The Chemistry of Polycyclic Arene Imines. V. Reactions of Phenanthrene 9,10-Imine with Nucleophiles under Phase Transfer Conditions [1]

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Reactions of phenanthrene 9,10-imine (**1**) with alkyl halides, sodium azide and ammonium thiocyanate in two liquid phase systems were investigated. In the presence of aqueous sodium hydroxide and alkyl halides triethylbenzylammonium (TEBA) salts promote *N*-alkylation of **1** with preservation of the aziridine ring. Tetrabutylammonium (TBA) salts catalyze nucleophilic substitutions in which the three membered ring is cleaved. Aqueous sodium azide reacts with **1** to give *trans*-10-azido-9,10-dihydro-9-phenanthrenamine (**2**). Ammonium and potassium thiocyanate cause expansion of the aziridine ring; while the unsubstituted imine **1** yields the 2-thiazolamine derivative **4**, *N*-butylphenanthrene 9,10-imine (**8**) froms *trans*-3a,11b-dihydro-3-butylphenanthro[9,10-*d*]thiazol-2-imine (**9**) with an exocyclic C=N bond. The structure of **9** was established by X-ray crystal analysis.

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In a previous paper [2] we have shown that phenanthrene 9,10-imine (1a,9b-dihydro-1*H*-phenanthro[9,10-*b*]azirine) (**1**) undergoes *N*-alkylation by alkyl halides, sodium hydroxide and triethylbenzylammonium (TEBA) salts under phase transfer conditions. We now find that by replacing the highly accessible [3] phase transfer catalyst by one of low accessibility [*e.g.*, a tetrabutylammonium (TBA) salt], **1** becomes less susceptible to *N*-alkylation but tends, instead to undergo nucleophilic aziridine ring opening. The superiority of TEBA in the alkylation reactions is demonstrated by the examples given in Table 1. It can be seen that in general TEBA leads to substantially higher yields than TBA salts even when the TEBA-promoted processes are conducted at lower temperature and for shorter periods. In fact TBA is completely inactive in reactions in which the alkylation agent is allyl chloride, benzyl chloride or isopropyl bromide. The relatively small difference between the activities of TEBA and TBA salts in *N*-butylation by 1-iodobutane may be attributed to the large excess of the phase transfer catalyst that had to be employed in order to overcome the "poisoning effect" of the lipophilic iodide anion [4].

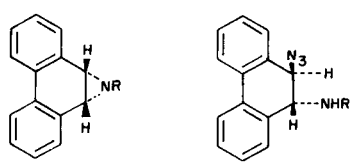
Table 1

Alkylation of **1** under Phase Transfer Catalysis Conditions [a]

Alkyl halide	Phase transfer catalyst [b]	Reaction temperature (°C)	Reaction time (hours)	Yield (%)
CH_2=$CHCH_2Cl$	A	37	48	66
CH_2=$CHCH_2Cl$	B	37	48	0
$(CH_3)_2CHBr$	A	37	48	22
$(CH_3)_2CHBr$	B	37	48	0
$CH_3(CH_2)_3Br$	A	20	24	37
$CH_3(CH_2)_3Br$	B	37	24	9
$CH_3(CH_2)_3I$	A	20	24	72
$CH_3(CH_2)_3I$	B	20	24	61
$C_6H_5CH_2Cl$	A	20	24	20
$C_6H_5CH_2Cl$	B	37	24	0
$C_6H_5CH_2Br$	A	20	8	94
$C_6H_5CH_2Br$	B	37	24	48

[a] Reaction conditions: except for the reactions in which 1-iodobutane was used, a mixture of 1.3 mmoles of **1**, 0.3 mmole of the phase transfer catalyst, 33 mmoles of alkyl halide in 15 ml of dichloromethane and 20 ml of 50% aqueous sodium hydroxide was stirred with a magnetic stirring unit operating at *ca.* 300 rpm. The reactions with 1-iodobutane were carried out in the presence of 6 mmoles of the phase transfer catalyst. [b] A = triethylbenzylammonium chloride or bromide; B = tetrabutylammonium hydrogensulfate.

Although TEBA salts were found to be very active alkylation catalysts, they proved completely inactive for nucleophilic ring opening of the aziridine moiety of **1** by neutral or basic sodium azide solutions. TBA salts, however, promoted under phase transfer conditions, smooth and quantitative conversion of **1** at room temperature (24 hours) into *trans*-9,10-dihydro-10-azido-9-phenanthrenamine (**2**). The latter labile compound could be transformed into its *N*-acetyl derivative **3** by acetic anhydride and pyridine.



1 R = H
8 R = $(CH_2)_3CH_3$

2 R = H
3 R = $COCH_3$

The pronounced difference in the activities of TEBA and TBA salt in the two phase transfer reactions could be explained in terms of the different mechanisms of the two processes. In analogy to some other phase transfer alkylations by alkyl halides and aqueous sodium hydroxide [3], the reaction of **1** is assumed to involve initial abstraction of the nitrogen-bound proton by the hydroxide ion. Since

the more active catalyst is the one of the higher accessibility, it can be concluded that the proton abstraction takes place at the layers' interface [3] and that the hydroxide ion transfer follows Makosza's phase transfer mechanism [5] (Scheme 1).

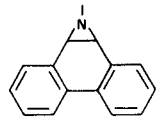
Scheme 1

Step 1: $Na^+aq + OH^-aq + GNH\ org \rightleftharpoons [Na^+GN^-]\ int + H_2O$

Step 2: $[Na^+GN^-]\ org + [Q^+X^-]\ org \rightleftharpoons [Q^+GN^-]\ org + Na^+aq + X^-aq$

Step 3: $[Q^+GN^-]\ org + RX'\ org \rightarrow GNR\ org + [Q^+X^-]\ org$

Q^+X^- = quarternary ammonium salt
RX' = alkyl halide

GN = 

Stark's mechanism [6] [7], which suggests hydroxide ion transfer from the aqueous layer *into* the organic phase in the initial step (Scheme 2) can at most play a minor role in the alkylation process.

Scheme 2

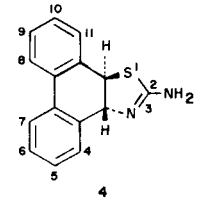
Step 1: $[Q^+X^-]\ org + OH^-\ aq \rightleftharpoons [Q^+OH^-]\ org + X^-\ aq$

Step 2: $[Q^+OH^-]\ org + GNH\ org \rightleftharpoons [Q^+GN^-]\ org + H_2O$

On the other hand in the reaction of **1** with sodium azide, the nucleophile is transferred into the substrate-containing layer by Stark's mechanism for which TBA is a much better catalyst than TEBA [3]. We assume, therefore, that the attack of the "naked" nucleophile by an S_N2 mechanism takes place entirely in the organic phase.

Thiocyanate ion was found to react with **1** similarly to azide under phase transfer conditions. This reagent causes, however, expansion of the aziridine ring to give a five membered thiazoline structure. In this process both TEBA and TBA proved active, though the latter led to considerably higher yields. E.g., while 92% of *trans*-3a,11b-dihydrophenanthro[9,10-*d*]thiazol-2-amine (**4**) was formed upon treatment of **1** in dichloromethane with excess ammonium thiocyanate and catalytic amounts of TBA hydrogensulfate (molar ratio 1:20:0.01, respectively) for 48 hours at 20°, only 3% of **4** was obtained when TEBA bromide was used as the phase transfer catalyst.

A *trans* configuration for the fused thiazoline ring in **4** was suggested on basis of both the indicative H3a,H11b coupling constant and the unequivocal X-ray analysis of the analogous thiocyanation product of *N*-butylphenanthrene 9,10-imine described below. By heating **4** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), the heterocyclic ring was dehydrogenated to give phenanthro[9,10-*d*]-thiazol-2-amine (**5**).



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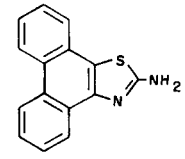

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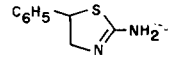
Although all reactions of aziridines and thiocyanate reported previously were performed in acidic media [8] [9], we found that the acids that rearrange arene imines [10] [11] are unnecessary, provided the reactions are carried out under phase transfer conditions. In fact nucleophilic ring opening in **1** by ammonium thiocyanate (as well as by sodium azide) was best performed under neutral or basic conditions. We now find that this applies also to simple ethylenimine derivatives that are not fused to aromatic moieties. Thus, we obtained 4,5-dihydro-5-phenyl-2-thiazolamine (**6**) from a dichloromethane solution of phenylethylenimine and TBA hydrogensulfate in the presence of ammonium thiocyanate in either water or 5% aqueous sodium bicarbonate.

The structure of 2-thiazolamines raised some controversy in the early literature. While Gabriel and Colman [12] described their reaction product of 1-phenyl-2-chloroethylamine hydrochloride and potassium thiocyanate as 4,5-dihydro-5-phenyl-2(3*H*)-thiazolimine (**7**) [13], and Mousseron *et al.* [14] [15] formulated the corresponding product of *cis*-2-chlorocyclohexylamine as *trans*-3a,4,5,6,7,7a-hexahydro-2-benzothiazolimine, Wohl and Headley [16] argued that the more stable 2-thiazolamine tautomers, with endocyclic double bonds, should always prevail.



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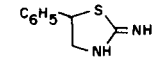

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The fact that the pmr singlets of **4** and **6** which disappear by deuterium oxide addition integrate exactly for two protons, and that the ir spectra include typical NH_2 bands at ~3420-3430 and 1590-1600 cm^{-1}, [14] indicates that both compounds exist as thiazolamines rather than as thiazolimines.

Reaction of *n*-butylphenanthrene 9,10-imine (**8**) [2] with aqueous potassium thiocyanate in the presence of TBA hydrogen sulfate gave, as in the above mentioned thiocyanation of **1**, a thiazoline derivative. However, as no alkyl migration from N3 to N2 took place the resulting product contained an exocyclic rather than an endocyclic C=N bond. The compound was unequivocally identified as *trans*-9a,11b-dihydro-3-butylphenanthro[9,10-*d*]thiazol-2-imine (**9**) on basis of analytical and spectral data (See Experimental) and on X-ray structure determination. Crystal

data are given in Table 2, atomic coordinates in Table 3 and selected bond lengths and angles in Table 4. Figure 1 shows a stereoscopic view of **9** in which the *trans* fusion of the thiazoline and dihydrophenanthrene moieties can be clearly visualized [17].

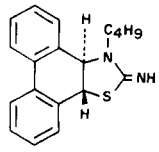

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Table 2

Crystallographic Data of Compound **9**

formula: $C_{19}H_{20}N_2S$	Z = 8
molecular weight = 308.448	ϱ_{calcd} = 1.27 g cm^{-3}
space group: I/2c	μ(Mo Kα) = 0.79 cm^{-1}
a = 21.908 Å	number of unique reflections 2799
b = 7.996 Å	number of reflections with I ≥ 3σ(I) 1857
c = 19.286 Å	R = 0.053
β = 106.84°	R_w = 0.089
V = 3234 Å^3	

Table 3

Final Positional Parameters for **9** with Estimated Standard Deviations in Parenthesis

Atom	X	Y	Z
S(1)	.18165(4)	.3777(1)	.64629(5)
C(2)	.1135(2)	.3284(5)	.5732(2)
N(2a)	.0577(2)	.3124(7)	.5780(2)
N(3)	.1290(1)	.3002(3)	.5094(1)
C(3a)	.1980(1)	.2763(4)	.5232(1)
C(3b)	.2277(1)	.3150(4)	.4635(2)
C(4)	.1946(2)	.3482(4)	.3912(2)
C(5)	.2274(2)	.3755(5)	.3408(2)
C(6)	.2930(2)	.3691(5)	.3611(2)
C(7)	.3265(2)	.3382(4)	.4328(2)
C(7a)	.2953(1)	.3126(3)	.4849(2)
C(7b)	.3300(1)	.2935(4)	.5633(2)
C(8)	.3934(2)	.2392(4)	.5868(2)
C(9)	.4254(2)	.2361(6)	.6598(2)
C(10)	.3953(2)	.2849(6)	.7101(2)
C(11)	.320(2)	.3367(5)	.6881(2)
C(11a)	.2994(1)	.3391(4)	.6145(2)
C(11b)	.2307(1)	.3925(4)	.5854(2)
C(12)	.0852(2)	.1906(4)	.4558(2)
C(13)	.0299(1)	.2869(5)	.4051(2)
C(14)	−.0151(2)	.1721(5)	.3497(2)
C(15)	−.0682(2)	.2673(6)	.2964(2)

Table 4

Selected Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

Bond Lengths

S(1)-C(2)	1.776(3)	C(7)-C(7a)	1.386(5)
S(1)-C(11b)	1.811(3)	C(7a)-C(7b)	1.490(4)
C(2)-N(2a)	1.259(5)	C(7b)-C(8)	1.399(4)
C(2)-N(3)	1.386(5)	C(7b)-C(11a)	1.393(5)
N(3)-C(3a)	1.468(3)	C(8)-C(9)	1.381(5)
N(3)-C(12)	1.479(4)	C(9)-C(10)	1.379(6)
C(3a)-C(3b)	1.510(4)	C(10)-C(11)	1.391(5)
C(3a)-C(11b)	1.522(3)	C(11)-C(11a)	1.392(4)
C(3b)-(C4)	1.398(4)	C(11a)-C(11b)	1.508(4)
C(3b)-C(7a)	1.418(4)	C(12)-C(13)	1.526(4)
C(4)-C(5)	1.383(5)	C(13)-C(14)	1.531(4)
C(5)-C(6)	1.377(5)	C(14)-C(15)	1.515(5)
C(6)-C(7)	1.386(4)		

Bond Lengths

C(2)-S(1)-C(11b)	91.2(2)	C(3b)-C(7a)-C(7b)	118.7(3)
S(1)-C(2)-N(2a)	125.1(4)	C(7)-C(7a)-C(7b)	122.5(3)
S(1)-C(2)-N(3)	111.9(3)	C(7a)-C(7b)-C(8)	121.8(3)
N(2a)-C(2)-N(3)	122.9(4)	C(7a)-C(7b)-C(11a)	118.9(3)
C(2)-N(3)-C(3a)	111.7(3)	C(8)-C(7b)-C(11a)	119.2(3)
C(2)-N(3)-C(12)	116.1(3)	C(7b)-C(8)-C(9)	120.0(3)
C(3a)-N(3)-C(12)	118.4(2)	C(8)-C(9)-C(10)	120.5(4)
N(3)-C(3a)-C(3b)	118.9(3)	C(9)-C(10)-C(11)	120.5(4)
N(3)-C(3a)-C(11b)	106.7(2)	C(10)-C(11)-C(11a)	119.1(3)
C(3b)-C(3a)-C(11b)	105.5(2)	C(7b)-C(11a)-C(11)	120.7(3)
C(3a)-C(3b)-C(4)	125.9(3)	C(7b)-C(11a)-C(11b)	116.3(3)
C(3a)-C(3b)-C(7a)	114.8(3)	C(11)-C(11a)-C(11b)	123.0(3)
C(4)-C(3b)-C(7a)	119.3(3)	S(1)-C(11b)-C(3a)	103.8(2)
C(3b)-C(4)-C(5)	120.4(4)	S(1)-C(11b)-C(11a)	117.1(2)
C(4)-C(5)-C(6)	120.4(4)	C(3a)-C(11b)-C(11a)	108.2(2)
C(5)-C(6)-C(7)	119.9(3)	N(3)-C(12)-C(13)	112.5(3)
C(6)-C(7)-C(7a)	121.3(4)	C(12)-C(13)-C(14)	112.0(3)
C(3b)-C(7a)-C(7)	118.7(3)	C(13)-C(14)-C(15)	112.6(4)

EXPERIMENTAL

trans-10-Azido-9,10-dihydro-9-phenanthrenamine (**2**).

A mixture of 300 mg (1.55 mmoles) of **1**, 100 mg (0.29 mmole) of TBA hydrogensulfate, 1.5 g (23.4 mmoles) of sodium azide, 10 ml of dichloromethane and 5 ml of deionized water (or 5% aqueous sodium bicarbonate) was stirred at room temperature for 5 hours. The orange precipitate was extracted with dichloromethane, and the combined organic layers were washed with water, dried and concentrated. Flash chromatography on Wolem neutral alumina of activity III (a mixture of 80% ether and 20% hexane served as eluent) afforded 290 mg (79%) of **2** as a colorless oil that darkened on prolonged exposure to air; ir (neat): 3360, 3290 (NH_2), 2093 cm^{-1} (N_3); uv (dichloromethane): λ max (log ϵ) 229.7 (4.03), 271.6 nm (4.19); 300 MHz pmr (deuteriochloroform): δ 1.628 (s, 2H, NH_2), 3.958 (d, 1H, $J_{9,10}$ = 4.8 Hz, H9 or H10), 4.451 (d, 1H, $J_{9,10}$ = 4.8 Hz, H9 or H10), 7.228-7.443 (m, 6H, H1, H2, H3, H6, H7, H8), 7.767 (dd, 1H, J_o = 7.0 Hz, J_m = 1.5 Hz, H4 or H5), 7.808 (dd, 1H, J_o = 7.4 Hz, J_m = 0.8 Hz, H4 or H5); ms: (70 eV, 25°) m/e (relative intensity) 236 ($M^{+\cdot}$, 9), 207 ($C_{14}H_{11}N_2^+$, 20), 193 ($C_{14}H_{13}N^{+\cdot}$, 14), 180 ($C_{13}H_{10}N^+$, 100), 178 ($C_{14}H_{10}^{+\cdot}$, 18), 165 ($C_{13}H_9^+$, 21), 152 ($C_{12}H_8^{+\cdot}$, 17).

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.13; H, 5.12; N, 23.71. Found: C, 70.86; H, 5.29; N, 24.19.

No **2** was formed when either the reaction mixture was stirred without the phase transfer catalyst or when the TBA salt was replaced by TEBA chloride.

trans-*N*-Acetyl-10-azido-9,10-dihydro-9-phenanthrenamine (**3**).

To a cooled solution (0°) of 120 mg (0.51 mmole) of **2** in 10 ml of dichloromethane was added 1.5 ml of dry pyridine and 1.0 ml of acetic anhydride. The mixture was allowed to warm to room temperature, stirred for 3 hours, diluted with 10 ml of chloroform and washed successively

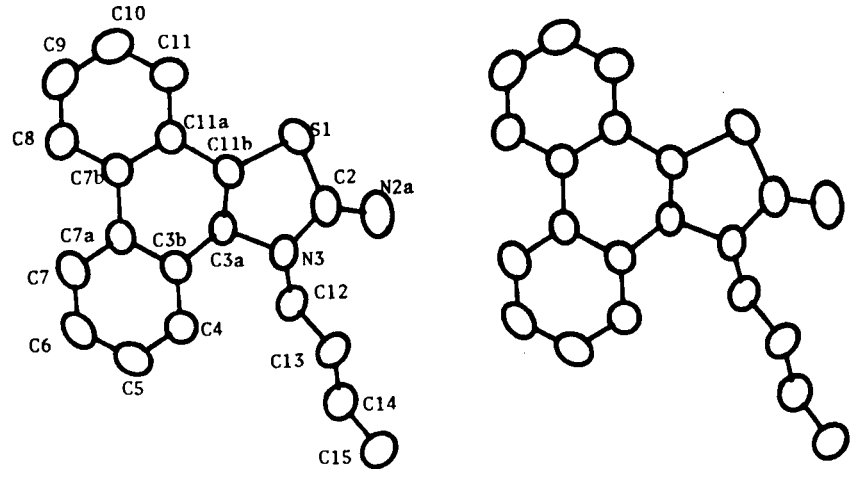

Figure 1. Stereoscopic view of compound **9**

with 5% hydrochloric acid, water, 3% aqueous sodium hydroxide and water. The organic solution was dried and concentrated. Upon addition of ether and hexane (1:1) 138 mg (98%) of colorless **3** separated, mp 176-177° (from ether); ir (nujol): 3225 (NH), 2103 (N_3), 1649 cm^{-1} (C=O); 300 MHz pmr (deuteriochloroform): δ 1.836 (s, 3H, CH_3), 4.745 (d, 1H, $J_{9,10}$ = 3.7 Hz, H10), 5.185 (dd, 1H, $J_{9,10}$ = 3.7 Hz, $J_{9,NH}$ = 7.4 Hz, H9), 5.547 (br d, 1H, $J_{9,NH}$ = 7.4 Hz), 7.344-7.541 (m, 6H, H1, H2, H3, H6, H7, H8), 7.852 (d, 1H, J_o = 7.7 Hz, H4 or H5), 7.895 (d, 1H, 8.1 Hz, H4 or H5); ms: (70 eV, 160°) m/e (relative intensity) 250 [$(M-N_2)^{+\cdot}$, 17], 220 ($C_{15}H_{10}NO^{+\cdot}$, 17), 208 ($C_{14}H_{10}NO^+$, 79), 192 ($C_{14}H_{10}N^+$, 63), 180 ($C_{13}H_{10}N^+$, 100), 165 ($C_{13}H_9^+$, 20), 152 ($C_{12}H_8^{+\cdot}$, 17).

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07. Found: C, 68.76; H, 4.99.

trans-3a,11b-Dihydrophenanthro[9,10-*d*]thiazol-2-amine (**4**).

A mixture of 250 mg (1.30 mmoles) of **1**, 50 mg (0.15 mmole of TBA hydrogensulfate, 2.0 g of either ammonium or potassium thiocyanate, 20 ml of dichloromethane and 6 ml of deionized water was stirred at room temperature for 48 hours. Dichloromethane was added until all the precipitate had dissolved. The organic solution was washed with water, dried over magnesium sulfate and filtered first through a 5 cm thick layer of active carbon and then through 5 cm of silica gel (type Merck-9385, 230-400 mesh) by applying a vacuum pump and ether as eluent. Upon concentration of the filtrate 300 mg (92%) of **4** separated as colorless crystals, mp 210° (from chloroform-ether); ir (nujol): 3428, 3405, 1600, 1590 (NH_2), 1310, 1209 cm^{-1} (CN); uv (dichloromethane): λ max (log ϵ) 229.2 (4.04), 269.2 (4.12), 293.5 nm (3.58 sh); 300 MHz pmr (hexadeuteriodimethylsulfoxide): δ 4.560 and 4.661 (ABq, 2H, J_{AB} = 14.7 Hz, H3a, H11b), 6.92 (s, 2H, disappears by deuterium oxide NH_2), 7.122 (d, 1H, $J_{4,5}$ = 7.3 Hz, H4), 7.319-7.451 (m, 4H, H5, H6, H9, H10), 7.678 (dd, 1H, $J_{10,11}$ = 5.1 Hz, $J_{9,11}$ = 12 Hz, H11), 7.834 (dd, 1H, $J_{8,9}$ = 5.0 Hz, $J_{8,10}$ = 1.5 Hz, H8); 7.870 (d, 1H, $J_{6,7}$ = 8.1 Hz, H7); ms: (70 eV, 150°) m/e (relative intensity) 252 ($M^{+\cdot}$, 100), 219 ($C_{15}H_{11}N_2^+$, 32), 210 ($C_{14}H_{10}S^{+\cdot}$, 70), 193 ($C_{14}H_{11}N^{+\cdot}$, 40), 178 ($C_{14}H_{10}^{+\cdot}$, 51), 165 ($C_{13}H_9^+$, 68).

Anal. Calcd. for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79; N, 11.10; S, 12.70. Found: C, 71.65; H, 4.88; N, 10.75; S, 12.27.

In the absence of the phase transfer catalyst no **4** was formed.

Phenanthro[9,10-*d*]thiazol-2-amine (**5**).

A solution of 150 mg (0.595 mmole) of **4** and 147 mg (0.633 mmole) of DDQ in 40 ml of toluene was refluxed for 18 hours. The solvent was removed *in vacuo*, and the residue chromatographed on silica gel (a mixture of 80% ether and 20% hexane served as eluent) to yield 31 mg (21%) of **5**, as red-brown crystals, mp 245-246°; ir (nujol): 3439, 3295, 1640, 1563 cm^{-1} (NH_2); uv (dichloromethane): λ max (log ϵ) 261.3 (4.56), 318.1 (3.98), 326.0 (3.98), 340 (3.49), 364 nm (2.97); 300 MHz pmr (deuteriochloroform): δ 5.297 (s, 2H, NH_2), 7.566-7.672 (m, 4H, H2, H3, H6, H7), 7.756 (dd, 1H, J_o = 7.0 Hz, J_m = 1.9 Hz, H1 or H8), 8.579 (dd, 1H, J_o = 7.0 Hz, J_m = 1.9 Hz, H1 or H8), 8.697 (superimposed d, 2H, $J_{3,4}$ = $J_{5,6}$ = 7.0 Hz, H4, H5); ms: (70 eV, 70°) m/e (relative intensity) 250 ($M^{+\cdot}$, 100), 222 ($C_{14}H_8NS^+$, 12), 190 ($C_{14}H_8N^+$, 26), 178 ($C_{14}H_{10}^{+\cdot}$, 9), 111 ($C_5H_5NS^{+\cdot}$, 23), 98 ($C_4H_4NS^+$, 30).

Anal. Calcd. for $C_{15}H_{10}N_2S$: C, 71.97; H, 4.03; N, 11.19; S, 12.81. Found: C, 72.28; H, 4.22; N, 10.86: S, 12.95.

4,5-Dihydro-5-phenyl-2-thiazolamine (**6**).

As for **4**, a mixture of 304 mg (2.55 mmoles) of phenaylethylenimine, 2.0 g (26.3 mmoles) of ammonium thiocyanate, 30 mg (0.09 mmole) of TBA hydrogensulfate, 10 ml of dichloromethane, and 4 ml of deionized water was stirred vigorously for 14 hours. The resulting solids were extracted with dichloromethane and the combined organic solutions dried and the solvent removed by distillation. The residue was extracted with dry ether, filtered from some inorganic salts and concentrated. The resulting oil was crystallized from a mixture of hexane and dichloromethane (20:1) to yield 186 mg (33%) of analytically pure **4**, mp 111-112° (lit [13] 111-112°); uv (dichloromethane): λ max (log ϵ) 229.2 nm (4.10); 300 MHz pmr (deuteriochloroform): δ 4.042 (dd, 1H, $J_{4,4'}$ = 13.6 Hz, $J_{4,5}$ = 5.9 Hz, H4), 4.297 (dd, 1H, $J_{4,4'}$ = 13.6 Hz, $J_{4,5}$ = 8.1 Hz, H4'), 5.022 (dd, 1H, $J_{4,5}$ = 5.9 Hz, $J_{4',5}$ = 8.1 Hz, H5), 7.250-7.383 (m, 5H, Ar*H*); ms: (70 eV, 50°) m/e (relative intensity) 178 ($M^{+\cdot}$, 100), 136 ($C_8H_8S^{+\cdot}$, 64), 135 ($C_8H_7S^+$, 66), 123 ($C_7H_7S^+$, 69), 121 ($C_7H_5S^+$, 32), 119 ($C_8H_9N^{+\cdot}$, 38), 118 ($C_8H_8^{+\cdot}$, 36), 103 ($C_8H_7^+$, 30), 91 ($C_7H_7^+$, 81). The absence of a benzylamine ion and the presence of highly abundant benzyl mercaptan and phenylthiocarbonyl fragments indicates that the phenyl group in **6** is attached to C5 rather than to C4 of the thiazoline ring.

trans-3a,11b-Dihydro-3-butylphenanthro[9,10-*d*]thiazol-2-imine (**9**).

A mixture of 50 mg (2 mmoles) of **8** [2], 2.9 g (32.6 mmoles) of potassium thiocyanate, 200 mg (0.6 mmole) of TBA hydrogensulfate, 20 ml of dichloromethane, and 5 ml of water was stirred vigorously for 48 hours. The dichloromethane soluble compounds were separated by flash chromatography on Wolem alumina for dry columns of activity III (hexane-ether mixtures served as eluents) to give **9** as an oil that crystallized from *n*-hexane, yield 296 mg (41%), mp 96-97° (from *n*-hexane); ir (nujol): 3320, 3240, 1608, 1480, 1300, 1282, 1265, 1183, 1145, 1097, 1080, 932, 750 cm^{-1}; 300 MHz pmr (deuteriochloroform): δ 0.927 (t, 3H, J = 7.4 Hz, CH_3), 1.346 (sextet, 2H, J = 7.4 Hz, CH_2CH_3), 1.685-1.876 (m, 2H, $CH_2C_2H_5$), 3.342 (ddd, 1H, J_a = 13.9 Hz, J_b = 9.6 Hz, J_c = 5.5 Hz,

NCHH), 3.848 (ddd, 1H, J_a = 13.9, J_b = 9.6 Hz, J_c = 5.5 Hz, NCHH), 4.500 and 4.644 (ABq, 2H, J_{AB} = 13.7 Hz, H3a, H11b), 7.086 (d, 1H, $J_{4,5}$ = 7.4 Hz, H4), 7.314, 7.460 (m, 4H, H5, H6, H9, H10), 7.556 (d, 1H, $J_{10,11}$ = 7.0 Hz, H11), 7.737 (dd, 1H, J_8 = 7.8 Hz, $J_{8,10}$ = 1.6 Hz, H8), 7.797 (dd, 1H, $J_{6,7}$ = 7.4 Hz, $J_{5,7}$ = 0.9 Hz, H7); ms: (70 eV, 120°) m/e (relative intensity) 308 ($M^{+\cdot}$, 3), 252 ($C_{15}H_{12}N_2S^{+\cdot}$, 25), 251 ($C_{15}H_{11}N_2S^+$, 15), 219 ($C_{15}H_{11}N_2S^+$, 12), 210 ($C_{14}H_{10}S^{+\cdot}$, 100), 193 ($C_{14}H_{13}N^{+\cdot}$, 17), 178 ($C_{14}H_{10}^{+\cdot}$, 79), 165 ($C_{13}H_9^+$, 22).

Anal. Calcd. for $C_{19}H_{20}N_2S$: C, 73.99; H, 6.54. Found: C, 73.85; H, 6.56.

X-Ray Crystal Structure Analysis of **9**.

Data were measured on a PW 1100/20 Philips four-circle computer-controlled diffractrometer. Mo K_α (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. the unit cell dimensions were obtained by a least-squares fit of 20 centered reflexions in the range of $10 > \theta > 13°$. Intensity data were collected using the $\omega - 2\theta$ technique to a maximum of 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was 0° with a scan time of 20 seconds. Background measurements were made for other 20 seconds at both limits of each scan. Three standard reflections were monitored every 60 minutes. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the MULTAN direct method analysis [18]. After several cycles of refinements [19] the positions of the hydrogen atoms were calculated, and added with a constant isotropic temperature factor of 0.5 Å, to the refinement process. Refinement proceeded to convergence by minimizing function $\Sigma w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(f)^{-2}$. A final difference Fourier synthesis map showed several peaks less than 0.4 e $Å^{-3}$ scattered about the unit cell without a significant feature.

The discrepency indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table 2. Selected positional parameters, bond lengths and angles are given in Table 3 and Table 4 [17].

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