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Synthesis and reactions of 9,10-dihydro-9,10-ethanoanthracene-11,12-diacid hydrazides

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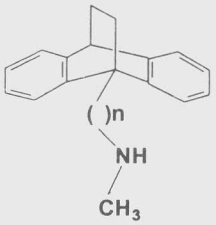
The cycloadducts **3a,b** have been synthesized from adduct **2** by hydrolysis with HCl/alcohol. **3a** on treatment with hydrazine hydrate or phenyl hydrazine yield diacid hydrazides **5a,b**. The cycloadduct **5a,** is converted readily to the corresponding 9,10-dihydro-9,10-ethanoanthracene-11,12-di-heterocyclic derivatives in variant yields.

Anthracene-9,10-*endo*-α,β-succinic anhydride **2** was prepared several years ago by Diels-Alder reaction. Several cycloadducts of anthracene and aromatic or antiaromatic hydrocarbons have been investigated[1-3].

Benzoctamine A and Maprotiline B are neuroleptics which are used clinically for the treatment of mental disorders such as schizophrenia and depression[4].

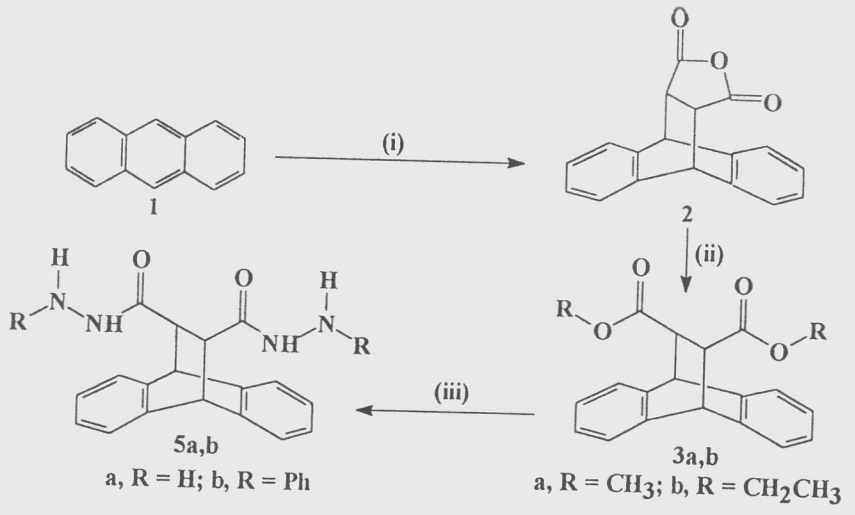


A, n = CH_2; B, n = $(CH_2)_3$

A variety of 9,10-dihydro-9,10-ethano/propanoanthracenes have also been prepared from anthracenes using [4+2] or [4+3] cycloaddition reactions[5,6]. In this paper we present a novel approach for the synthesis of 9,10-dihydro-9,10-ethanoanthracene-11,12-diheterocyclic ring derivatives as combination between 9,10-dihydro-9,10-ethanoanthracene and heterocyclic moieties such as pyrazole, thiazole and triazole rings. 9, 10-Dihydro-9, 10-ethanoanthracene-11, 12-diacid esters **3a,b** were prepared by hydrolysis of cycloadduct anhydride **2** using HCl/alcohol as colourless crystals in 85-86% yield. Refluxing of the diacid esters **3a,b** in ethanol containing an excess of hydrazine hydrate or phenyl hydrazine afforded the corresponding diacid hydrazide derivatives **5a,b.** Condensation of the diacid ester **3a** with aromatic amines gave the expected 11,12-dianilide derivatives **6a-c** in 68-74% yield (cf. Scheme I).

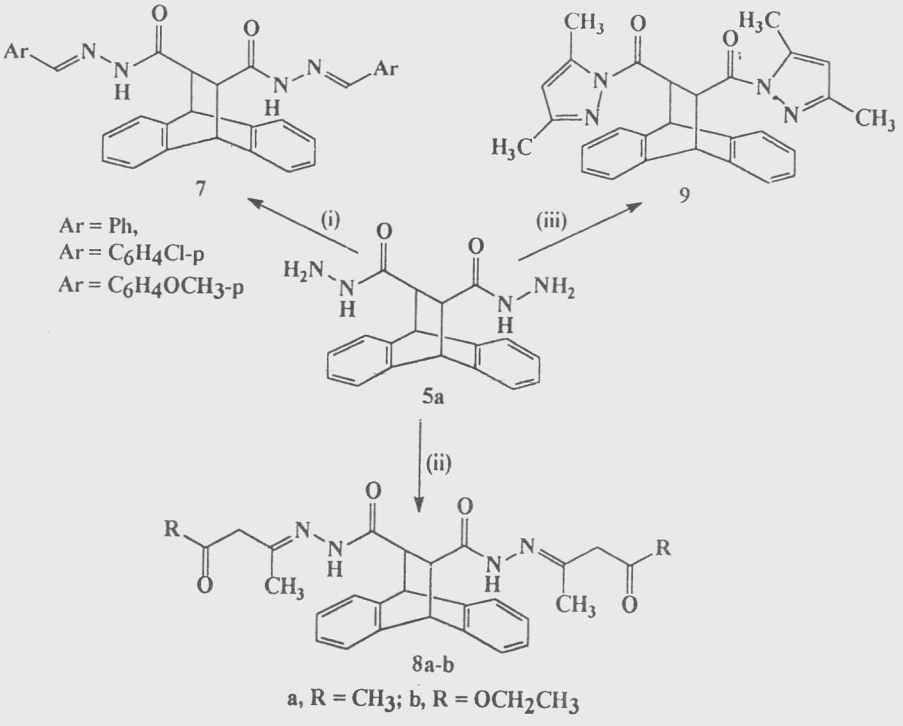
On the other hand, condensation of 11,12-dihydrazide derivative **5a** with aromatic aldehydes under neat conditions afforded the corresponding 11,12-diarylmethylidine hydrazone derivatives **7a-c** in good yield. Further, **5a** when condensed with acetyl acetone in refluxing ethanol gave an unseparable mixture of the uncyclized form **8a** and the dipyrazolyl derivative **9.** While **5a** on refluxing with ethyl acetoacetate in ethanol gave the product **8b** only in 80% yield. In addition, when **5a** was refluxed with acetyl acetone in ethanol/acetic acid mixture, 11,12-dipyrazolyl derivative **9** was obtained in 71% yield (cf. Scheme II).

Attempts to prepare the cycloadduct **10** by boiling **5a** in a mixture of acetic anhydride and acetic acid[7] were unsuccessful, and instead the acetylated derivative **11** was isolated in 85% yield. The structure of **11** was confirmed from spectral (IR, ^{1}H NMR) data. The IR spectrum revealed the presence of the NH group (3290-3260 cm^{-1}) and CO group (1707 and at 1657 cm^{-1}). The ^{1}H NMR spectrum of **11** showed signal at δ 1.8 (s, 6H, 2 CH_3) besides the other signals. Compound **5a** on direct heating over its melting point did not give the expected pentacyclic componds **12** but the starting anthracene **1** was obtained (cf. Scheme III). Formation of the anthracene **1** was



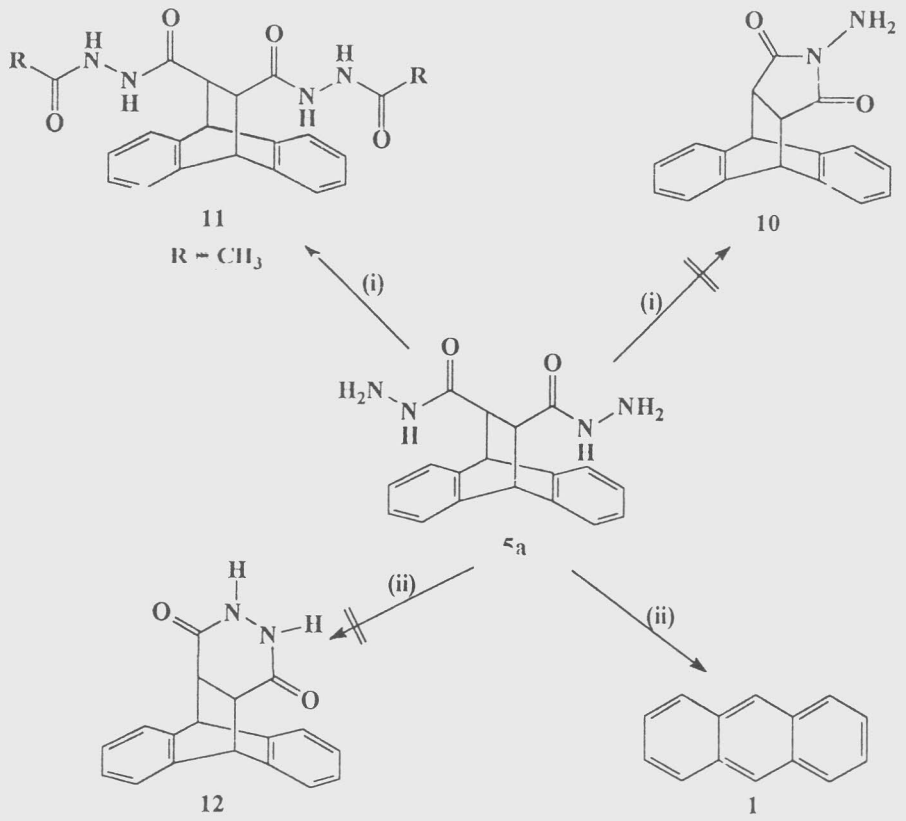
(i) maleic anhydride/Benzene, reflux 6h. (ii) HCl/ROH, reflux 4h
(iii) $RNHNH_2$, neat, 1h, a, R = H, b, R = Ph (iv) $ArNH_2$, neat 1h.

Scheme I



(i) Aromatic aldehyde (benzaldehyde, p-chlorobenzaldehyde, p-anisaldehyde neat, 30 minutes.
(ii) Ethyl acetoacetate/ethanol. reflux, 3h.
(iii) Acetylacetone/ethanol.acetic acid, reflux, 3h.

Scheme II



(i) Ac_2O/AcOH, 4h (ii) neat, 1h

Scheme III

confirmed by melting point and mixed melting point and spectral (IR, ^{1}H NMR) data.

Moreover, the reaction of the dihydrazide derivative **5a** with isothiocyanate derivatives furnished the corresponding dithiosemicarbazide derivatives **13a-c** in good yields. The cycloadducts **13a-c** on cyclization with alc. KOH followed by acidification with dil. HCl gave 11,12-ditriazolyl derivatives **14a-c**. Alkylation of **14a,b** with EtI/EtOH/KOH afforded the 9,10-dihydro-11,12-di[(3`-(4′-methyl/phenyl-5′-ethylthio-1′, 2′, 4′-triazolyl)]-9,10-ethanoanthracenes (**15a-b**) in good yields (cf. Scheme IV).

Experimental Section

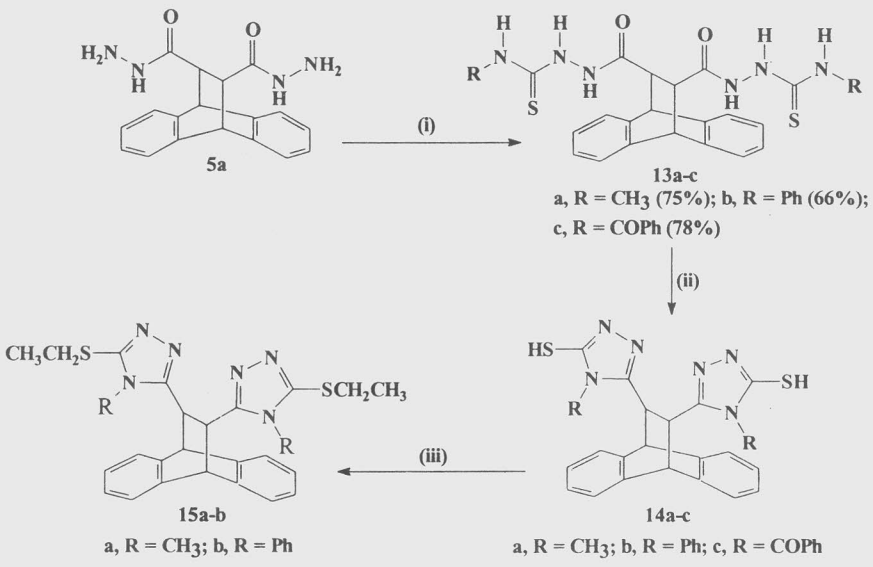
Melting points are uncorrected. IR spectra were recorded on a Shimadzu 1470 spectrophotometer, ^{1}H NMR (90MHz) spectra on a Varian EM-390 spectrometer using TMS as internal standard (chemical shifts in δ, ppm) and the mass spectra on MS 30 and MS 9 (AEI) at 70 eV. Elemental analyses were obtained by the microanalytical unit.

Anthracene-9,10-*endo*-α,β-succinic anhydride **2** was prepared by a well-known method.

9, 10-Dihydro-9, 10-ethanoanthracene-11,12-diacid esters 3a,b. A suspension of **2** (2.8 g, 1.0 mmoles) in methanol or ethanol (50 ml) was treated with conc. HCl (5 mL) and heated under reflux for 4 hr. The reaction mixture was poured into ice water. The precipitate thus obtained was filtered and crystallized from ethanol to give diacid esters **3a,b** as colourless crystals.

3a (R = CH_3); yield 86%; m.p. 150°C; IR (KBr): 3050-3070 (CH aromatic), 2990-2910 (CH aliphatic), 1740 (ester CO); ^{1}H NMR ($CDCl_3$, 90 MHz): δ 3.5 (bs, 2H, H-11, H-12), 3.7 (s, 6H, 2 CH_3), 4.8 (bs, 2H, H-9, H-10), 7.1-7.8 (m, 8H, Ar-H) (Found: C, 74.60; H, 5.70. $C_{20}H_{18}O_4$ requires C, 74.52; H, 5.63%).

3b (R = CH_2CH_3); yield 85%; m.p. 88°C, IR



(i) Isothiocyanate derivatives/ethanol, 6h. (ii) KOH alc. (2N), reflux, 1h
(iii) EtI/KOH alc. (2N0, room temperature, 2h

Scheme IV

(KBr): 3050 (CH aromatic), 2950 (CH aliphatic), 1720 (ester CO); ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.2 (t, J = 7 Hz, 6H, 2×CH_3), 3.3 (bs, 2H, H-11, H-12), 4.0 (q, J = 7 Hz, 4H, 2×CH_2), 4.6 (bs, 2H, H-9, H-10); 7.1-7.6 (m, 8H, Ar-H) (Found: C, 75,60; H, 6.50. $C_{22}H_{22}O_4$ requires C, 75.41; H, 6.33%).

9, 10-Dihydro-9, 10-ethanoanthracene-11,12-diacid hydrazides 5a,b. A mixture of **3a** (3.22 g, 10 mmoles) and hydrazine hydrate or phenyl hydrazine (50 mmoles) was heated under neat conditions for 1 hr. It was cooled and then refluxed in ethanol (50 mL) for another 1 hr. The reaction mixture on cooling gave a precipitate which was filtered, washed with alcohol and crystallized from dioxane to give **5a,b** as colourless crystals.

5a; yield 75%; m.p. 310°C; IR (KBr): 3400-3300 (NH, NH_2), 1650 (2 CO); ^{1}H NMR (DMSO-d_6): δ 3.0 (bs, 2H, H-11, H-12), 3.9 (br, 4H, 2×NH_2), 4.4 (bs, 2H, H-9, H-10), 6.95-7.30 (m, 8H, Ar-H), 9.2 (b, 4H, 2×NH); MS: 322 (M^+) (Found: C, 67.20; H, 5.80; N, 17.50. $C_{18}H_{18}N_4O_2$ requires C, 67.07; H, 5.63; N, 17.38%).

5b; yield 77%; m.p. 330°C; IR (KBr): 3350-3200 (NH); 1700 (CO); ^{1}H NMR (DMSO-d_6): δ 3.4 (bs, 2H, H-11, H-12), 4.8 (bs, 2H, H-9, H-10), 5.5 (bs, 2H, 2×NH), 6.5-7.5 (m, 18H, Ar-H), 8.2 (bs, 2H, 2×NH) (Found: C, 76.1; H, 5.70; N, 12.00. $C_{30}H_{26}N_4O_2$ requires C, 75.93; H, 5.52; N, 11.81%).

9, 10-Dihydro-11, 12-diarylamino-9, 10-ethanoanthracenes 6a-c. Compounds **6a-c** were prepared by a similar method as reported for the preparation of **5a,b** except aromatic amines were used instead of the hydrazines. The cycloadducts **6a-c** were obtained as white crystals from dioxane or ethanol.

6a (Ar = Ph); yield 72%; m.p. 265°C; IR (KBr): 3300-3250 (NH), 1700 (CO); ^{1}H NMR (DMSO-d_6): δ 3.3 (bs, 2H, H-11, H-12), 4.8 (bs, 2H, H-9, H-10), 7.2-8.2 (m, 18H, Ar-H), 8.6 (bs, 2H, 2×NH); MS 444(M^+) (Found: C, 81.3; H, 5.7; N, 6.5. $C_{30}H_{24}N_2O_2$ requires C, 81.06; H, 5.44; N, 6.30%).

6b (Ar = C_6H_4Cl-p); yield 68%; m.p. 285°C; IR (KBr): 3400-3300 (NH), 3320-3280 (NH), 1700 (CO); MS 513 (M^+) Found: C,70.3; H, 4.5; N, 5.5. $C_{30}H_{22}N_2O_2Cl_2$ requires C, 70.18; H, 4.32; N, 5.46%).

6c (Ar = $C_6H_4OCH_3$-p); yield 74%; m.p. 258°C; IR (KBr): 3300-3200 (NH), 1690 (CO);. MS 504 (M^+) (Found: C, 76.3; H, 5.8; N, 5.6. $C_{32}H_{28}N_2O_4$ requires C, 76.17; H, 5.59; N, 5.55%).

9, 10-Dihydro-11, 12-di[arylidinehydrazonyl]-9,10-ethanoanthracene 7a-c. A mixture of diacid

hydrazide **5a** (3.22 g, 10 mmoles) and aromatic aldehyde (20 mmole) was heated for 20 min and then refluxed in ethanol for 1hr. The resulting precipitate was collected by filtration and recrystallized from the proper solvent to give the cycloadducts **7a-c.**

7a (Ar = Ph); crystallised from dil. DMF; yield 92%; m.p 325°C; IR (KBr): 3190 (NH), 1650 (CO); ^{1}H NMR (insoluble in all deutrated solvents); Mol.wt. 498.4 (Found: C, 76.80; H, 5.34; N, 10.89. $C_{32}H_{26}N_4O_2$ requires C, 77.08; H, 5.22; N, 11.23 %).

7b (Ar = C_6H_4-Cl-*p*); crystallised from diluted acetic acid; yield 86%; m.p 358°C; IR (KBr): 3150 (NH), 1660 (CO); ^{1}H NMR (insoluble in all deutrated solvents); Mol. wt. 567.4 (Found: C, 68.06; H, 4.55; N, 10.15; Cl, 12.06. $C_{32}H_{24}N_4O_2Cl_2$ requires C, 67.71; H, 4.26; N, 9.87; Cl, 12.51 %).

7c (Ar = *p*-anisyl); crystallised from dil. DMF; yield73%; m.p. 325 °C; IR (KBr): 3200-3100 (NH), 3050 (CH aromatic), 2950 (CH aliphatic), 1650 (CO); ^{1}H NMR (TFA): δ 3.3 (bs, 2H, H-11, H-12), 4.1 (s, 6H, 2×OCH_3), 4.8 (bs, 2H, H-9, H-10), 7.2-8.1 (m, 8H, Ar-H), 8.9 (s, 1H, N = CH); Mol.wt. 558 (Found: C, 73.30; H, 5.40; N, 10.30. $C_{34}H_{30}N_4O_4$ requires C, 73.10; H, 5.41; N, 10.30%).

Reaction of 5a with acetyl acetone. A mixture of **5a** (3.22 g, 10 mmoles) and acetyl acetone (15 mmoles) was refluxed in ethanol (30 mL) for 3hr. The resulting precipitate was collected by filtration and recrystallized from dioxane to give a mixture of cycloadducts **8a** and **9**.

Reaction of 5a with ethyl acetoacetate. A mixture of **5a** (3.22 g, 10 mmoles) and ethyl acetoacetate (15 mmoles) was refluxed in ethanol (30 mL) for 3hr. The resulting precipitate was filtered and crystallized from dioxane to give colourless crystals of cycloadduct **8b** in 80% yield.

8b (R = OCH_2CH_3); yield 80%; m.p. 225°C; IR (KBr): 3400-3250 (NH), 3050 (aromatic CH), 2995 (aliphatic CH), 1720 (ester CO), 1650 (CO); ^{1}H NMR (DMSO-d_6): δ 1.3 (t, J = 7 Hz, 6H, 2×CH_3), 2.4 (bs, 2H, H-11, H-12), 2.7 (s, 6H, 2×CH_3), 3.8 (s, 4H, 2×CH_2), 4.0 (bs, 2H, 2×NH), 4.3 (q, J = 7 Hz, 4H, 2×CH_2), 4.8 (bs, 2H, H-9, H-10), 7.2-7.6 (m, 8H, Ar-H); MS: 546 (M^+); Mol.wt. 546.4 (Found: C, 66.20; H, 6.40; N, 10.30. $C_{30}H_{34}N_4O_6$ requires C, 65.92; H,6.27; N, 10.25%).

9, 10-Dihydro-11, 12-di(3′,5′-dimethylpyrazolyl)carbonyl-9,10-ethanoanthracene 9. A mixture of **5a** (3.22 g, 10 mmoles) and acetyl acetone (20 mmoles) was refluxed in ethanol/acetic acid mixture (1:1) (30 mL) for 3hr. The resulting precipitate was collected by filtration and recrystallized from ethanol to give the corresponding dipyrazolyl derivative **9** as colourless crystals in 71% yield; m.p. 265°C; IR (KBr): 3050 (aromatic CH), 2990 (aliphatic CH) 1705 (CO); ^{1}H NMR ($CDCl_3$): δ 2.1 (t, 6H, 2×CH_3), 2.4 (s, 6H, 2×CH_3), 4.4 (bs, 2H, H-11, H-12), 4.8 (bs, 2H, H-9, H-10), 5.8 (s, 2H, pyrazol H), 7.0-7.5 (m, 8H, Ar-H), MS: 450 (M^+); Mol. wt. 450.6 (Foun: C, 74.80; H, 6.00; N, 12.60. $C_{28}H_{26}N_4O_2$ requires C, 74.65; H, 5.81; N, 12.44%).

9, 10-Dihydro-11, 12-diacetylhydrazono-9,10-ethanoanthracene (11). 5a (3.22 g, 10 mmoles) was refluxed in acetic acid/acetic anhydride mixture (20 : 5 mL) for 4 hr. The reaction mixture was cooled for 2 hr, the resulting precipitate was collected by filtration and crystallized from ethanol to give colourless crystals of the diacetylated derivative **11** in 85% yield; m.p. 185°C; IR (KBr): 3290-3260 (NH), 3000 (CH aromatic), 2950 (CH aliphatic) 1707 (CO), 1657 (CO), ^{1}H NMR (DMSO-d_6): δ 1.9 (s, 6H, 2×CH_3), 3.3 (bs, 2H, H-11, H-12), 4.7 (bs, 2H, H-9, H-10), 7.0-7.5 (m, 8H, Ar-H), 9.8 (s, 2H, 2×NH), 10.2 (s, 2H, 2×NH); Mol. Wt. 406.6 (Found: C, 65.30; H, 5.50; N, 13.90. $C_{22}H_{22}N_4O_4$ requires C, 64.98; H, 5.46; N, 13.78%).

Reaction of 5a with methyl- and phenyl-isothiocyanates. Formation of 9, 10-Dihydro-9, 10-ethanoanthracenes-11, 12-di-methyl/phenyl-thiosemicarbazides 13a-b. A mixture of **5a** (3.22 g, 10 mmoles) and methyl- or phenyl-isothiocyanate (11 mmoles) was refluxed in ethanol (50 mL) for 6hr. The reaction mixture was cooled at room temperature and the resulting precipitate was collected by filtration and recrystallized from dilute DMF to give colourless crystals of **13a,b**.

13a (R = CH_3); yield 75%; m.p. 258°C; IR (KBr): 3300-3150 (NH), 3060 (aromatic CH), 2950 (CH aliphatic), 1650 (CO), 1600 (CS); ^{1}H NMR (DMSO-d_6): δ 2.8 (d, 6H, 2×CH_3), 3.3 (bs, 2H, H-11, H-12), 4.8 (bs, 2H, H-9, H-10), 6.9-7.5 (m, 8H, aromatic-H), 7.7 (q, 2H, 2×$NHCH_3$), 9.0 (bs, 2H, 2×NH); 9.9 (bs, 2H, 2×NH). MS: 468

(M^+); Mol. wt. 468.4 (Found: C, 56.50; H, 5.30; N, 18.10; S, 13.80. $C_{22}H_{24}N_6O_2S_2$ requires C, 56.39; H, 5.16; N, 17.93; S, 13.68%).

13b (R = Ph); yield 66%; m.p. 270°C; IR (KBr): 3320-3200 (NH), 3020 (aromatic CH), 2950 (aliphatic CH), 1660 (CO), 1590 (CS); ^{1}H NMR (DMSO-d_6): δ 3.3 (s, 2H, H-11, H-12), 4.8 (bs, 2H, H-9, H-10), 7.0-7.6 (m, 18H, Ar-H), 9.5 (b, 3H, 3×NH), 10.5 (b, 3H, 3×NH); MS: 592 (M^+); Mol. wt. 592.5 (Found C, 65.10; H, 5.00; N, 14.30; S, 11.00. $C_{32}H_{28}N_6O_2S_2$ requires C, 64.84; H, 4.76; N, 14.18; S, 10.80%).

9, 10-Dihydro-11, 12-dibenzoylthiosemicarbazido-9,10-ethanoanthracene 13c. Equimolecular amounts of **5a** (3.22 g, 10 mmoles) and benzoyl isothiocyanate (20 mmoles) (prepared *in situ* by reaction of ammonium thiocyanate and benzoyl chloride) in dry acetone were refluxed for 3 hr. The reaction mixture was cooled gradually and then diluted with cold water. The resulting precipitate was collected by filtration, washed with water, dried and recrystallized from ethanol to give the corresponding dibenzoylthiosemicarbazide derivative **13c** as yellow crystals in 78% yield, m.p. 248°C; IR (KBr): 3200-3100 (NH), 3050 (aromatic CH), 2950 (aliphatic CH), 1660 (CO), 1590 (CS); ^{1}H NMR (DMSO-d_6): δ 3.3 (bs, 2H, H-11, H-12), 4.7 (bs, 2H, H-9, H-10), 7.05-7.95 (m, 24H, Ar-H and 6×NH); Mol. Wt. 648.5 (Found: C, 63.10; H, 4.50; N, 13.20; S, 10.00. $C_{34}H_{28}N_6O_4S_2$ requires C, 62.95; H, 4.35; N, 12.95; S, 9.88%).

9, 10-Dihydro-11, 12-di[3′-(4′-phenyl-5′-mercapto-1′,2′,4′-triazolyl)]-9,10-ethanoanthracenes 14a-c. A mixture of **13a-c** (5.0 mmoles) in alcoholic solution of 2*N* KOH (40 ml) was refluxed for one hr. The reaction mixture was poured into ice water and acidified with dil. HCl. The resulting precipitate was collected by filtration and crystallized from dioxane or ethanol to give the corresponding 11,12-ditriazolyl derivatives **14a-c**.

14a (R = CH_3); yield 73%; m.p > 360°C; IR (KBr): 3100 (NH), 3000 (aromatic CH), 2900 (aliphatic CH), 1580 (C = N); ^{1}H NMR (DMSO-d_6): δ 3.5 (s, 6H, 2×NCH_3), 3.7 (bs, 2H, H-11,H-12), 4.7 (bs, 2H, H-9, H-10), 7.0-7.6 (m, 8H, Ar-H), 10.5 (s, 2H, 2NH); Mol. wt. 432.4 (Found: C, 60.81; H, 4.83; N, 18.84; S, 14.99. $C_{22}H_{20}N_6S_2$ requires C, 61.09; H, 4.63; N, 19.44; S, 14.80%).

14b (R = Ph); yield 70%; m.p. > 360°C; IR (KBr): 3350-3300 (NH), 3050 (aromatic CH), 2950 (aliphatic CH), 1590 (CS); ^{1}H NMR (DMSO-d_6): δ 3.3 (bs, 2H, H-11, H-12), 4.6 (bs, 2H, H-9, H-10), 6.7-7.4 (m, 18H, Ar-H), 10.5 (s, 2H, 2×NH); MS: 556 (M^+); Mol. wt. 556.5 (Found: C, 69.10; H, 4.50; N, 15.30; S, 11.70. $C_{32}H_{24}N_6S_2$ requires C, 69.04; H, 4.35; N, 15.10; S, 11.52%).

14c (R = COPh); yield 68%; m.p. 175°C; IR (KBr): 3360-3175 (NH), 1668 (CO), 1598 (CS); ^{1}H NMR (DMSO-d_6):δ 3.4 (bs, 2H, H-11, H-12), 4.7 (s, 2H, H-9, H-10), 7.0-7.5 (m, 18H, Ar-H), 8.0 (s, 2H, 2×NH); MS: 588 (M^+) (Found: C, 65.40; H, 4.40; N, 14.30; S, 11.00. $C_{32}H_{24}N_6O_2S_2$ requires C, 65.29; H, 4.11; N, 14.28; S, 10.89%).

9, 10-Dihydro-11, 12-di[3′-(4′-phenyl-5′-ethylthio-1′, 2′, 4′-triazolyl)]-9, 10-ethanoanthracenes 15a,b. To a solution of **14a,b** (1.0 mmoles) in 2*N* alcoholic KOH, ethyl iodide (3 mL) was added dropwise. The reaction mixture was stirred at room temperature for 2 hr. The resulting precipitate was separated on standing, collected by filtration and recrystallized from ethanol to give colourless crystals of the cycloadduct **15a,b** in good yield.

15a (R = CH_3); yield 58%; m.p. 288°C; IR (KBr): 3000 (arom. CH), 2900 (aliphatic CH), 1580 (C = N); ^{1}H NMR ($CDCl_3$): 1.3-1.5 (t, 6H, 2×CH_3CH_2), 3.0-3.3 (q, 4H, 2×CH_3CH_2), 3.7 (s, 6H, 2×NCH_3), 4.2 (bs, 2H, H-11, H-12), 4.65 (bs, 2H, H-9, H-10), 7.0-7.6 (m, 8H, Ar-H); Mol. wt. 488.5 (Found: C, 64.33; H, 5.95; N, 16.90; S, 13.20. $C_{26}H_{28}N_6S_2$ requires C, 63.91; H, 5.78; N, 17.20; S, 13.10%).

15b (R = Ph); yield 43%; m.p. 230°C; IR (KBr): 3050 (aromatic. CH), 2980 (aliphatic CH). ^{1}H NMR ($CDCl_3$): δ 1.2 (t, 3H, CH_3), 3.4 (bs, 2H, H-11, H-12), 4.2 (q, 2H, CH_2), 4.8 (bs, 2H, H-9, H-10), 6.9-7.6 (m, 18H, Ar-H); Mol. wt. 612.6 (Found: C, 70.70; H, 5.40; N, 13.50; S, 10.60. $C_{36}H_{32}N_6S_2$ requires C, 70.56; H, 5.26; N, 13.72; S, 10.46%).

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