

ture of the corresponding two isomers, the 2-substituted product predominating. In contrast, benzotriazole is usually substituted at the 1-position [6-8].

Negative charge distributions of phenanthro[9,10-*d*]triazole and benzotriazole anions were estimated by semiempirical MO calculation [9]. The values obtained are as follows: phenanthro[9,10-*d*]triazole N1 and N3-0.174, N-2-0.115; benzotriazole N1 and N3-0.222, N-2-0.088 using AM1 Hamiltonian [10]; phenanthro[9,10-*d*]triazole N1 and N3-0.188, N2-0.112; benzotriazole N1 and N3-0.256, N2-0.059 using PM3 Hamiltonian [11]. Negative charge is more localized on N1 and N3 in benzotriazole anion compared with phenanthro[9,10-*d*]triazole anion. Furthermore, the phenanthro[9,10-*d*]triazole HOMO (-4.491 eV) is localized on N-2, whereas the benzotriazole HOMO (-4.110 eV) is on N1 and N3. The calculated results are consistent with the different behavior between phenanthro[9,10-*d*]triazole and benzotriazole in the substitution reactions.

The substitution reactions of phenanthro[9,10-*d*]triazole potassium salt with other benzyl chlorides having a methyl, a chloro or a nitro group gave the corresponding products, 1-(*X*-benzyl)-1*H*-phenanthro[9,10-*d*]triazoles **1b-j** and 2-(*X*-benzyl)-2*H*-phenanthro[9,10-*d*]triazoles **2b-j**. In all cases, **2b-j** are the major products in 13-62% yields, and **1b-j** are the minor products in 1.4-8.0% yields. The isolated yields are summarized in Table 1. There is no reasonable regularity in the relationship between the yields and the groups introduced into the benzyl chlorides. All the products could be isolated easily by preparative tlc and were identified similarly to **1a** and **1b** by tlc, uv and nmr spectra. Evaluation of the activities as an herbicide, an insecticide and a fungicide is now in progress.

In order to confirm the structural assignment, X-ray analyses of 1-(*o*-nitrobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (**1h**) and 2-(*o*-chlorobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (**2e**) were carried out. The two compounds, **1h** and **2e**, were preferred for their large crystal sizes. The perspective view of the molecules are shown in are shown in Figures 1 and 2.

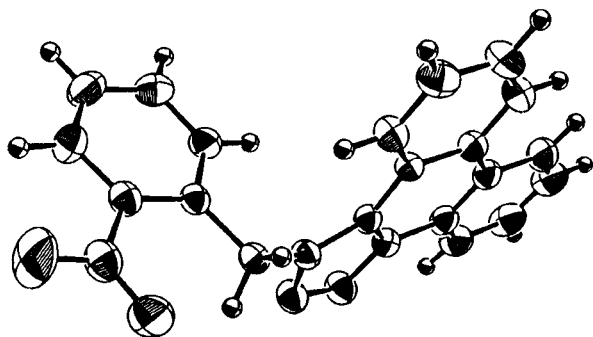


Figure 1. ORTEP drawing of molecule **1h**.

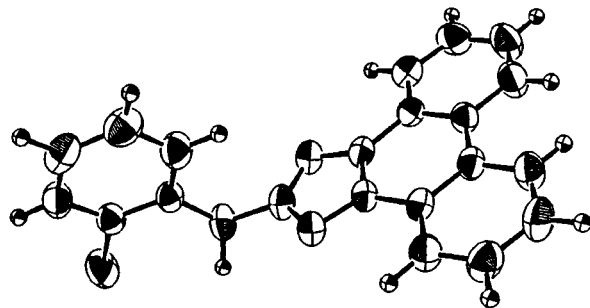


Figure 2. ORTEP drawing of molecule **2e**.

The data collection was achieved at 23°. The structure was solved by direct methods and was refined by full-matrix least-squares. The crystal data and selected bond distances of the triazole rings are listed in Table 2. Estimated standard deviations in the least significant figure are given in parentheses in the Table. The triazole ring of **1h** is apparently different from that of **2e**. The N1-N2 bond length of **1h** is longer than that of **2e**, and the N2-N3 bond of **1h** is shorter than that of **2e**.

Table 2
Crystal Data and Bond Distances of the Triazole Ring

	1h	2e
Crystal dimension (mm)	0.5 x 0.3 x 0.6	0.8 x 0.2 x 0.8
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n z = 4	P2 ₁ /c z = 4
a (Å)	13.796(4)	12.474(3)
b (Å)	8.545(2)	5.955(3)
c (Å)	14.491(2)	22.106(2)
β (°)	109.09(2)	90.64(1)
R (agreement factor)	0.044	0.043
Rw (weighted agreement factor)	0.049	0.050
Bond distance (Å)		
N-1—N-2	1.360(3)	1.332(3)
N-2—N-3	1.311(3)	1.337(3)
N-3—C-4	1.360(3)	1.351(3)
N-1—C-5	1.364(3)	1.344(3)
C-4—C-5	1.375(3)	1.385(3)

The phenanthrene nucleus of **1h** is essentially planar with a mean deviation of 0.031 Å from the least-squares plane. Three nitrogens, N1, N2 and N3, of the triazole ring are nearly in the plane with deviations of 0.065 Å, 0.100 Å and 0.083 Å, respectively. The methylene carbon has a deviation of 0.154 Å from the plane.

The phenanthrene nucleus of **2e** is planar with a mean deviation of 0.012 Å from the least-squares plane. Three nitrogens, N1, N2 and N3, of the triazole ring are in the plane with deviations of 0.070 Å, 0.099 Å and 0.065 Å, respectively. The methylene carbon has a deviation of 0.131 Å from the plane.

EXPERIMENTAL

Melting points are uncorrected. The ir as potassium bromide discs and the uv spectra in methanol were recorded on Shimadzu IR-408 and UV-240 spectrometers, respectively. The ^1H nmr spectra were recorded on a Jeol JNM-PMX60SI spectrometer in chloroform-*d* using tetramethylsilane as an internal reference. The mass spectral data were obtained on a Hitachi M-80 B spectrometer by electron-impact ionization at 70eV. The X-ray crystal analysis was performed on a Rigaku AFC5R diffractometer with graphite monochromated Mo $K\alpha$ radiation. The preparative tlc was performed using Merck Kieselgel 60 PF254.

According to the procedure described in the literature, 9-bromophenanthrene was prepared by bromination of phenanthrene, mp 61-62° (lit [12] 54-56°), yield 76%. Substituted benzyl chlorides were purchased from commercial sources and used without further purification.

Phenanthro[9,10-*d*]triazole.

To a solution of 2.57 g (0.01 mole) of 9-bromophenanthrene in 45 ml of dimethyl sulfoxide were added 4.48 g (0.03 mole) of potassium *t*-butoxide which was freshly prepared according to the literature [13], and 1.30 g (0.02 mole) of sodium azide with rapid stirring at ambient temperature. The stirring was continued for 12 hours and then the solvent was evaporated under reduced pressure. The residual material was washed with water, acetic acid and methanol, and then dried. Recrystallization from ethanol gave an off-white solid, 1.32 g (60%) mp 298-305° (lit [1] 306°, lit [2] 294-298°).

Substitution of Phenanthro[9,10-*d*]triazole with Benzyl Chloride.

To a solution of 12 g (0.21 mole) of potassium hydroxide in 50 ml of water, was dissolved 1.32 g (0.006 mole) of phenanthro[9,10-*d*]triazole, and was allowed to stir overnight. The potassium salt crystallized as silvery leaflets was collected by filtration and dried.

A solution of 500 mg (1.95 mmole) of the potassium salt and 246.1 mg (1.95 mmole) of benzyl chloride in 20 ml of ethanol was heated at reflux for 8 hours. After the solvent was removed by evaporation, the residual material was washed with three 10 ml portions of chloroform. The washings were combined and evaporated to dryness. The residual material was subjected to preparative tlc and developed with dichloromethane. The lower part of silica gel was removed from the tlc plate and was washed with three 10 ml portions of chloroform. After evaporation of the solvent, the residual material was recrystallized from ethanol to give 1-(benzyl)-1*H*-phenanthro[9,10-*d*]triazole (1a) as colorless needles, 23.6 mg (3.9%), mp 181-182°; tlc: Rf = 0.50; ir: ν 1450, 1230, 1025, 756, 735, 725, 700 cm^{-1} ; uv: λ max 243 nm (ϵ 47,900), 250 nm (ϵ 61,700); ^1H nmr: δ 7.5-8.9 (m, 5H, phenyl), 7.2-7.4 (m, 8H, phenanthrene), 6.22 ppm (s, 2H, CH_2); ms: m/z (relative intensity) 309 (82) [M^+], 280 (24) [$\text{M}^+\text{-HN}_2$], 190 (62) [$\text{C}_{14}\text{H}_8\text{N}^+$], 91 (100) [C_7H_7^+].

Anal. Calcd. for $\text{C}_{21}\text{H}_{15}\text{N}_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.72; H, 4.83; N, 13.75.

The upper part of silica gel was treated with chloroform as described above and the crude product was recrystallized from ethanol to give 2-(benzyl)-2*H*-phenanthro[9,10-*d*]triazole (2a) as colorless needles, 89.5 mg (15%), mp 171-172°; tlc: Rf = 0.77; ir: ν 1455, 1387, 1331, 835, 760, 735, 697 cm^{-1} ; uv: λ max 241 nm (ϵ 52,500), 248 nm (ϵ 61,700); ^1H nmr: δ 7.5-8.8 (m, 5H,

phenyl), 7.2-7.5 (m, 8H, phenanthrene), 5.92 ppm (s, 2H, CH_2); ms: m/z (relative intensity) 309 (53) [M^+], 280 (29) [$\text{M}^+\text{-HN}_2$], 190 (72) [$\text{C}_{14}\text{H}_8\text{N}^+$], 91 (100) [C_7H_7^+].

Anal. Calcd. for $\text{C}_{21}\text{H}_{15}\text{N}_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.69; H, 4.82; N, 13.67.

This procedure is representative of all other substitution reactions with substituted benzyl chlorides. The following products were obtained.

1-(*o*-Methylbenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1b).

This compound was obtained as light brown plates (ethanol), 47.9 mg (7.6%), mp 196-198°; tlc: Rf = 0.52; ir: ν 1386, 1226, 1095, 1038, 775, 751, 720 cm^{-1} ; uv: λ max 241 nm (ϵ 57,500), 249 nm (ϵ 93,300); ^1H nmr: δ 8.5-9.0 (m, 4H, phenyl), 6.9-7.9 (m, 8H, phenanthrene), 6.2 (s, 2H, CH_2), 2.6 ppm (s, 3H, CH_3); ms: m/z (relative intensity) 323 (46) [M^+], 294 (29) [$\text{M}^+\text{-HN}_2$], 280 (16) [$\text{M}^+\text{-Me-N}_2$], 190 (96) [$\text{C}_{14}\text{H}_8\text{N}^+$], 105 (100) [C_8H_9^+], 104 (74) [C_8H_8^+], 77 (29) [C_6H_5^+].

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3$: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.73; H, 5.38; N, 13.09.

2-(*o*-Methylbenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2b).

This compound was obtained as colorless needles (ethanol), 391.1 mg (62%), mp 164-165°; tlc: Rf = 0.83; ir: ν 1461, 1436, 1306, 1238, 1000, 760, 747 cm^{-1} ; uv: λ max 239 nm (ϵ 35,500), 246 nm (ϵ 51,300); ^1H nmr: δ 8.3-8.6 (m, 4H, phenyl), 7.1-7.7 (m, 8H, phenanthrene), 5.85 (s, 2H, CH_2), 2.5 ppm (s, 3H, CH_3); ms: m/z (relative intensity) 323 (36) [M^+], 294 (4) [$\text{M}^+\text{-HN}_2$], 190 (31) [$\text{C}_{14}\text{H}_8\text{N}^+$], 105 (54) [C_8H_9^+], 104 (100) [C_8H_8^+], 77 (18) [C_6H_5^+].

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3$: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.86; H, 5.30; N, 13.13.

1-(*m*-Methylbenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1c).

This compound was obtained as light brown plates (ethanol), 22.1 mg (3.5%), mp 152-155°; tlc: Rf = 0.48; ir: ν 1534, 1465, 1387, 1228, 785, 756, 723 cm^{-1} ; uv: λ max 242 nm (ϵ 38,900), 249 nm (ϵ 58,900); ^1H nmr: δ 8.5-9.1 (m, 4H, phenyl), 6.9-8.3 (m, 8H, phenanthrene), 6.26 (s, 2H, CH_2), 2.26 ppm (s, 3H, CH_3); ms: m/z (relative intensity) 323 (72) [M^+], 294 (36) [$\text{M}^+\text{-HN}_2$], 280 (21) [$\text{M}^+\text{-Me-N}_2$], 190 (90) [$\text{C}_{14}\text{H}_8\text{N}^+$], 105 (100) [C_8H_9^+], 77 (24) [C_6H_5^+].

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3$: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.84; H, 5.36; N, 13.15.

2-(*m*-Methylbenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2c).

This compound was obtained as light yellow plates (ethanol), 132.5 mg (21%), mp 134-135°; tlc: Rf = 0.84; ir: ν 1448, 1418, 1308, 1236, 1005, 787, 725 cm^{-1} ; uv: λ max 239 nm (ϵ 28,200), 246 nm (ϵ 70,800); ^1H nmr: δ 8.4-8.7 (m, 4H, phenyl), 7.0-7.8 (m, 8H, phenanthrene), 5.95 (s, 2H, CH_2), 2.3 ppm (s, 3H, CH_3); ms: m/z (relative intensity) 323 (78) [M^+], 294 (24) [$\text{M}^+\text{-HN}_2$], 280 (10) [$\text{M}^+\text{-Me-N}_2$], 190 (85) [$\text{C}_{14}\text{H}_8\text{N}^+$], 105 (100) [C_8H_9^+], 77 (27) [C_6H_5^+].

Anal. Calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_3$: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.97; H, 5.49; N, 13.27.

1-(*p*-Methylbenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1d).

This compound was obtained as light brown prisms, 12.6 mg (2.0%), mp 177-179°; tlc: Rf = 0.65; ir: ν 1387, 1228, 1098, 795, 755, 721 cm^{-1} ; uv: λ max 242 nm (ϵ 33,100), 249 nm (ϵ 47,900); ^1H nmr: δ 8.0-9.0 (m, 4H, phenyl), 7.0-7.8 (m, 8H,

phenanthrene), 6.26 (s, 2H, CH₂), 2.3 ppm (s, 3H, CH₃); ms: m/z (relative intensity) 323 (76) [M⁺], 280 (20) [M⁺-Me-N₂], 190 (88) [C₁₄H₈N⁺], 105 (100) [C₈H₉⁺], 77 (20) [C₆H₅⁺].

Anal. Calcd. for C₂₂H₁₇N₃: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.90; H, 5.19; N, 13.18.

2-(*p*-Methylbenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2d)

This compound was obtained as colorless plates, 282.8 mg (45%), mp 193-194°; tlc: R_f = 0.88; ir: ν 1525, 1465, 1427, 1312, 802, 760, 728 cm⁻¹; uv: λ max 239 nm (ε 23,400), 246 nm (ε 36,300); ¹H nmr: δ 8.3-8.7 (m, 4H, phenyl), 7.0-7.9 (m, 8H, phenanthrene), 5.90 (s, 2H, CH₂), 2.3 ppm (s, 3H, CH₃); ms: m/z (relative intensity) 323 (78) [M⁺], 294 (26) [M⁺-HN₂], 280 (12) [M⁺-Me-N₂], 190 (66) [C₁₄H₈N⁺], 105 (100) [C₈H₉⁺], 77 (17) [C₆H₅⁺].

Anal. Calcd. for C₂₂H₁₇N₃: C, 81.71; H, 5.30; N, 13.00. Found: C, 81.48; H, 5.24; N, 13.14.

1-(*o*-Chlorobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1e)

This compound was obtained as yellow plates, 26.8 mg (4.0%), mp 200-201°; tlc: R_f = 0.63; ir: ν 1452, 1387, 1228, 1053, 1040, 753, 720 cm⁻¹; uv: λ max 241 nm (ε 23,400), 248 nm (ε 63,100); ¹H nmr: δ 8.6-9.1 (m, 4H), 6.9-8.0 (m, 8H, phenanthrene), 6.36 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 345 (13) [M⁺], 343 (34) [M⁺], 280 (27) [M⁺-Cl-N₂], 190 (100) [C₁₄H₈N⁺], 127 (25) [C₇H₆Cl⁺], 125 (65) [C₇H₆Cl⁺].

Anal. Calcd. for C₂₁H₁₄N₃Cl: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.64; H, 4.37; N, 12.48.

2-(*o*-Chlorobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2e)

This compound was obtained as colorless prisms, 173.1 mg (26%), mp 132-134°; tlc: R_f = 0.85; ir: ν 1425, 1237, 1065, 1043, 840, 757, 727 cm⁻¹; uv: λ max 238 nm (ε 35,500), 246 nm (ε 51,300); ¹H nmr: δ 8.3-8.7 (m, 4H, phenyl), 6.8-7.8 (m, 8H, phenanthrene), 6.05 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 345 (31) [M⁺], 343 (85) [M⁺], 308 (25) [M⁺-Cl], 280 (32) [M⁺-Cl-N₂], 190 (87) [C₁₄H₈N⁺], 127 (33) [C₇H₆Cl⁺], 125 (100) [C₇H₆Cl⁺], 89 (20).

Anal. Calcd. for C₂₁H₁₄N₃Cl: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.46; H, 4.31; N, 12.38.

1-(*m*-Chlorobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1f)

This compound was obtained as brown plates, 30.2 mg (4.5%), mp 161-163°; tlc: R_f = 0.35; ir: ν 1449, 1387, 1230, 868, 787, 754, 720 cm⁻¹; uv: λ max 242 nm (ε 38,000), 249 nm (ε 58,900); ¹H nmr: δ 8.5-9.1 (m, 4H, phenyl), 6.9-8.2 (m, 8H, phenanthrene), 6.26 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 345 (40) [M⁺], 343 (100) [M⁺], 280 (32) [M⁺-Cl-N₂], 190 (99) [C₁₄H₈N⁺], 127 (65) [C₇H₆Cl⁺], 125 (98) [C₇H₆Cl⁺], 89 (63).

Anal. Calcd. for C₂₁H₁₄N₃Cl: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.21; H, 3.90; N, 12.34.

2-(*m*-Chlorobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2f)

This compound was obtained as colorless needles, 136.2 mg (20%), mp 151-152°; tlc: R_f = 0.80; ir: ν 1424, 1240, 1098, 998, 790, 757, 725 cm⁻¹; uv: λ max 238 nm (ε 39,800), 245 nm (ε 56,200); ¹H nmr: δ 8.4-8.8 (m, 4H, phenyl), 7.3-7.9 (m, 8H, phenanthrene), 5.90 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 345 (32) [M⁺], 343 (85) [M⁺], 280 (60) [M⁺-Cl-N₂], 190 (100) [C₁₄H₈N⁺], 127 (26) [C₇H₆Cl⁺], 125 (85) [C₇H₆Cl⁺], 89 (27).

Anal. Calcd. for C₂₁H₁₄N₃Cl: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.17; H, 3.96; N, 12.07.

1-(*p*-Chlorobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1g)

This compound was obtained as light brown plates, 9.4 mg (1.4%), mp 161-164°; tlc: R_f = 0.35; ir: 1491, 1385, 1100, 1016, 795, 770, 722 cm⁻¹; uv: λ max 243 nm (ε = 114,800), 250 nm (ε 144,500); ¹H nmr: δ 8.5-9.1 (m, 4H, phenyl), 7.0-8.2 (m, 8H, phenanthrene), 6.26 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 345 (10) [M⁺], 343 (30) [M⁺], 190 (100) [C₁₄H₈N⁺], 127 (24) [C₇H₆Cl⁺], 125 (60) [C₇H₆Cl⁺], 89 (20).

Anal. Calcd. for C₂₁H₁₄N₃Cl: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.29; H, 4.05; N, 12.28.

2-(*p*-Chlorobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2g)

This compound was obtained as colorless needles, 97.3 mg (15%), mp 193-194°; tlc: R_f = 0.77; ir: ν 1493, 1449, 1235, 1094, 798, 755, 724 cm⁻¹; uv: λ max 237 nm (ε 42,700), 246 nm (ε 66,100); ¹H nmr: δ 8.4-8.8 (m, 4H, phenyl), 7.2-7.9 (m, 8H, phenanthrene), 5.90 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 345 (20) [M⁺], 343 (53) [M⁺], 190 (83) [C₁₄H₈N⁺], 127 (22) [C₇H₆Cl⁺], 125 (100) [C₇H₆Cl⁺], 89 (24).

Anal. Calcd. for C₂₁H₁₄N₃Cl: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.48; H, 4.01; N, 12.41.

1-(*o*-Nitrobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1h)

This compound was obtained as yellow prisms, 41.4 mg (6.0%), mp 203-206°; tlc: R_f = 0.56; ir: ν 1534, 1339, 1023, 861, 792, 756, 721 cm⁻¹; uv: λ max 242 nm (ε 125,900), 249 nm (ε 169,800); ¹H nmr: δ 8.2-9.3 (m, 4H, phenyl), 7.3-7.9 (m, 8H, phenanthrene), 6.75 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 354 (42) [M⁺], 281 (10), 190 (100) [C₁₄H₈N⁺], 165 (10).

Anal. Calcd. for C₂₁H₁₄N₄O₂: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.32; H, 4.22; N, 16.03.

2-(*o*-Nitrobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2h)

This compound was obtained as light brown plates, 283.7 mg (41%), mp 138-144°; tlc: R_f = 0.85; ir: ν 1526, 1330, 1305, 862, 791, 755, 722 cm⁻¹; uv: λ max 238 nm (ε 5,600), 245 nm (ε 67,600); ¹H nmr: δ 8.1-8.8 (m, 4H, phenyl), 7.3-7.9 (m, 8H, phenanthrene), 6.4 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 354 (100) [M⁺], 190 (69) [C₁₄H₈N⁺], 164 (37), 78 (26).

Anal. Calcd. for C₂₁H₁₄N₄O₂: C, 71.18; H, 3.98; N, 15.81. Found: C, 70.98; H, 3.86; N, 15.75.

1-(*m*-Nitrobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1i)

This compound was obtained as colorless needles, 27.6 mg (4.0%), mp 201-203°; tlc: R_f = 0.52; ir: ν 1538, 1385, 1357, 788, 754, 723 cm⁻¹; uv: λ max 242 nm (ε 8,100), 248 nm (ε 17,400); ¹H nmr: δ 8.3-9.0 (m, 4H, phenyl), 7.2-8.3 (m, 8H, phenanthrene), 6.37 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 354 (25) [M⁺], 190 (100) [C₁₄H₈N⁺], 90 (11).

Anal. Calcd. for C₂₁H₁₄N₄O₂: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.21; H, 4.00; N, 15.85.

2-(*m*-Nitrobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2i)

This compound was obtained as colorless plates, 93.2 mg (14%), mp 201-204°; tlc: R_f = 0.78; ir: ν 1529, 1449, 1354, 1313, 806, 754, 727 cm⁻¹; uv: λ max 238 nm (ε 9,100), 245 nm (ε 11,500); ¹H nmr: δ 8.0-8.7 (m, 4H, phenyl), 7.2-8.0 (m, 8H, phenanthrene), 6.00 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 354 (100) [M⁺], 190 (60) [C₁₄H₈N⁺], 90 (20).

Anal. Calcd. for C₂₁H₁₄N₄O₂: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.35; H, 4.17; N, 15.95.

1-(*p*-Nitrobenzyl)-1*H*-phenanthro[9,10-*d*]triazole (1j).

This compound was obtained as colorless plates, 17.3 mg (2.5%), mp 183-186°; tlc: R_f = 0.57; ir: ν 1606, 1520, 1348, 1108, 755, 753, 722 cm⁻¹; uv: λ max 242 nm (ε 64,600), 249 nm (ε 97,700); ¹H nmr: δ 8.4-9.0 (m, 4H, phenyl), 7.2-8.4 (m, 8H, phenanthrene), 6.40 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 354 (30) [M⁺], 190 (100) [C₁₄H₈N⁺].

Anal. Calcd. for C₂₁H₁₄N₄O₂: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.28; H, 3.70; N, 15.80.

2-(*p*-Nitrobenzyl)-2*H*-phenanthro[9,10-*d*]triazole (2j).

This compound was obtained as colorless needles, 199.5 mg (29%), mp 145-147°; tlc: R_f = 0.78; ir: ν 1605, 1522, 1450, 1423, 1347, 757, 725 cm⁻¹; uv: λ max 238 nm (ε 22,900), 245 nm (ε = 29,500); ¹H nmr: δ 7.8-8.7 (m, 4H, phenyl), 7.1-7.8 (m, 8H, phenanthrene), 5.93 ppm (s, 2H, CH₂); ms: m/z (relative intensity) 354 (100) [M⁺], 190 (73) [C₁₄H₈N⁺], 163 (10).

Anal. Calcd. for C₂₁H₁₄N₄O₂: C, 71.18; H, 3.98; N, 15.81. Found: C, 70.20; H, 3.88; N, 15.39.

REFERENCES AND NOTES

[1] R. Epsztein, *Mém. services Chim.*, **36**, 353 (1951); *Chem. Abstr.*, **48**, 8204i (1954).

[2] J. W. Barton and A. R. Grinham, *J. Chem. Soc., Perkin Trans. I*, 634 (1972).

[3a] American Cyanamid Co., Belgian Patent Appl., 853,179 (1977); *Chem. Abstr.*, **88**, 190843q (1978); [b] R. E. Diehl and R. V. Kendall, US Patent, 4,086,242 (1978); *Chem. Abstr.*, **89**, 109512g (1979).

[4a] F. Sparatore, M. I. La Rotonda, G. Paglietti, E. Ramundo, C. Silipo and A. Vittoria, *Farmaco. Ed. Sci.*, **33**, 901 (1978); *Chem. Abstr.*, **90**, 103903j (1979); [b] F. Sparatore, M. I. La Rotonda, E. Ramundo, C. Silipo and A. Vittoria, *Farmaco. Ed. Sci.*, **33**, 924 (1978); *Chem. Abstr.*, **90**, 98454g (1979); [c] R. E. Diehl and R. V. Kendall, US Patent, 4,240,822 (1980); *Chem. Abstr.*, **94**, 134160b (1981); [d] F. Sparatore, M. I. La Rotonda, G. Caliendo, E. Novellino, C. Silipo and A. Vittoria, *Farmaco. Ed. Sci.*, **43**, 29 (1988); *Chem. Abstr.*, **109**, 128916q (1988).

[5] G. Yasuda and T. Hori, *Nippon Kagaku Kaishi*, 1912 (1988); *Chem. Abstr.*, **111**, 23442v (1989).

[6] F. R. Benson and W. L. Savel, *Chem. Rev.*, **46**, 1 (1950).

[7] A. R. Katrizky, J. Wu, W. Kuzmierkiewicz and S. Rachwal, *Liebigs Ann. Chem.*, 1 (1994).

[8] A. R. Katrizky and J. Wu, *Synthesis*, 597 (1994).

[9] J. J. P. Stewart, *QCPE Bull.*, **10**, 86 (1990): CAChe MOPAC Version 94.10, derived from MOPAC 6.00, QCPE program 455.

[10] J. J. P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989).

[11] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

[12] C. A. Dornfeld, J. E. Callen and G. H. Coleman *Organic Syntheses, Coll. Vol III*, 134 (1955).

[13] W. S. Johnson and G. H. Daub, *Organic Reactions*, Vol VI, 44 (1951).