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Phenanthrene 9,10-imine (**1**) was shown to react with allyl bromide and 50% aqueous sodium hydroxide under phase transfer catalysis conditions to give the title compound **3** as the only product. The starting imine **1** is assumed to undergo initially bis alkylation to form an *N,N*-di-(2-propenyl)phenanthrene 9,10-iminium salt (**4**) which, in turn, is attacked by a deprotonated phenanthrene imine anion (**5**). The structure of **3** has been determined by a single crystal X-ray diffraction analysis.

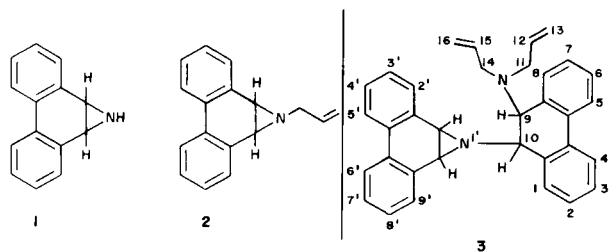
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Recently [2] we reported that phenanthrene 9,10-imine (1a,9b-dihydro-1*H*-phenanthro[9,10-*b*]azirine) (**1**) can be *N*-alkylated by alkyl halides both under unhydrous conditions in the presence of sodium hydride or methylsulfinylmethide, and in a two liquid phase system of a dichloromethane solution of the two reactants and aqueous sodium hydroxide. Thus, by using allyl chloride as alkylating agent we obtained *N*-(2-propenyl)phenanthrene 9,10-imine (**2**) regardless of which of the two systems was employed. However, by substitution of the allyl *chloride* by the corresponding *bromide* we obtained a compound that has the correct elemental analysis but shows an entirely different pmr spectrum than **2**. (See Figure 1). Owing to the complex nature of this spectrum in which the ratio of aromatic to nonaromatic protons is 8:7 and to the mass spectral data that suggests a dimeric structure, we subjected the compound to single crystal X-ray analysis. The crystallographic data are given in Table 1.

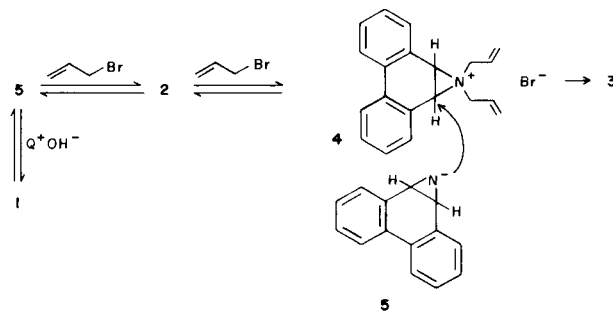
The results indicate cell units of two pairs of similar enantiomers of 1[*N,N*-di-(2-propenyl)-9-phenanthreneamine-10-yl]-1a,9b-phenanthro[9,10-*b*]azirine (**3**). The atomic coordinates for one of the molecules in the cell unit is given in Table 2 and selected bond lengths and angles in Table 3 [3]. ORTEP and stereoscopic drawings are presented in Figure 2 and Figure 3, respectively. In **3** one of

stereoscopic drawing shows that the two nitrogens are in a *trans* configuration which means that the molecules of the analyzed crystal exist as the *threo* isomer [4]. The fact that the pmr spectrum of the single crystal and that of the entire crop are completely identical proves that no geometric isomer other than *threo*-**3** was formed in our reaction of **1** and allyl bromide.

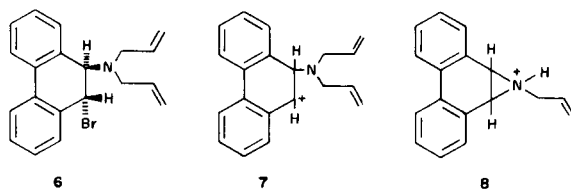
The different products obtained by alkylation of **1** with allyl chloride and bromide can be explained in terms of the higher nucleophilicity of the latter reagent towards the initial product, *N*-(2-propenyl)phenanthrene 9,10-imine (**2**) [2]. Intermediate *N,N*-di-(2-propenyl)phenanthrene 9,10-iminium bromide (**4**) is assumed to be attacked by anion **5** (generated from **1** and the quat-hydroxide ion pair in the presence of the phase transfer catalysis [1]) at position 10 with ring cleavage of the aziridinium structure. Although the quaternary ammonium ion **4** could not be isolated, we have established the intermediacy of **2** by application of the mono-allyl compound as starting material.



the nitrogen atoms is part of an aziridine moiety [C(1')-N(1')-C(9'b) 60.6°; N(1')-C(1'a)-C(9'b) 59.1°; N(1')-C(9'b)-C(1'a) 60.2°] while the other has the characteristics of a tris-alkylated amine [C(9)-N(9a)-C(11) 113.1°; C(11)-N(9a)-C(14) 112.3°; C(9)-N(9a)-C(14) 111.6°]. The



An alternative mechanism in which Br<sup>-</sup> reacts with **4** to form the bromoamine **6** can be excluded by virtue of the stereoselectivity of the process. An S<sub>N</sub>2 reaction of **5** with **6** should have given *erythro*-**3** and the generation of a benzylium ion **7** by an S<sub>N</sub>1 process should have led to a mixture of the *threo*- and *erythro*-isomers rather than to a single compound with a *threo* configuration.



Since no reaction takes place between **1** and allyl bromide in the absence of a base it can also be concluded that the formation of **3** does not involve a pathway in which **1** adds first one molecule of allyl bromide to give **8**, followed by interaction with **5** prior to the final interaction with a second molecule of the allylation reagent.

Table 1  
Crystallographic Data of Compound 3

formula: $C_{34}H_{30}N_2$	$\gamma = 79.51^\circ$
molecular weight = 466.6	$V = 2620 \text{ \AA}^3$
space group P 1	$Z = 4$
$a = 14.532 \text{ \AA}$	$\rho_{\text{calcd}} = 1.18 \text{ cm}^{-3}$
$b = 14.588 \text{ \AA}$	$\mu(\text{Mo K}\alpha) = 0.36 \text{ cm}^{-1}$
$c = 12.688 \text{ \AA}$	number of unit reflections 6712
$\alpha = 93.33^\circ$	reflections with $I \geq 3\sigma(I)$ 4283
$\beta = 97.52^\circ$	$R = 0.098$

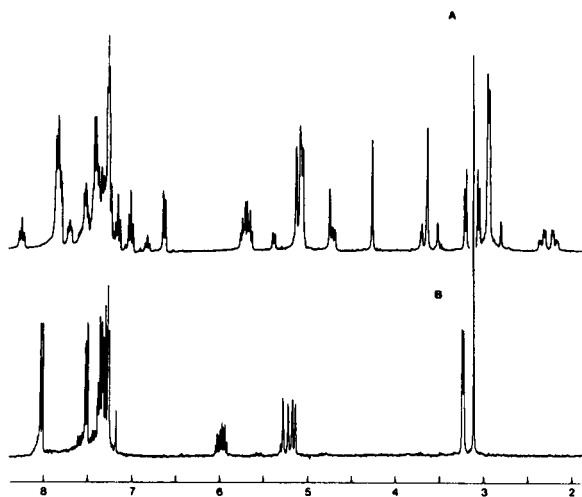


Figure 1. 300 MHz pmr spectra of the alkylation products of phenanthrene 9,10-imine by (A) allyl bromide, (B) allyl chloride.

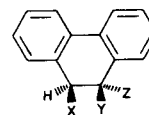
In this study we prepared the starting imine **1** by the Hassner aziridine synthesis [5] which involves reduction of a *trans*-halo azide. So far no chloro azide has yet been converted into an arene imine [6]. Treatment of *trans*-10-azido-9,10-dihydrophenanthren-9-ol (**9**) [7] with thionyl chloride in benzene [8] gave a 1:1 mixture of *cis*- and *trans*-10-azido-9-chloro-9,10-dihydrophenanthrene (**10** and **11**, respectively). While the *trans*-isomer (**11**) proved stable un-

Table 2

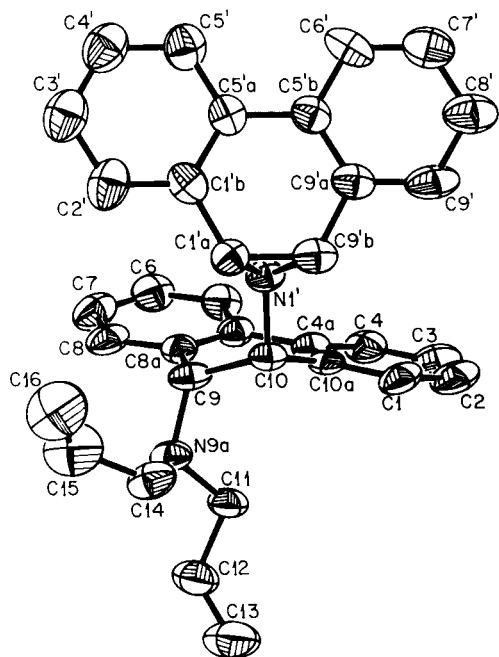
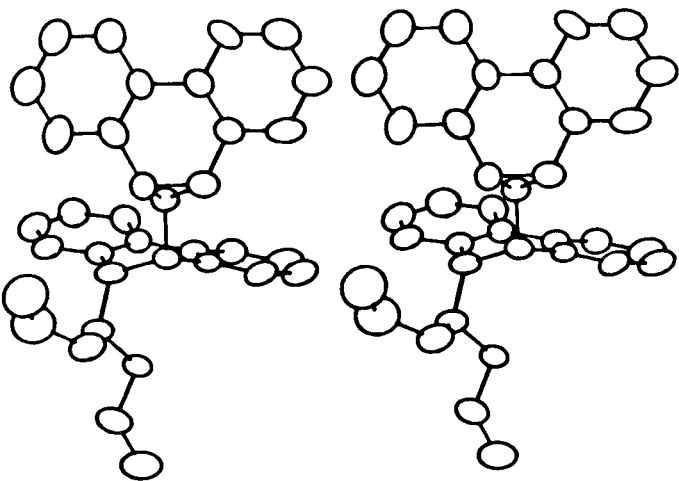
Final Positional Parameters for **3** with Estimated Standard Deviations in Parentheses

Atom	X	Y	Z
C(1)	.4868 (6)	.6961 (5)	.9024 (6)
C(2)	.4005 (7)	.6946 (6)	.9410 (7)
C(3)	.3148 (7)	.7343 (6)	.8826 (7)
C(4)	.3162 (5)	.7739 (5)	.7848 (6)
C(4a)	.4015 (5)	.7749 (5)	.7445 (6)
C(4b)	.4034 (5)	.8190 (5)	.6421 (5)
C(5)	.3197 (6)	.8401 (5)	.5703 (6)
C(6)	.3205 (6)	.8862 (5)	.4771 (7)
C(7)	.4052 (7)	.9112 (6)	.4528 (6)
C(8)	.4882 (6)	.8867 (5)	.5239 (6)
C(8a)	.4869 (5)	.8401 (5)	.6175 (5)
C(9)	.5805 (5)	.8111 (5)	.6858 (5)
C(10)	.5783 (5)	.7300 (4)	.7580 (5)
C(10a)	.4866 (5)	.7371 (4)	.8034 (5)
N(9a)	.6123 (4)	.8941 (4)	.7433 (5)
C(11)	.5590 (6)	.9286 (5)	.8340 (6)
C(12)	.5756 (6)	1.0269 (6)	.8675 (8)
C(13)	.5997 (7)	1.0504 (8)	.9704 (9)
C(14)	.7164 (5)	.8771 (6)	.7752 (6)
C(15)	.7656 (6)	.8782 (7)	.6765 (9)
C(16)	.8329 (7)	.8126 (9)	.6493 (9)
N(1')	.5846 (4)	.6437 (4)	.6876 (4)
C(1'a)	.6827 (5)	.6025 (5)	.6645 (6)
C(1'b)	.6839 (5)	.5576 (5)	.5550 (6)
C(2')	.7282 (6)	.5971 (6)	.4822 (7)
C(3')	.7257 (6)	.5607 (7)	.3758 (7)
C(4')	.6798 (7)	.4836 (7)	.3470 (7)
C(5')	.6376 (6)	.4424 (6)	.4218 (7)
C(5'a)	.6382 (5)	.4803 (5)	.5268 (6)
C(5'b)	.5955 (5)	.4373 (5)	.6066 (6)
C(6')	.5529 (6)	.3588 (5)	.5783 (8)
C(7')	.5142 (6)	.3169 (6)	.6567 (8)
C(8')	.5193 (6)	.3521 (6)	.7619 (8)
C(9')	.5627 (6)	.4305 (5)	.7907 (7)
C(9'a)	.5979 (5)	.4728 (5)	.7118 (6)
C(9'b)	.6362 (5)	.5596 (5)	.7440 (6)

der ambient conditions, **10** underwent spontaneous *trans*-elimination of hydrogen chloride to yield 9-azidophenanthrene (**12**) [7] [9]. Lithium aluminium hydride reduction of **11** (that could be separated readily from **12** by column chromatography) gave **1** in quantitative yield.



- 9** X = OH, Y = H, Z = N<sub>3</sub>  
**10** X = Cl, Y = N<sub>3</sub>, Z = H  
**11** X = Cl, Y = H, Z = N<sub>3</sub>

Figure 2. ORTEP drawing of **3**.Figure 3. Stereoscopic view of **3**.

## EXPERIMENTAL

*trans*-9-Azido-10-chloro-9,10-dihydrophenanthrene (**11**) and 9-Azidophenanthrene (**12**).

A solution of 1.5 g of *trans*-10-azido-9,10-dihydrophenanthren-9-ol (**7**) and 9.5 ml of thionyl chloride in 40 ml of dry benzene was stirred under argon at room temperature. After 48 hours the reaction mixture was diluted with 30 ml of ether and poured on ice. The aqueous layer was extracted with ether and the combined organic solutions were washed with aqueous sodium bicarbonate, dried and concentrated. The yellow oily residue was flash chromatographed on silica gel [10]. The first fraction that was eluted with a mixture of 95% of hexane and 5% of ether yielded

Table 3

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

Bond Lengths			
C(1)-C(2)	1.41 (1)	C(12)-C(13)	1.35 (1)
C(1)-C(10a)	1.42 (1)	C(14)-C(15)	1.52 (1)
C(2)-C(3)	1.41 (1)	C(15)-C(16)	1.30 (1)
C(3)-C(4)	1.40 (1)	N(1')-C(1'a)	1.502 (8)
C(4)-C(4a)	1.40 (1)	N(1')-C(9'b)	1.485 (8)
C(4a)-C(4b)	1.49 (1)	C(1'a)-C(1'b)	1.50 (1)
C(4a)-C(10a)	1.397 (9)	C(1'a)-C(9'b)	1.51 (1)
C(4b)-C(5)	1.42 (1)	C(1'b)-C(2')	1.40 (1)
C(4b)-C(8a)	1.38 (1)	C(1'b)-C(5'a)	1.42 (1)
C(5)-C(6)	1.40 (1)	C(2')-C(3')	1.42 (1)
C(6)-C(7)	1.42 (1)	C(3')-C(4')	1.42 (1)
C(7)-C(8)	1.41 (1)	C(4')-C(5')	1.41 (1)
C(8)-C(8a)	1.41 (1)	C(5')-C(5'a)	1.41 (1)
C(8a)-C(9)	1.519 (9)	C(5'a)-C(5'b)	1.48 (1)
C(9)-C(10)	1.55 (1)	C(5'b)-C(6')	1.41 (1)
C(9)-N(9a)	1.491 (9)	C(5'b)-C(9'a)	1.40 (1)
C(10)-C(10a)	1.50 (1)	C(6')-C(7')	1.42 (1)
C(10)-N(1')	1.497 (8)	C(7')-C(8')	1.40 (1)
N(9a)-C(11)	1.48 (1)	C(8')-C(9')	1.41 (1)
N(9a)-C(14)	1.493 (9)	C(9')-C(9'a)	1.40 (1)
C(11)-C(12)	1.52 (1)	C(9'a)-C(9'b)	1.49 (1)

## Bond Angles

C(2)-C(1)-C(10a)	119.5 (8)	N(9a)-C(14)-C(15)	108.9 (7)
C(1)-C(2)-C(3)	120.3 (8)	C(14)-C(15)-C(16)	124 (1)
C(2)-C(3)-C(4)	119.3 (8)	C(10)-N(1')-C(1'a)	114.4 (5)
C(3)-C(4)-C(4a)	121.2 (8)	C(10)-N(1')-C(9'b)	112.4 (5)
C(4)-C(4a)-C(4b)	121.3 (7)	C(1'a)-N(1')-C(9'b)	60.6 (4)
C(4)-C(4a)-C(10a)	119.5 (7)	N(1')-C(1'a)-C(1'b)	112.2 (6)
C(4b)-C(4a)-C(10a)	119.2 (6)	1(1')-C(1'a)-C(9'b)	59.1 (4)
C(4a)-C(4b)-C(5)	120.2 (6)	C(1'b)-C(1'a)-C(9'b)	118.0 (6)
C(4a)-C(4b)-C(8a)	119.8 (7)	C(1'a)-C(1'b)-C(2')	117.6 (7)
C(5)-C(4b)-C(8a)	120.0 (6)	C(1'a)-C(1'b)-C(5'a)	120.4 (6)
C(4b)-C(5)-C(6)	120.1 (7)	C(2')-C(1'b)-C(5'a)	122.0 (8)
C(5)-C(6)-C(7)	120.4 (9)	C(1'b)-C(2')-C(3')	119.5 (8)
C(6)-C(7)-C(8)	118.4 (7)	C(2')-C(3')-C(4')	118.7 (8)
C(7)-C(8)-C(8a)	120.8 (7)	C(3')-C(4')-C(5')	121.4 (8)
C(4b)-C(8a)-C(8)	120.2 (7)	C(4')-C(5')-C(5'a)	119.6 (8)
C(4b)-C(8a)-C(9)	122.5 (6)	C(1'b)-C(5'a)-C(5')	118.7 (7)
C(8)-C(8a)-C(9)	117.2 (6)	C(1'b)-C(5'a)-C(5'b)	120.9 (7)
C(8a)-C(9)-C(10)	112.0 (5)	C(5')-C(5'a)-C(5'b)	120.4 (7)
C(8a)-C(9)-N(9a)	110.4 (6)	C(5'a)-C(5'b)-C(6')	120.3 (7)
C(10)-C(9)-N(9a)	114.4 (6)	C(5'a)-C(5'b)-C(9'a)	120.9 (6)
C(9)-C(10)-C(10a)	113.6 (6)	C(6')-C(5'b)-C(9'a)	118.8 (7)
C(9)-C(10)-N(1')	106.2 (5)	C(5'b)-C(6')-C(7')	119.5 (8)
C(10a)-C(10)-N(1')	104.8 (5)	C(6')-C(7')-C(8')	120.8 (8)
C(1)-C(10a)-C(4a)	120.2 (7)	C(7')-C(8')-C(9')	119.8 (8)
C(1)-C(10a)-C(10)	119.0 (7)	C(8')-C(9')-C(9'a)	118.7 (8)
C(4a)-C(10a)-C(10)	120.5 (6)	C(5'b)-C(9'a)-C(9')	122.3 (7)
C(9)-N(9a)-C(11)	113.1 (5)	C(5'b)-C(9'a)-C(9'b)	120.9 (6)
C(9)-N(9a)-C(14)	111.6 (6)	C(9')-C(9'a)-C(9'b)	116.8 (7)
C(11)-N(9a)-C(14)	112.3 (6)	N(1')-C(9'b)-C(1'a)	60.2 (5)
N(9a)-C(11)-C(12)	109.2 (6)	N(1')-C(9'b)-C(9'a)	114.3 (6)
C(11)-C(12)-C(13)	121.1 (9)	C(1'a)-C(9'b)-C(9'a)	118.5 (6)

495 mg (36%) of **12** [7] [9]. A second fraction of 620 mg (38%) of **11** was eluted by a mixture of 85% of hexane and 15% of ether. When finally a 1:1 mixture of the solvents was applied, 300 mg of unreacted azido-alco-

hol **9** was recovered. The chloro-azide (**11**) was obtained as a pale yellow oil that solidified on standing, mp 79-81°; ir (nujol): 2100 cm<sup>-1</sup> (N<sub>3</sub>); 300 MHz pmr (deuteriochloroform): δ 4.783 (d, 1H, J<sub>9,10</sub> = 2.9 Hz, H10), 5.140 (d, 1H, J<sub>9,10</sub> = 2.9 Hz, H9), 7.328-7.563 (m, 6H, H1, H2, H3, H6, H7, H8), 7.867 (dd, 1H, J<sub>3,4</sub> = 1.6 Hz, J<sub>3,4</sub> = 7.5 Hz, H4), 7.918 (d, 1H, J<sub>5,6</sub> = 7.7 Hz, H5); ms: (70 eV, 30°) m/e (relative intensity), 257, 255 (M<sup>+</sup>, 20, 61), 229, 227 [(M-N<sub>2</sub>)<sup>+</sup>, 4, 12], 215, 213 [(M-N<sub>2</sub>)<sup>+</sup>, 33, 98], 193 (C<sub>14</sub>H<sub>11</sub>N<sup>+</sup>, 40), 192 (C<sub>14</sub>H<sub>10</sub>N<sup>+</sup>, 99), 191 (C<sub>14</sub>H<sub>9</sub>N<sup>+</sup>, 22), 179 (C<sub>13</sub>H<sub>9</sub>N<sup>+</sup>, 29), 178 (C<sub>14</sub>H<sub>10</sub><sup>+</sup>, 100), 177 (C<sub>14</sub>H<sub>9</sub><sup>+</sup>, 44), 167 (C<sub>13</sub>H<sub>11</sub><sup>+</sup>, 21), 165 (C<sub>13</sub>H<sub>9</sub><sup>+</sup>, 99).

Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>ClN<sub>3</sub>: C, 65.76; H, 3.91; Cl, 13.88; N, 16.44. Found: C, 66.05; H, 4.09; Cl, 13.67; N, 16.00.

#### 1a,9b-Dihydro-1H-phenanthro[9,10-b]azirine (**1**).

To a cooled solution (0°) of 0.5 g of lithium aluminium hydride in 20 ml of dry tetrahydrofuran was added dropwise under argon a solution of 350 mg of **11** in 15 ml of the same solvent. The mixture was stirred at room temperature for 3 hours, and then successively treated with 0.5 ml of water, 0.5 ml of 15% aqueous sodium hydroxide and once again with 1.5 ml of water. The solids were filtered off and washed with 100 ml of dichloromethane. The organic solution was washed with water, and dried on magnesium sulfate. Upon concentration of the solution pure **1** separated in quantitative yield; mp 163-164° (lit [11] mp 163-164°).

#### 1-[N,N-Di-(2-propenyl)-9-phenanthrenamine-10-yl]-1a,9b-dihydrophenanthro[9,10-b]azirine (**3**).

A mixture of 350 mg of **1**, 1.2 g of allyl bromide, 50 mg of triethylbenzylammonium chloride, 10 ml of dichloromethane and 20 ml of 50% aqueous sodium hydroxide was stirred vigorously at 25° for 5.5 hours. The mixture was cooled to 0°, diluted with methylene chloride, washed with water and the organic layer stirred for 2 hours with 100 ml of 10% ammonium hydroxide, washed with water, dried over magnesium sulfate and activated charcoal. The solvent was removed by distillation and the residue recrystallized from a 20:1 mixture of ether and hexane to yield 384 mg (91%) of **3** as colorless crystals, mp 170-172° (ether); ci ms: (isobutane) m/e 467 (M + 1)<sup>+</sup>; ei ms: (70 eV, 160°) m/e (relative intensity) 466 (M<sup>+</sup>, 2), 425 [(M-C<sub>3</sub>H<sub>5</sub>)<sup>+</sup>, 2], 384 [(M-C<sub>6</sub>H<sub>10</sub>)<sup>+</sup>, 2], 370 [C<sub>28</sub>H<sub>20</sub>N<sup>+</sup>, 4], 369 [C<sub>28</sub>H<sub>19</sub>N<sup>+</sup>, 7], 368 [C<sub>28</sub>H<sub>18</sub>N<sup>+</sup>, 4], 287 [C<sub>20</sub>H<sub>10</sub>N<sub>2</sub><sup>+</sup>, 8], 193 [C<sub>14</sub>H<sub>11</sub>N<sup>+</sup>, 100], 178 [C<sub>14</sub>H<sub>10</sub><sup>+</sup>, 40], 165 [C<sub>13</sub>H<sub>9</sub><sup>+</sup>, 50].

Anal. Calcd. for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.36; H, 6.44; N, 5.92.

#### X-Ray Crystal Structure Analysis of **3**.

A suitable crystal was obtained by slow concentration (14 days) of an acetone solution of pure **3**.

Data were measured on a PW 1100/20 Phillips four-circle computer-controlled diffractometer. Mo K<sub>α</sub> (λ = 0.71069 Å) radiation with graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-square fit of 22 centered reflexions in the range of 10 < θ < 12°. Intensity data were controlled using the ω-2θ technique to a maximum of 2θ of 45°. The scan with Δω, for each reflexion was 1° with a scan time of 20 seconds. Background measurements were made for another 20 seconds at both limits of each scan. Three standard reflexions 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 [12]. Hydrogen atoms were not included in the refinement process. Refinement proceeded to convergence by minimizing the function Σ ||F<sub>o</sub>| - |F<sub>c</sub>|| / Σ |F<sub>o</sub>|.

The discrepancy indices R = Σ ||F<sub>o</sub>| - |F<sub>c</sub>|| / Σ |F<sub>o</sub>| is presented with other pertinent crystallographic data in Table 1. Selected positional parameters, bond lengths and angles are given in Table 2 and Table 3 [3] [13].

#### Acknowledgement.

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