Aziridines. 76 [1]

Neglected Aspects of Anthracenide (Anthracenidyl) Chemistry – Reactions with two *N*-Benzoylaziridines

Pen-Yuan Lin

Taipei (Taiwan), School of Pharmacy, Pharmaceutical Chemistry, Taipei Medical College

Rainer Weiß, Jürgen Werry, Reinhard Falkenstein, and **Helmut Stamm***

Heidelberg, Faculty of Pharmacy, University

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Abstract. Reaction of anthracenide $\mathbf{A}^{\cdot-}$ with *N*-benzoylaziridines **1a**,**b** forms charged radicals **3a**,**b** by single electron transfer and homolytic ring opening. Reactions follow that are known or expected as *e.g.* coupling with position 9 of $\mathbf{A}^{\cdot-}$ forming dihydroanthracene anions **9a**,**b** that yield amidoethylated dihydroanthracenes **10a**,**b**, or react with **1a**,**b** giving finally 9,10-bis-amidoethylated dihydroanthracenes **11a**,**b**. Results depend on experimental conditions and on the counter ions Na^+ or Li^+. Coupling is not regiospecific: contributions by positions 2 and 1 reach 29% or 4%, respectively, of total coupling with the primary radical **3a**; much higher contributions are possible with Li. Product **21s** (probably 3,3'-disubstituted tetrahydrobianthryl) may arise by hydrogen detachment from the first intermediate (**29**) of coupling with position 2 and dimerization of the formed 2-substituted $\mathbf{A}^{\cdot-}$ (**30**). Coupling products may be fully aromatized or may be hydroxylated in one of the benzylic positions. With counter ion Li^+ a non-SET reaction of **1a** with the dimer of $\mathbf{A}^{\cdot-}$ is indicated by the isolation of 9-benzoyl-dihydroanthracene **15** and by 19% yield of **16a** (aromatized **10a**). Reaction of **3b** with anthracene is indicated by 10,10'-disubstituted tetrahydrobianthryl **37**.

Single electron transfer (SET) reactions of *N*-acylaziridines with radical anions and other electron sources were prompted by a mechanistic problem [2]. Usually aziridino ketyls arise and homolyze to amidatoalkyl radicals [2–7]. The final result can depend on substituents of the aziridine ring, on the acyl group and on the radical anion. 2-Phenylaziridines present a special case [6–7]. Reactions with *N*-pivaloylaziridines were reported both with naphthalenidyl $N^{\cdot-}$ (naphthalenide) and with $\mathbf{A}^{\cdot-}$ [3], reactions of *N*-aroylaziridines with $N^{\cdot-}$ only [5]. After a very short notice [2], reactions of **1a**,**b** with $\mathbf{A}^{\cdot-}$ are now fully described with steps and types of products usually ignored or even unknown in $\mathbf{A}^{\cdot-}$ chemistry and therefore of possible importance for reactions with alkylating agents RX [8] (*cf.* introduction in [3]) that give alkylation in position 9 (and 10) of $\mathbf{A}^{\cdot-}$ besides reduction ($\rightarrow$ RH) and multi-step dimerization ($\rightarrow$ RR) (Scheme 1).

Results and Discussion

Tables 1 and 2 present the most important ones of many experiments with **1a**,**b** and $\mathbf{A}^{\cdot-}$. Main products (Scheme 1) are **6a**,**b**, **8**, **10a**,**b** and **11a**,**b**. In contrast to RX above, **1a** (Table 1) provided more **6a** (corresponding to RH) than **10a** and **11a** taken together. It had been conluded [3] that the amidatoalkyl radicals (here **3a**,**b**) are reduced to the carbanions (here **4a**,**b**) by the aziridino ketyl (here **2a**,**b**), a path not possible with RX. Subsequent steps to **6a**,**b** and **8** are known from reactions with other electron sources [5]. Since **6a** and ketone **8** are very difficult to chromatographically separate from one another run 1 includes a laborious technique to overcome this problem. A question-mark for the yield of **13** in Table 1 indicates that this nearly insoluble product may have been lost during work-up [5]. This does not disturb a discussion of the other products. Counter ion Na^+ has been replaced by Li^+ in runs 6 and 7 that are dealt with separately.

The product of two-fold SET (**6a**) was always the main product of Table 1 in contrast to the results from reactions of $\mathbf{A}^{\cdot-}$ with RX [8] or with *N*-pivaloylaziridines [3]. This is in accord with the electron source **2a** for the conversion **3a** $\rightarrow$ **4a** since **2a** has a longer lifetime than aliphatic aziridino ketyls and can better compete with $\mathbf{A}^{\cdot-}$. This SET from **2a** to **3a** may further profit from the reported [5] reversible dimerization of **2a** if one ketyl of the separating pair undergoes ring opening before it diffuses away. The yields of **6a** (and also of **6b** in Table 2) may be a bit low in long term runs since **5a**,**b** and analogous precursors can eliminate [5] the *N*-substituent as olefine (ethene from **5a**) when Na^+ is the counter ion.

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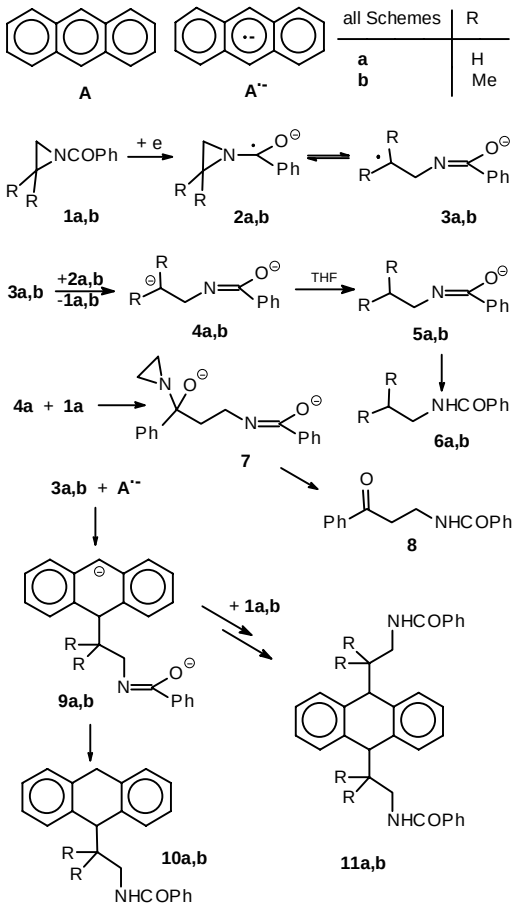
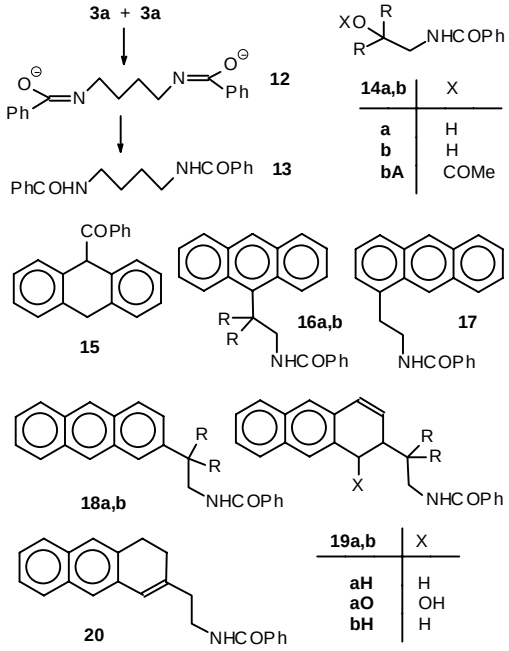


Scheme 1 Formation of main products: 1) SET from $A^{\cdot-}$ to 1; 2) homolytic ring opening **2** → **3**; 3) either reduction of radicals **3** to carbanions **4** or coupling of **3** with $\mathbf{A}^{\cdot-}$ to yield **9** and finally products **10** and **11**; 4) **4a**,**b** are protonated by THF to **5a**,**b** yielding finally products **6a**,**b** although part of **4a** forms product **8** *via* carbonyl attack (intermediate 7) on **1a**



Scheme 2 Dimerization of radical **3a** (product **13**); artifacts **14** of **1a**,**b**; product **15** from short-term carbonyl attack and product **16a** from nucleophilic ring opening by dimer (see Scheme 3) of $\mathbf{A}^{\cdot-}\,\mathrm{Li}^{+}$; products **17**–**20** from coupling of **3a**,**b** with positions 2 or 1 of $\mathbf{A}^{\cdot-}$

While formation of RR from RHal and an aromatic radical anion proceeds by reduction of the radical $R^{\cdot}$ ($\rightarrow R^{-}$) and SET reaction of the generated carbanion R^{-} with RHal providing a radical pair that collapses to RR [9], the precursor **12** of dimer **13** arises by a direct dimerization of radical **3a** without intermediacy of **4a** [5]. The highest yield of **13** comes from a run (9) that favours a high conversion **1a** → **2a**. Encounter of **4a**

Table 1 Reactions of **1a** with $A^{\cdot-}$ in THF[a)] at room temperature. Influence of experimental conditions.

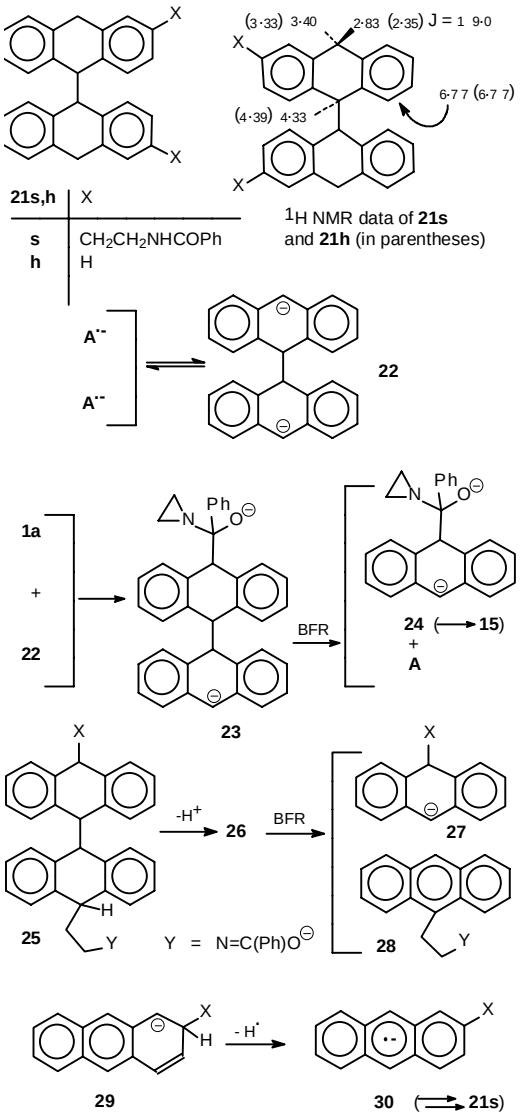
run	mmol of reagents			time [b)]	yields [c)] of products						
	metal	**A**	**1a**		**6a**	**8**	**10a**	**11a**	**13**	**1a** [d)]	further products
1	15 Na	15	15	15 min [e)]/40 h	37	19					
2	6.3 Na	6	3.2	30 min/30 min	(39)	(5)	(6)	(11)	?		
3	6.3 Na	6	5.6	30 min/30 min	(36)	(18)	4	(16)	(5)		
4	5.4 Na	7.5	4	2 layers [f)]/2 h	(34)	(1)	14	(4)	–	39 **14a**	
5	6 Na	6.5	5.2	ca.10 s [g)]/–	(24)	(17)	2	(11)	6	29 **1a**, 3 **14a**	
6	6 Li	6.5	5.3	ca.10 s [g)]/–	11	tr	2	–	–	67 **1a**, 9 **14a**	7 **15**
7	17 Li	20	6.8	inj. [h)]/3 d	57	10	(1)	–	?		19 **16a**, (1) **17**, (>0.5) **18a**, (1) **19aH**, (4) **19aO** [i)], (0.3) **20**
8	17 Na	20	6.8	inj. [h)]/1 d	>28 [j)]	tr	(2)	15	4		(0.5) **17**, >4 **19aO** [i)]
9	12 Na	14	2	36 min/–	(41)	(13)	(18)		17		1 **16a**, **17**, **19aH**, **19aO** [i)], 2 **20**, (4) **21s**

[a)] Anthracene **A** and metal in 100 ml, **1a** in 20 or 30 ml. [b)] Specification before the slant is the time required for the addition (dropwise unless otherwise stated) of **1a**. Reactions were quenched (except run 1) with $MeCO_2H$. [c)] Yields in parentheses are from ^1H NMR of product mixtures. tr = trace. A product number without yield in the last column indicates a trace. For „?“ see text. [d)] And artifacts of **1a**. [e)] At –10 °C. [f)] **1a** solution slowly poured over $\mathbf{A}^{\cdot-}$ solution, no stirring. [g)] Fastest possible flux from a dropping funnel. [h)] Rapid injection of **1a** solution. [i)] Mixture of diastereomers *α*-**19aO** and *β*-**19aO** where the former predominated. [j)] 28–29%.

with **1a** would not lead to **12** but give ketone **8** *via* **7** [5] as is also supported by the influence (runs 2–3) of the molecular ratio $\mathbf{A}^{\cdot-}$: 1a that needs to be ≥2:1 for the products **6a** and **10a** (from coupling of **3a** with $\mathbf{A}^{\cdot-}$) but only 1:1 for **8** and **11a**. An „addition" of dissolved **1a** to dissolved $\mathbf{A}^{\cdot-}$ nearly without mixing describes run 4; slowing bimolecular reactions by thermal diffusion across the interface makes **3a** live long enough [5] to form **5a** with THF and to react with $\mathbf{A}^{\cdot-}$ when this is regenerated from **A** by SET. Formation of **11a** (bis-imidate) proceeds by fast (cf. short-term run 5 with high concentrations of **1a** and **9a** during rapid mixing) nucleophilic ring opening of **1a** through **9a** (counter ion Na^+) that possibly is preceded by an even faster reversible attack of **9a** (carbanionic site) on the carbonyl group of **1a** [10, 11]. Run 9 shows that this reaction can be suppressed by a large excess of $\mathbf{A}^{\cdot-}$ combined with slow dropwise addition of **1a**, conditions that simultaneously favour strongly the reaction of **30** with $\mathbf{A}^{\cdot-}$ (total coupling reaches 25%). In contrast, moderate excess, long reaction time and very fast mixing (run 8) provided the highest yield ratio (7.5) of **11a** : **10a** in Table 1. The pivaloyl analogue of **1a** yielded under similar conditions no analogue of **10a** at all but 26% of the analogue of **11a** [3] in accord with a reaction time of three days. From runs 5 and 9 follows that even with counter ion Na^+ the carbanion **4a** reacts much faster with **1a** than with THF taking into account the difference in concentrations. **14a** arose by hydrolytic ring opening of unreacted **1a**.

Elaborate chromatography in runs 7–9 led to the detection of several by-products where the benzamidoethyl chain is attached to position 1 or 2 of the anthracene ring system. Apart from two pivaloyl analogues of **18a** [3] this seems to be without precedence in $\mathbf{A}^{\cdot-}$ chemistry. Most of these by-products are not obtained in a pure state but their structures are deduced from unambiguous ^{1}H NMR signals. Protons in positions 9 and 10 of anthracene compounds show singlets near 8.4 ppm, a region usually without signals. Two singlets of equal intensity at 8.42 and 8.69 ppm indicate structure **17** since the downfield shift for one of these protons points to a substituent in the neighbouring position 1. Isomer **16a** is one of the main products in Li run 7. Pure isomer **18a** shows the two singlets at 8.37 and 8.42 ppm. The structure of **19aH** follows from signals of the olefinic double bond and from a multiplet at 3.1 ppm (NCCCH–C=C). The 3,4-dihydro isomer **20** shows a C=CH singlet at 6.52 ppm. The hydroxy compound **19aO** is found as two diastereomers α and β. Their structure was deduced, among others, from the OCH signals. Signals for ArH and CH_2CH_2NH are always seen but usually difficult to distinguish from one another and from signals of other products.

Coupling of $\mathbf{A}^{\cdot-}$ with a radical is clearly not regiospecific, and run 8 shows that at least coupling in position 2 cannot be neglected since it reached 29% (much higher in the Li run 7, see below) of the total coupling with **3a** but only 4% for position 1. The 2 isomer of **9a** is certainly not so stable as **9a** and may easily be oxygenated when oxygen enters the reaction vessel during quenching. Dehydration of the final product **19aO** would form **18a**. An analogous path to **17** is possible (for an alternative path to **17** and **18a** see below) but **16a** may arise from a special mechanism discussed below. Of course, one cannot exclude a hydroxylation during work-up. The assigned structure of product **21s** will be dealt with later.



Scheme 3 Proposed structure of by-product **21s** and ^{1}H NMR comparison with known **21h**; dimerization of $\mathbf{A}^{\cdot-}$ and reaction of the dimer **22** with **1a** forming either **23** (and hence **15**) or **25** (X = H or CH_2CH_2Y) and hence **28** and **16a**.

Na run 5 and Li run 6 have been performed identically except for the counter ion. A comparison shows that

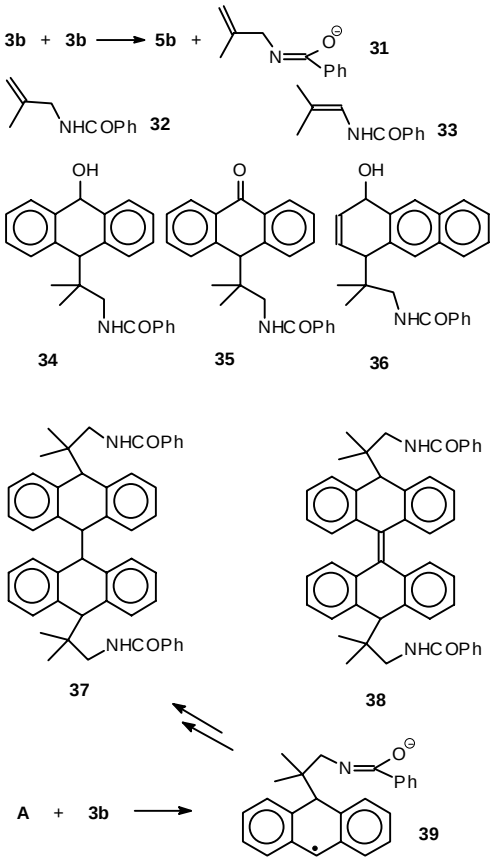
the SET step **1a** → **2a** as well as the reaction of **1a** both with **4a** (→→ **8a**) and **9a** (→→ **11a**) proceeds more slowly with Li, the latter due to a deactivating carbanion stabilization. **15** was found only with Li after a very short reaction time (run 6) but not in the long-term Li run 7. One reaction of $\mathbf{A}^{\cdot-}$, namely its (reversible) dimerization (Scheme 2), is usually ignored or even denied in spite of Schlenk's evidence (mol. mass after carbonization and methylation of the dicarbonic acid) [12], later independent confirmation [13] and theoretical arguments for a special behaviour of this radical anion. The equilibrium will be shifted by Li^+ in favour of the dimer **22** due to the carbanion stabilization by Li^+. The lowered concentration of monomer $\mathbf{A}^{\cdot-}$ may explain the slow SET step at least in part as well as the decrease of coupling (at most ca. 1% of **16a** in run 7 may have been formed by radical coupling, see run 9). This dimerization explains the formation of **15** in run 6 and the high yield of **16a** in run 7. Fast attack of the lithiated „monomeric **22**", *i.e.* of 9-lithio-9,10-dihydroanthracene, on the carbonyl of **1a** is known [10,11]. Thus, formation of **23** from **22** can be expected, followed by heterolytic (Scheme 3) benzylic fragmentation (BFR) to give **A** and **24** that yields **15** if the time until quenching is too short for a homolytic BFR of **24** that would provide $\mathbf{A}^{\cdot-}$ and **2a**. Lack of **15** in the long term Li run 7 may be considered evidence that this inner-sphere SET path to **2a** [11b] plays a role and perhaps even an important role with Li. This is underlined by the high yields of **6a**,**b** in Li runs 6, 7 and 13 (Table 2): the yield in run 6 is 46% of converted **1a**. Homolytic BFR of **24** (counter ion Li^+) and its dimethyl analogue gives much more **6a**,**b** than **10a**,**b** [11].

The high yield of **16a** in run 7 can be explained in a similar manner with a slight modification, already described for the pivaloyl analogue of **16a** [3]. The rapid injection of **1a** in run 7 may enable a reaction of both carbanion sites in **22** forming **25** that by deprotonation in the lower part (H indicated in the formula) gives carbanion **26** that undergoes heterolytic BFR yielding **27** and **28**, the precursor of **16a**. The fate of **27** depends on X. **27** arises from **22** and **1a** either by carbonyl attack or by ring opening. More likely appears the path **23** → **25** to **27** that in this long-term run would undergo homolytic BFR to $\mathbf{A}^{\cdot-}$ and **2a**.

Run 7 and 8 have been performed identically except for counter ion and reaction time that certainly was unnecessarily long in run 7. Material balance (ca. 94%) and yield of **6a** are high in run 7. Lower yield and poorer balance in run 8 point to the mentioned ethene elimination from **5a**Na^+ [5]. **5a**Li^+ in run 7 is much more stable as already shown by the yields of **6a** [11]. The excess of $\mathbf{A}^{\cdot-}$ and the rapid injection of **1a** in runs 7 and 8 are unfavourable for the formation of **8** since carbanion **4a**, once it is formed, will find only small concentrations of **1a** in contrast to the situation in run 9. The result is more pronounced in run 8. The 10% yield in run 7 may be ascribed to the stabilization of **4a** by Li^+ that retards the protonation much more than the carbonyl attack which perhaps even may be faster with the lithiumorganic reagent. Surprising are the high contributions of coupling with positions 2 and 1 in the Li run 7. The above given maximum estimate (1%) of **16a** arising from coupling *via* **9a** gives a total of 8.8% for all coupling products. This total coupling is then composed of the contributions 23%, 66% and 11% for coupling in postition 9, 2 and 1, respectively. It appears as if the spin distribution in $\mathbf{A}^{\cdot-}$ changes markedly on going from Na^+ to Li^+. This may be correlated to changes in the fast equilibria between different kinds of $\mathbf{A}^{\cdot-}$ ion pairs including that one of the paramagnetic dimer of $\mathbf{A}^{\cdot-}$ [14].

A late chromatographic fraction of run 9 contained **8** together with a further product. Its ^1H NMR spectrum (see Scheme 3) showed two 19.0 Hz doublets and a singlet at 4.33 ppm pointing to a dihydroanthracene compound substituted in position 9 by a substituent *Z* that does not show vicinal coupling. The shift rules out *Z* = COPh and *Z* = OH, OR but all these signals as well as a kind of doublet at 6.77 ppm of this uncommon product, proposed structure **21s**, match nicely the respective signals in **21h** [15] except for 10-H *pseudo ax*. This shift difference may arise from the side chain $CH_2CH_2NHCOPh$ in **21s** whose CH_2 signals (for an easier understanding discussed here for one half of this symmetrical molecule only) show diastereotopism as expected from structure **21s**: multiplets at 2.16 ppm (1H of $NCCH_2$), 2.62 ppm (1H of $NCCH_2$), 3.15 ppm (1H of NCH_2) and 3.60 ppm (1H of NCH_2). Additionally, these multiplets, NCH_2 less clear than $NCCH_2$, appear as doubled more simple sub-multiplets of unequal intensity within each sub-multiplet pair. This doubling is compatible with an unequal mixture of *meso*-**21s** and *rac*-**21s**. If the assumed structure is correct, how can it arise? A reasonable sequence follows. Coupling of **3a** with $\mathbf{A}^{\cdot-}$ is favoured in run 9 (see above) and should form some carbanion **29**. This is less stable than isomer **9a** and should be a good hydrogen donor in reactions with a radical, *e.g.* **3a**. The high yield of **13** simultaneously indicates particularly high concentrations of **3a** in this run. Thus, abstraction of the allylic hydrogen atom in **29** by **3a** may generate **30** whose dimerization gives the tetra-anion of **21s**, both when the side chains point in the same or in the opposite direction during dimerization. The reverse dimerization would be less effective than the conversion **22** → $\mathbf{A}^{\cdot-}$ if it is slowed down by some stabilizing interaction of the side chain from one half to the other half in the charged precursor of **21s**, *e.g.* by chelating the counter ion of the carbanion. The hydrogen detachment from **29** or its 1-isomer may also be a simple path to products **18a** and **17** when

the arising **30** (or its 1-isomer) transfers the unpaired electron to **A**. Due to the high excess of $\mathbf{A}^{\cdot-}$ in run 9 would this SET be less effective thus allowing some dimerization. A positional isomer of **21s** can be ruled out by the following arguments. Coupling in position 1 of $\mathbf{A}^{\cdot-}$ is generally less important than in position 2. Moreover, ^{1}H NMR signal (4H) at 6.77 ppm excludes substitution in positions 1, 1', 8 or 8' while substitution in positions 4, 4', 5 or 5' should influence the 19.0 Hz doublets relative to **21h** more than observed. Substitution in positions 2, 2', 7 or 7' would make the signal at 6.77 ppm a singlet with perhaps some fine splitting and could for steric reasons not exert the observed shift of the 2.35 doublet in **21h** to 2.83 ppm in the new product.



Scheme 4 Disproportionation of **3b** forming **32** and in part **33**; artifacts **34**–**36** of coupling products; addition of radical **3b** to anthracene **A** and dimerization of the adduct **39** yielding finally **37** and its artifact **38**.

Some reactions of **1b** are listed in Table 2. Except for run 13, **6b** was not the main product, even taken together with **32** and **33**. The tertiary radical **3b** does not dimerize; its self reaction is disproportionation to **5b** and **31**, the precursor of **32** and **33** (*via* slow base catalyzed isomerization of **31** [16]). It is not clear how much of **32** is an artifact of **1a**. Product **33** in run 13 indicates that here at worst only a part of **32** is an artifact. **10b** is always the main or the second important product. Surprising is the formation of **11b** that even is the main product in the equimolar long-term run 10. No pivaloyl analogue of **11b** has previously been found, although a nucleophilic ring opening of the pivaloylaziridine is faster than that one of **1b** [17]. Anions of 9-substituted dihydroanthracenes are known to prefer the *cis* conformation [18]. We suspect therefore that the pivaloyl analogue (Ph replaced by *t*-Bu) of **9b** exerts a stronger shielding of the carbanionic centre than **9b** does. The slowness of the reaction of **9b** with **1b** can be recognized from a comparison of runs 10 and 11. **11b** may exist as *cis* or *trans* isomer. It was isolated in three runs, showing the same melting point and mixed melting point but indicating two isomers by the ^{1}H NMR spectra.

Again, several „irregular“ products were detected. **18b** and **19bH** are recognizable from ^{1}H NMR comparison with **18a** or **19aH**, respectively. An olefinic doublet of doublet at 6.17 ppm (J = 9.9/3.8 Hz) indicates that there is only one vicinal aliphatic proton in **19bH**. Lack of **16b** in the Li run 13 contrasts with the high yield of **16a** in run 7. This is expeccted from steric hindrance of a nucleophilic ring opening by **22** (*cf.* [17]). Part of **10b** in run 13 was found hydroxylated (**34**) giving rise to *cis*–*trans*-isomerism. One isomer (α-**34**) was obtained pure while β-**34** was only found in mixture with **36** from which a single crystal could be picked out. The CHO singlet of α-**34** is downfield from that of β-**34** indicating that this H stands *pseudo-axial* in α-**34** as expected for the *cis*-isomer. The rather high yield of

Table 2 Reactions of **1b** with $\mathbf{A}^{\cdot-}$ in THF at room temperature. Influence of experimental conditions

run	mmol of reagent/ml of THF		time [a])	yields [b]) of products						
	metal + **A**/THF	**1b**/THF		**6b**	**32**	**33**	**10b**	**11b**	**1b** [c])	further products
10	15 Na + 15/150	15/30	15 min [d])/40 h	(18)	(7)	–	21	40		
11	5.6 Na + 7.5/100	5/30	15 min/1d	(15)	(10)		32	9	12 Oxa [e]) 12 **14bA**	
12	11 Na + 20/150	10/20	inj. [f])/2d	4	8	–	13	5	3 Oxa [e]) (1) **14b**	1 **18b**, (3) **19bH**, (3) **35**, 0.5 **37**, 3 **38**
13	15 Li + 18/150	6/10	inj. [f])/1d	34	4	3	17	0		6 **18b**, 10 α-**34**, 1 β-**34**, 0 **35**, 0.5 **36**

[a]) Specification before the slant is the time required for the addition of dissolved **1b**. Addition was dropwise unless otherwise stated. Reactions were quenched (except run 1) with acetic acid (run 2) or methanol (run 3 and 4). [b]) Yields in parentheses are from ^{1}H NMR of product mixtures. [c]) Artifacts of **1b**. [d]) At –10 °C. [e]) Oxa = 5,5-Dimethyl-2-phenyl-4,5-dihydrooxazole. [f]) Rapid injection of dissolved **1b**.

34 may result from the carbanion stability of **9b**$(Li^+)_2$ that slows protonation by methanol used to quench this run. Anthrone **35** in run 12 may arise from **34** or its peroxidic precursor. The only 1-substituted anthracene product obtained from **1b** was **36**. Its most characteristic and structure proving ^{1}H NMR signals are those for the olefinic double bond: doublets of doublets at 6.37 ppm and 6.48 ppm (J = 10.4/5.2 Hz). The total coupling of **3b** with $\mathbf{A}^{\cdot-}$ in the Li run 13 amounted to 34.5% with a distribution of 81%, 17% and 1.4%, respectively, for positions 9, 2 and 1.

A real surprise were the dimeric products **37** and **38**. ^{1}H NMR showed a slow conversion **37** → **38** of the crystals during storage or handling. The structures were deduced from ^{1}H NMR and MS, the dimeric nature proven by a FAB spectrum of **37**. How can **37** arise? A path similar to that one proposed for **21s** is obviously unlikely. However, 2-cyano-2-propyl radical (Me_2C–CN radical), structurally resembling **3b**, is known [19] to add to position 9 of **A**; one reaction of the arising substituted dihydroanthryl radical is dimerization to yield an analogue of **37**. Thus, we propose that **3b** and **A** form **39** which dimerizes to the *N*-deprotonated **37**.

This paper shows that reactions of $\mathbf{A}^{\cdot-}$ with substituting reagents can strongly depend on the counter ion, that they may include reactions of dimerized $\mathbf{A}^{\cdot-}$, that generated radicals may couple with $\mathbf{A}^{\cdot-}$ not exclusively in position 9 and that position 2 is more prone to coupling than position 1. $\mathbf{A}^{\cdot-}Li^+$ may couple even more in position 2 than 9. Furthermore, the products may be fully aromatized. Even bianthryl derived products may arise and radical addition to A may occur.

Experimental

^{1}H NMR: Bruker WM 250, AC 200, AC 300, $CDCl_3$. – IR: Perkin-Elmer 283, KBr tablets unless otherwise stated. – MS: Varian MAT 311-A. Chromatography: silica gel Merck, 0.063–0.2 mm, column dimensions in cm are given with each run, mixtures analyzed by ^{1}H NMR. Abbreviations: Chr. (chromatography), dic. (CH_2Cl_2), EA (ethyl acetate), B (benzene), T (toluene).

General Procedure

See Tables. All reactions were performed in dry THF under dry N_2 (Ar with Li) with continuous stirring (except run 4). The mixture of **A**, THF, and metal was stirred for 0.5–1 d (2 d with Li). Addition of **1a** or **1b** and quenching is stated in the Tables. On evaporation of THF usually some **A** precipitated that was removed. The residue of evaporation was taken up in dic., washed with water and evaporated. Further treatment is given below. Some products are known: **8**, **13** and **33** [5]; **6a**, **6b**, **10a**, **10b**, and **15** [11]; **11a** [20]; **32**, Oxa [21].

Run 1

Chr. (35 × 3, dic.) provided hydrocarbons and a mixture of **6a** and **8** that was dissolved in CCl_4 and 5 times washed with water. Evaporation of the organic layer yielded 360 mg (19%) of **8**. The wash water was twice extracted with dic. to give 830 mg (37%) of **6a**.

Run 2

Chr. (80 × 2, dic.) removed hydrocarbons. Elution with EA provided 363 mg of a mixture consisting of 189 mg (39%) of **6a**, 20 mg (5%) of **8**, 66 mg (6%) of **10a** and 87 mg (11%) of **11a**.

Run 3

Chr. (40 × 3, dic.) provided hydrocarbons and 70 mg (4%) of **10a**. Elution with dic./EA 1:1 yielded 642 mg of a mixture consisting of 302 mg (36%) of **6a**, 129 mg (18%) of **8** and 211 mg (16%) of **11a**. Elution with MeOH gave 178 mg of a mixture that was boiled out with EA/MeOH 3:1. Hot filtration yielded an extract containing (calibrated ^{1}H NMR) 41 mg (5%) of **13**.

Run 4

Chr. (40 × 3, dic.) removed hydrocarbons. Elution with dic./EA 10:1 yielded 182 mg (14%) of **10a**. Elution with dic./EA 1:1 gave 247 mg of a mixture consisting of 206 mg (34%) of **6a**, 7 mg (1%) of **8** and 34 mg (4%) of **11a**. Elution with MeOH yielded 259 mg (39%) of **14a**.

N-(2-Hydroxyethyl)benzamide (**14a**)

m.p. 55–57 °C (Lit. ca. 58 °C [22]). – ^{1}H NMR δ/ppm = 2.48 (s br, OH), 3.61–3.70 (m, NCH_2), 3.82–3.90 (m, OCH_2), 6.62 (s br, NH), 7.38–7.55 (m, *m*-H and *p*-H of Ph), 7.74–7.84 (m, *o*-H of Ph).

Run 5

Chr. (40 × 3, T) removed hydrocarbons. Elution with dic./EA 25:1 yielded 220 mg (29%) of **1a**. Elution with dic./EA 10:1 gave 39 mg (2%) of **10a** and 79 mg of unknown products. Elution with EA provided 433 mg of a mixture consisting of 184 mg (24%) of **6a**, 111 mg (17%) of **8** and 138 mg (11%) of **11a**. Elution with MeOH gave 102 mg of a mixture containing (calibrated ^{1}H NMR) 43 mg (6%) of **13** and 26 mg (3%) of **14a**.

Run 6

Chr. (40 × 3, T) provided hydrocarbons and 107 mg (7%) of **15**. Elution with dic./EA (25:1) yielded 519 mg (67%) of **1a** and (10:1) 35 mg (2%) of **10a** and 65 mg unknown products. Elution with EA provided 89 mg (11%) of **6a** containing traces of **8** and unknown products. Elution with MeOH yielded 78 mg (9%) of **14a**.

Run 7

Chr. (40 × 4, T/EA 10:1) provided hydrocarbons, 392 mg of **16a** and 85 mg of a mixture consisting of 21 mg (1%) of **10a**, 21 mg (total 413 mg, 19%) of **16a**, 21 mg (1%) of **17** and 21 mg (1%) of **19aH**. Treatment of the next fraction (36 mg) with a little MeOH left 18 mg of crystals consisting of 12 mg (0.5%) of **18a** and 6 mg (0.3%) of **20**; evaporation of the extract gave 18 mg of rather pure **19aO** (mainly α). The same treatment of the next fraction (210 mg) left a mixture of **18a** and unknown products undissolved while evaporation of the MeOH gave 72 mg (total 90 mg, 4%) of **19aO** (mainly α). Continued elution yielded 100 mg (10%) of **8**. Elution with

T/EA/MeOH 10:4:1 provided 567 mg (57%) of **6a** containing a trace of **8**.

9-(2-Benzamidoethyl)anthracene (**16a**)

m.p. 265–267 °C. – IR ν/cm^{-1} = 3 308, 1 642. – ^{1}H NMR: δ/ppm = 3.84 (m_c, $NCCH_2$), 4.02 (m_c, NCH_2), 6.19 (s br, NH), 7.22–7.58 (m, Ph and 2-H, 3-H, 6-H, 7-H), 8.03 (m_c, 4-H, 5-H), 8.40 (m_c, 1-H, 9-H), 8.42 (s, 10-H). – MS (174 °C): *m/z* = 325 (23, M^+), 204 (100, M – $PhCONH_2$), 191 (62), 189 (20), 105 (69, PhCO), 77 (30, Ph).

$C_{23}H_{19}NO$	Calcd.:	C 84.89	H 5.89	N 4.30
(325.41)	Found:	C 84.85	H 6.09	N 4.57.

1-(2-Benzamidoethyl)anthracene (**17**)

Only in mixture with **10a**, **16a** and **19aH**. – For ^{1}H NMR see text.

2-(2-Benzamidoethyl)anthracene (**18a**)

m.p. 236–238 °C. – IR: ν/cm^{-1} = 3 310, 1 638. – ^{1}H NMR: δ/ppm = 3.16 (t, *J* = 6.7, $NCCH_2$), 3.88 (q, *J* = 6.7, NCH_2), 6.18 (s br, NH), 7.32–7.50 (m, *m*-H and *p*-H of Ph), 7.51 (m_c, 3-H), 7.65–7.76 (m, *o*-H of Ph, 3-H, 6-H, 7-H), 7.83 (s, 1-H), 8.00 (m_c, 4-H, 5-H, 8-H), 8.37 (s, 10-H), 8.43 (s, 9-H). – MS (149 °C): *m/z* = 325 (12, M^+), 204 (100, M – $PhCONH_2$), 191 (16), 189 (10), 105 (49, PhCO), 77 (28, Ph).

$C_{23}H_{19}NO$	Calcd.:	C 84.89	H 5.89	N 4.30
(325.41)	Found:	C 84.68	H 6.13	N 4.13.

2-(2-Benzamidoethyl)-1,2-dihydroanthracene (**19aH**)

Only in mixture with **10a**, **16** and **17**. – ^{1}H NMR (recognizable signals only): δ/ppm = 3.10, m_c (NCCCH–C=C), 6.08 (dd, *J* = 10.1/4.5, NCCC–CH=C), 6.63 (d, *J* = 10.1, NCCC–C=CH).

2-(2-Benzamidoethyl)-1-hydroxy-1,2-dihydroanthracene (**19aO**)

Impure mixture of isomers α and β. – IR: ν/cm^{-1} = 3 100 br, 1 638. – MS (139 °C): *m/z* = 325 (25, M – H_2O), 204 (100, 325 – $PhCONH_2$), 191 (14, 235 – $PhCONHCH_2$), 189 (8), 105 (33, PhCO), 77 (19, Ph). – ^{1}H-NMR: δ = (α) 1.65–2.19 (m, $NCCH_2$), 3.08–3.74 (m, NCH_2CCH), 4.83 (d, *J* = 5.8, OCH), 6.00 (dd, *J* = 9.6/4.6, NCCCCH=C), 6.31 (t br, *J* ≈ 6, NH), 6.70 (d, *J* = 9.9, NCCCC=CH), 7.15–7.76 (m, ArH), 7.97 (m_c, *o*-H of PhCO), 8.26 (s, 9-H), 8.32 (s, 10-H); (β, only signals differing from the α signals) 5.26 (d, *J* = 6.6, OCH), 6.17 (dd, *J* = 9.8/4.7, NCCCCH=C), 8.07 (m_c, *o*-H of PhCO).

$C_{23}H_{21}NO_2$	Calcd.:	C 80.44	H 6.16	N 4.08
(343.43)	Found:	C 80.95	H 6.28	N 4.27.

2-(2-Benzamidoethyl)-3,4-dihydroanthracene (**20**)

Only in mixture with **18a**. – ^{1}H NMR: δ/ppm = 2.31 (t, *J* = 7.1, $C{=}CCH_2$), 2.59 (t, *J* = 6.8, $NCCH_2$), 3.02 (t, *J* = 7.0, $C{=}CCCCH_2$), 3.72 (q, *J* = 6.7, NCH_2), 6.52 (s, C=CH), 7.82 (s, 10-H), 7.99 (s, 9-H), other signals coincide or overlap with the respective ones of **18a**; assignment for the two CH_2CH_2 parts from decoupling.

Run 8

Chr. (40 × 4, T/EA 10:1) provided hydrocarbons, unknown products and 76 mg of a mixture containing (calibrated ^{1}H NMR) 36 mg (2%) **10a** and 11 mg (0.5%) **17**. Elution with T/EA (5:2) gave 95 mg (4%) of impure **19aO** (mainly α) and 39 mg of a mixture containing α-**19aO**. Further elution provided 57 mg of a mixture consisting of **6a** (main component), **8** and **11a**. The next fraction was 309 mg of a mixture consisting of 131 mg of **6a** and 178 mg of **11a**. Further elution provided 239 mg of a mixture consisting of 130 mg (total >286 mg, >28%) of **6a**, 67 mg (total 243 mg, 15%) of **11a** and 42 mg (4%) of **13**.

Run 9

Chr. (33 × 3, B/EA 9:1) provided hydrocarbons, 53 mg of unknown products, 85 mg of **10a** containing a trace of **19aH**, 32 mg (total >117 mg, >18%, see next fraction) of **10a** containing a trace of **19aO**, 17 mg of a mixture consisting of **10a** (main component), anthraquinone and some **18a**. Further elution yielded 31 mg of unknown products containing some **20** and a trace of **17**. Continued elution gave 31 mg of a mixture consisting of **20** (main component) and unknown products. The combined last two fractions contained (calibrated ^{1}H NMR) 16 mg (2%) of **20**. Further elution provided 22 mg of a mixture consisting of 10 mg of **8** and 12 mg (4% if structure is correct) of **21s**. Continued elution yielded 146 mg of a mixture consisting of 122 mg (41%) of **6a** and 24 mg (total 36 mg, 13%) of **8**. Further elution gave 49 mg (17%) of **13**.

3,3'-Bis-(2-benzamidoethyl)-9,9',10,10'-tetrahydro-bi-9,9'-anthryl (**21s**), proposed structure

Only in mixture with **8**. Structure proposed on the basis of ^{1}H NMR data in the text and in Scheme 3.

Run 10

Chr. (35 × 3, dic.) removed hydrocarbons and yielded mixture a. Elution with acetone provided mixture b. Chr. (40 × 3, dic.) of mixture a provided some unknown products and impure **10b**, that on recrystallization from cyclohexane yielded 1 140 mg (21%) of **10b**. Chr. (35 × 3, dic./EA) of mixture **b** yielded small fractions with unknown products and 680 mg of a mixture consisting of 489 mg (18%) of **6b** and 191 mg (7%) of **32**. Acetone yielded **11b** that was recrystallized (CCl_4, refrigerator) to give 1590 mg (40%) of pure **11b**.

Run 11

Chr. (40 × 4; dic.) removed hydrocarbons. Elution with dic./EA 10:1 provided 567 mg (32%) of **10b** and 215 mg of a mixture consisting of 131 mg (15%) of **6b** and 84 mg (10%) of **32**. Continued elution yielded 340 mg of mixture a and 107 mg (12%) of Oxa (see Table 2). Chr. (15 × 1.5, dic./EA 3:1) of mixture a yielded 123 mg (9%) of **11b** and 143 mg (12%) of **14bA**.

2-Benzamido-2-methylpropylacetate (**14bA**)

Oil. – IR (film): ν/cm^{-1} = 3 340, 1 739, 1 650, 1 540. – ^{1}H NMR: δ/ppm = 1.49 (s, CMe_2), 2.04 (s, MeCO), 3.70 (d, *J* = 6.1, NCH_2), 7.20–7.50 (m, NH, *m*-H and *p*-H of Ph), 7.75–7.90 (m, *o*-H of Ph).

$C_{13}H_{17}NO_3$	Calcd.:	C 66.36	H 7.28	N 5.95
(235.28)	Found:	C 66.23	H 7.07	N 5.64.

Run 12

Chr. (30 × 3, T/EA 9:1) yielded hydrocarbons and 314 mg of **10b** and 233 mg of a mixture consisting of 164 mg (total 478 mg, 13%) of **10b** and 69 mg of **19bH**. Further elution gave 43 mg of a mixture consisting of 29 mg (total 98 mg, 3%) of **19bH** and 14 mg (1%) of **18b**. The next fraction was a mixture of 81 mg of **32** and 8 mg of **6b**. Further elution gave 169 mg of a mixture consisting of 93 mg of **35**, 18 mg of **6b**, 46 mg of **32** and 12 mg of **37**. Further elution yielded 84 mg of a mixture consisting of 27 mg of **6b**, 11 mg (total 138 mg, 8%) of **32**, 26 mg (total 119 mg, 3%) of **35**, 7 mg (total 19 mg, 0.5%) of **37** and 13 mg of **38**. The next fraction (153 mg) consisted of 92 mg (total 105 mg, 3%) of **38**, 46 mg (3%) of Oxa (see Table 2) and 15 mg (total 68 mg, 4%) of **6b**. Further elution yielded 132 mg (5%) of **11b** and 201 mg of unknown products.

9,10-Bis-(2-benzamido-1-methyl-2-propyl)-9,10-dihydroanthracene (**11b**)

m.p. 215–217 °C (run 10 and 11, after washing with B/CCl_4). – IR: ν/cm^{-1} = 3 335, 3 320, 1 648, 1 527, 1 522.

11b from run 11. – ^{1}H NMR: δ/ppm = 1.21 (s, 4 Me), 3.61 (d br, J = 5.4, 2NCH_2), 4.06 (s, 9-H, 10-H), 5.93 (t br, J ca. 5.5, 2NH), 7.20–7.30 (m, 2-H, 3-H, 5-H, 6-H), 7.30–7.49 (m, *m*-H and *p*-H of 2Ph), 7.49–7.65 (m, 1-H, 4-H, 5-H, 8-H, 4 o-H of 2Ph).

$C_{36}H_{38}N_2O_2$	Calcd.:	C 81.48	H 7.22	N 5.28
(530.70)	Found:	C 81.67	H 7.13	N 5.44.

11b from run 12. – ^{1}H NMR: δ/ppm = 1.21 (s, 4Me), 3.61 (d br, J = 5.4, 2NCH_2), 4.06 (s, 9-H, 10-H), 5.93 (t br, J ca. 5.5, 2NH), 7.20–7.30 (m, 2-H, 3-H, 5-H, 6-H), 7.30–7.49 (m, *m*-H and *p*-H of 2Ph), 7.49–7.65 (m, 1-H, 4-H, 5-H, 8-H, 4 *o*-H of 2Ph). – MS (203 °C): *m/z* = 530 (0.1, M^+), 355 (2, M – 32), 354 (2), 219 (1, anthranylCMe_2), 176 (99, A), 105 (100, PhCO).

$C_{36}H_{38}N_2O_2$	Calcd.:	C 81.48	H 7.22	N 5.28
(530.70)	Found:	C 81.56	H 7.30	N 5.24.

2-(2-Benzamido-1-methyl-2-propyl)-1,2-dihydroanthracene (**19bH**)

Only in mixture with either **10b** or **18b**. – ^{1}H NMR: δ/ppm = 1.04 (s, 2Me), 2.49 (m_c, NCCCH), 3.08 (m_c, NCH_2), 3.46 (m_c, 1H of NCCCCH_2), 3.83 (m_c, 1H of NCCCCH_2), 6.10 (s br, NH), 6.17 (dd, J = 9.9/3.9, 3-H), 6.77 (d br, J = 9.9, 4-H), 7.30–7.73 (m, ArH indistinguishable from signals of **10b** or **18b**.

9-(2-Benzamido-1-methyl-2-propyl)-10-oxo-9,10-dihydroanthracene (**35**)

Only in mixture with **6b**, **32** and **37**. – ^{1}H NMR: δ/ppm = 0.76 (s, 2Me), 3.34 (d, J = 6.4, NCH_2), 4.06 (s, 9-H), 6.18 (t br, J ca 6, NH), 7.62 (m_c, 1-H, 8-H), 8.15 (m_c, 4-H, 5-H), other ArH cannot be assigned in the mixture. – MS (158 °C): *m/z* = 194 (33, anthrone), 176 (39, Oxa-H^+), 105 (100, PhCO).

10,10'-Bis(2-benzamido-1-methyl-2-propyl)-9,9',10,10'-tetrahydro-9,9'-bianthryl (**37**)

m.p. 280–281 °C (MeOH). – IR: ν/cm^{-1} = 3 300, 1 640, 1 530. – ^{1}H NMR: δ/ppm = 1.32 (s, 4Me), 3.90 (d, J = 6.4, 2NCH_2), 4.23 (s, 10-H, 10'-H), 4.49 (s, 9-H, 9'-H), 6.28 (t br, J ca. 6, 2NH), 6.35 (m_c, 1-H, 1'-H, 8-H, 8'-H), 6.77 (m_c, 2-H; 2'-H, 7-H, 7'-H), 7.21 (m_c, 3-H, 3'-H, 6-H, 6'-H), 7.42–7.60 (m, 4-H, 4'-H, 5-H, 5'-H, *m*-H and *p*-H of 2Ph), 7.67 (m_c, *o*-H of 2Ph). – MS (205 °C): *m/z* = 354 (0.5, M/2 or bianthryl), 219 (4, anthryl-CMe_2 cation), 178 (100, A), 176 (33, Oxa-H^+), 105 (58, PhCO). – MS-FAB (MNBA + 1% TFA): 709 (M + H^+).

$C_{50}H_{48}N_2O_2$	Calcd.:	C 84.71	H 6.82	N 3.95
(708.95)	Found:	C 84.56	H 6.88	N 3.98.

10,10'-Bis(2-benzamido-1-methyl-2-propyl)-9,9',10,10'-tetrahydro-9,9'-bianthrylidene (**38**)

m.p. 311–312 °C (MeOH), the red crystals became non-transparent near 73 °C. – IR: ν/cm^{-1} = 3 350, 3 460, 1 660, 1 650, 1 545, 1 530. – ^{1}H NMR: δ/ppm = 1.28 (s, 4Me), 3.82 (d, J = 6.3, 2NCH_2), 3.93 (s, 9-H, 9'-H), 6.20 (t br, J = 6.0, 2NH), 6.71 (t, J = 7.4, 2 × 2 ArH), 7.15 (t, J = 7.4, 2 × 2ArH), 7.24 (d, J = 7.4, 2 × 2 ArH), 7.35–7.55 (m, 2 × 2 ArH, *m*-H and *p*-H of 2Ph), 7.59 (m_c, *o*-H of 2Ph). – MS (277 °C): *m/z* = 706 (0.07, M^+), 395 (0.2, bianthrylyl-CMe_2 cation), 354 (9, bianthryl), 176 (92, Oxa-H^+), 105 (100, PhCO).

$C_{50}H_{48}N_2O_2$	Calcd.:	C 84.71	H 6.82	N 3.95
(708.95)	Found:	C 84.56	H 6.88	N 3.98.

Run 13

Chr. (30 × 3, T/EA 10:1) provided hydrocarbons and 394 mg of a mixture consisting of 362 mg (17%) of **10b** and 32 mg (3%) of **33**. Further elution gave 127 mg (6%) of **18b** and 436 mg of a mixture consisting of 357 mg (34%) of **6b**, 42 mg (4%) of **32** and 37 mg of α-**34**. Continued elution yielded 189 mg of a mixture consisting of 179 mg (total 216 mg, 10%) of α-**34** and 10 mg of β-**34**. Further elution gave 30 mg of a mixture consisting of 18 mg (total 28 mg, 1%) of β-**34** and 12 mg (0.5%) of **36**.

2-(2-Benzamido-1-methyl-2-propyl)anthracene (**18b**)

m.p. 152–154 °C. – IR: ν/cm^{-1} = 3 300, 1 640, 1 545. – ^{1}H NMR: δ/ppm = 1.55 (s, 2Me), 3.80 (d, J = 6.6, NCH_2), 5.80 (s br, NH), 7.30–7.70 (m, COPh), 7.73 (m_c, 3-H, 6-H, 7-H), 7.95 (s, 1-H), 8.02 (m_c, 4-H, 5-H, 8-H), 8.43 (s, 9-H, 10-H). – MS (134 °C): *m/z* = 353 (30, M^+), 232 (31, M – $PhCONH_2$), 219 (M – $PhCONHCH_2$), 204 (219 – Me), 191 (9), 178 (19, Oxa-H^+), 105 (25, PhCO).

$C_{25}H_{23}NO$	Calcd.:	C 84.95	H 6.56	N 3.96
(353.47)	Found:	C 84.73	H 6.70	N 4.04.

cis-9-(2-Benzamido-1-methyl-2-propyl)-10-hydroxy-9,10-dihydroanthracene (α-**34**)

m.p. 184–186 °C (MeOH/ether). – IR: ν/cm^{-1} = 3 340, 1 640, 1 535. – ^{1}H NMR: δ/ppm = 1.21 (s, 2Me), 3.17 (d, J = 6.7, NCH_2), 3.87 (s, NCCCH), 5.84 (s, CHO), 6.89 (t br, $J \approx 6$, NH), 7.11 (d, J = 8.0, 1-H, 8-H), 7.57 (d, J = 7.8, 4-H, 5-H), 7.22–7.45 (m, Ph). – MS (161 °C): *m/z* = 353 (0.3, M – H_2O), 178 (91, **A**), 176 (74, Oxa-H^+) 105 (100, PhCO).

$C_{25}H_{25}NO_2$	Calcd.:	C 80.83	H 6.78	N 3.77
(371.48)	Found:	C 80.90	H 6.69	N 3.80.

trans-9-(2-Benzamido-1-methyl-2-propyl)-10-hydroxy-9,10-dihydroanthracene (β-**34**)

m.p. 169–171 °C. – IR: ν/cm^{-1} = 3 340, 1 640, 1 535. –

^{1}H NMR (in mixture with **36**): δ/ppm = 1.17 (s, 2Me), 3.04 (d, J = 6.8, NCH_2), 3.82 (s, NCCCH), 5.30 (s, CHO), 7.03 (d, J = 8.0, 1-H, 8-H), 7.54 (d, J = 7.8, 4-H, 5-H), 7.20 – 7.43 (m, Ph together with Ph of **36**).

$C_{25}H_{25}NO_2$	Calcd.:	C 80.83	H 6.78	N 3.77
(371.48)	Found:	C 80.82	H 6.77	N insufficient material

1-(2-Benzamido-1-methyl-2-propyl)-4-hydroxy-1,4-dihydroanthracene (**36**)

Only in mixture with β-**34**. – ^{1}H NMR: δ/ppm = 1.20 (s, 1Me), 1.28 (s, 1Me), 3.23 (m_c, NCH_2), 3.45 (d br, J = 5.0, NCCCH), 5.45 (d br, J = 5.0, CHO), 6.37 (dd, J = 10.4/5.1, NCCCCH=C), 6.48 (dd, J = 10.4/5.1, NCCCC=CH), 6.95 (t br, J ca 5, NH), 7.77 (s, 9-H), 7.97 (s, 10-H).

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Address for correspondence:
Prof. Dr. H. Stamm
University of Heidelberg,
Faculty of Pharmacy
Tannenweg 26
D-69190 Walldorf
Fax: Internat. code (0)6227-81039