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1,3-Dipolar Cycloaddition Reactions of Polycyclic Aromatic Hydrocarbons with 3,5-Dichloro-2,4,6-trimethyl- and 2,4,6-Trimethylbenzonitrile Oxide.

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Abstract: Title 1,3-dipoles add to phenanthrene, pyrene, anthracene and perylene, but not to naphthalene and triphenylene, to give a regioisomeric monocycloadduct. Anthracene give also the two corresponding biscycloadducts. The site- and regio-selectivity of the reactions of the anthracene and pyrene is discussed in terms of FMO approximation.

Against the anticipation of their inertia, mainly due to the loss of aromaticity, several aromatic compounds undergo 1,3-dipolar cycloaddition reactions with nitrile oxides and imines.[1] Recently 5- and 6-membered aromatic heterocycles have been the object of extensive researches,[2-5] but aromatic carbocycles have received very little attention.

Polycyclic aromatic hydrocarbons (PAHs) undergo a very few cycloadditions when they act as a 2π-component. To our best knowledge, the only known cycloadditions are their reactions with ozone,[6] the Diels-Alder reactions with hexachlorocyclopentadiene[7] and 1,3-dipolar reactions with the azomethine ylid derived from 1-(4-methoxyphenyl)aziridine-2,3-(*trans*)-dicarboxylate.[8]

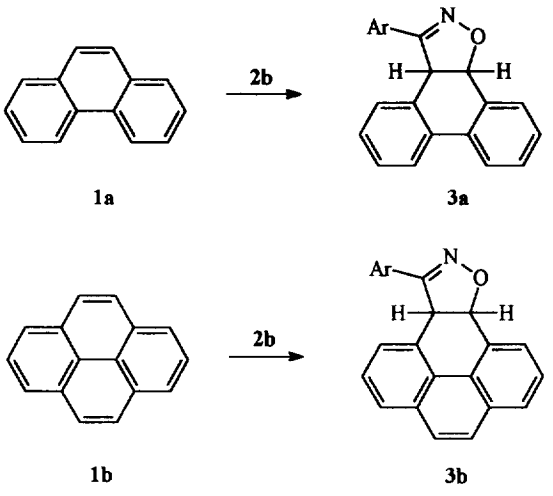
Following our initial studies on cycloaddition reactions of PAHs,[9,10] where we found that phenanthrene (**1a**) and pyrene (**1b**), but not naphthalene (**1c**) and perylene (**1d**), react with mesitonitrile oxide (**2a**) to give monocycloadducts, we have extended this study to the reactions with anthracene (**1e**) and triphenylene (**1f**) and to the reactions of these PAHs with 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide (**2b**). This latter 1,3-dipole proved to be more efficient than mesitonitrile oxide because of its greater stability. With the most reactive benzonitrile oxide, cycloadditions do not occur because the faster 1,3-dipole dimerization becomes the dominant process.

RESULTS AND DISCUSSION

Two equivalents of the 1,3-dipole were added portionwise to a refluxing solution of PAHs in toluene for one day. Chromatography of the reaction residue obtained by removing the solvent gave the following results.

Phenanthrene and Pyrene

These two PAHs showed with **2b** the same reactivity observed with **2a**[9] and gave the corresponding monocycloadducts **3a,b** with yields of 6.5 and 15.9%, respectively.



Ar = 3,5-dichloro-2,4,6-trimethylphenyl

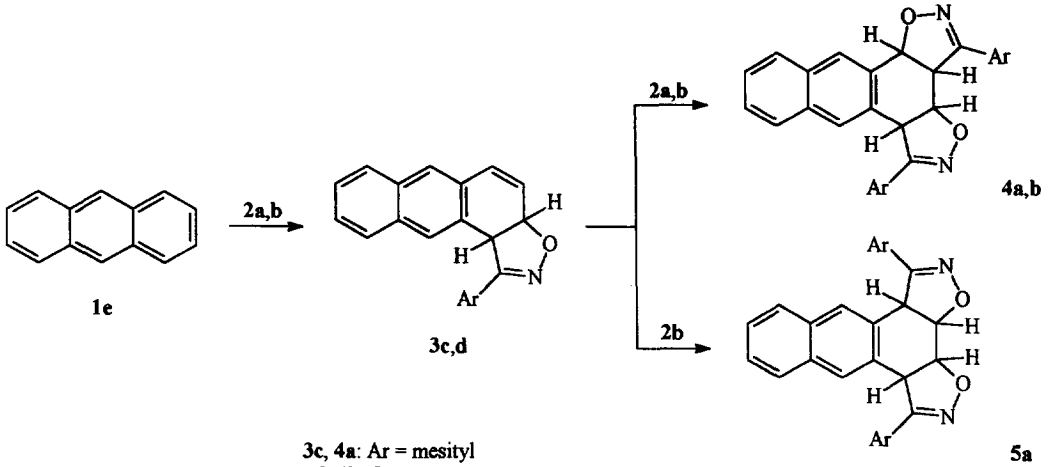
As in the case of reaction with **2a**,[9] pyrene did not give any biscycloadduct with **2b**, even when the reaction was conducted with a large excess (six equivalents) of the 1,3-dipole and/or for longer periods of time (2-4 days) neither when **3b** was used as starting material. In the former case moderate yields (29%) of monocycloadduct can be obtained.

The structural assignments of **3a,b** were deduced from their spectral and elemental data. Particularly, beside the signals of aromatic protons, ^{1}H-NMR spectra show three singlets at high field for the protons of the three methyl groups of the 3,5-dichloro-2,4,6-trimethylphenyl substituent and two doublets at 4.85 and 5.24 ppm and at 6.14 and 6.47 ppm for the 4- and 5-isoxazolinic protons of the dihydro-phenanthrene and -pyrene, respectively. The chemical shifts and coupling constants of doublets (J = 10.8 and 11.3 Hz) correspond to values already reported for isoxazolines.[11] ^{13}C-NMR spectra show three signals for the carbon atoms of methyl groups in the range 17.68-18.98 ppm and signals assignable to the isoxazolinic carbon atoms (53.69, 78.41 and 158.96 for **3a**; 53.45, 78.97 and 158.59 for **3b**) along with aromatic signals due to the remaining carbon atoms.

Anthracene

Anthracene (**1e**) reacts with **2a,b** to give a regioisomeric monocycloadduct **3c,d** (15.7 and 16.5% yield, respectively) and the two corresponding biscycloadducts **4a** (4.6% yield) and **4b** (4.3% yield). A symmetrical biscycloadduct **5a** with 4.3% yield was also formed in the case of the reaction of anthracene with **2b**. We confirmed that the biscycloadducts **4b** and **5a** derive from the monocycloadduct **3d** by exposing **3d** to an excess of **2b**.

Again ^{1}H-NMR spectra were the basis for their structural assignments along with their elemental data, ^{13}C-NMR and mass spectra. The structure of 3a,11a-dihydro-3-arylanthraceno[1,2-d]isoxazoles (**3c,d**) was given to monocycloadducts because their ^{1}H-NMR spectra contained a doublet [4.93 ppm (J = 11.4 Hz) and 4.96 ppm (J = 11.7 Hz)] for the 4-isoxazolinic proton and a double double doublet (5.80 and 5.86 ppm) for the 5-isoxazolinic proton which further couples with the adjacent proton (J = 3.0 and 2.8 Hz) and with the allylic proton (J = 1.2 and 1.3 Hz). A double doublet (6.05 and 6.06 ppm) and a doublet (6.79 and 6.81 ppm) for the two vinylic protons of the ring to which the 1,3-dipole is fused.



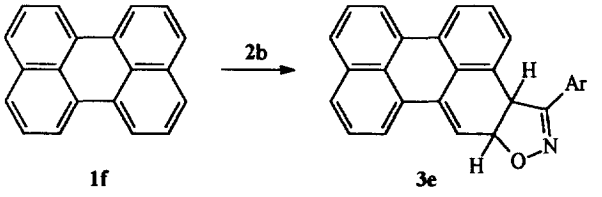
3c, **4a**: Ar = mesityl
3d, **4b**, **5a**: Ar = 3,5-dichloro-2,4,6-trimethylphenyl

^{1}H-NMR spectrum of **4a,b** show a double doublet and a doublet for the two 4-isoxazolinic protons at higher fields [(4.53 ppm (J = 2.4, 9.0 Hz), 4.44 ppm (J = 2.4, 9.2 Hz) and 4.67 ppm (J = 10.5 Hz), 4.65 ppm (J = 10.4 Hz)] and a double doublet and doublet for the two 5-isoxazolinic protons, [4.97 ppm (J = 2.4, 10.5 Hz), 5.00 ppm (J = 2.4, 10.4 Hz) and 5.99 ppm (J = 9.0 Hz) and 6.03 ppm (J = 9.2 Hz)], while the ^{1}H-NMR of the symmetrical biscycloadduct **5a** is characterized by a doublet at 4.90 (J = 8.3 Hz) and a double doublet at 5.47 (J = 1.0 and 8.3 Hz).

Presumably, bisadducts are *trans*-isomers with respect to the fusion of the two isoxazoline units to the six membered ring as it can be deduced by the little coupling constant (1.0 and 2.4 Hz) between the two isoxazolinic protons of the two pentatomic rings, which is indicative of a dihedral angle near to 90°. This latter was confirmed by computational molecular models.

Perylene

A monocycloadduct (**3e**) (8.5% yield) was isolated from the reaction mixture of perylene (**1f**) with **2b**, but not with **2a**. To this, the structure of 3a,13a-dihydro-3-(3,5-dichloro-2,4,6-trimethylphenyl)peryleno[4,5-d]isoxazole **3e** was given on the basis of their ^{1}H-NMR spectrum. This contains a doublet at 4.47 ppm (J = 8.9 Hz) for the 4-isoxazolinic proton, a double doublet at 5.03 ppm (J = 2.2 and 8.9 Hz) for the 5-isoxazolinic proton and a doublet at 5.45 ppm for the olefinic proton. Subjected to the exposition to **2b**, monocycloadduct **3e** did not give any biscycloadducts.



Ar = 3,5-dichloro-2,4,6-trimethylphenyl

Naphthalene and Triphenylene

These PAHs do not react with **2a,b** under the reaction conditions used for the other PAHs, neither with an excess of the 1,3-dipole and/or for longer periods of time.

Frontier Molecular Orbital analysis

Especially, in order to rationalise the site- and regio-selectivity observed in the cycloadditions of anthracene and perylene, we have performed a frontier molecular orbital analysis of PAHs **1a-f** and the two dipoles **2a,b**.

All compounds have been optimised using the PM-3 method[12] and energies of the HOMO and LUMO and orbital coefficient values are given (Figure 1, and 2).

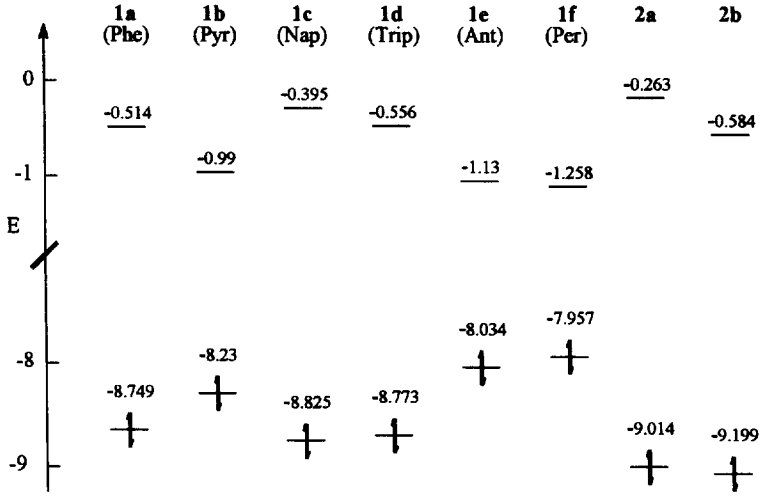


Figure 1. HOMO and LUMO Energies of PAHs **1a-f** and nitrile oxides **2a, b**

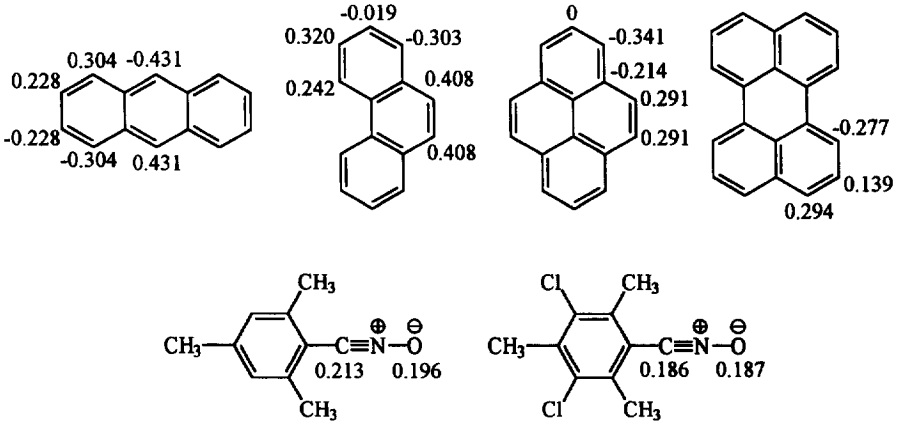


Figure 2. Orbital coefficients of PAHs **1a,b,e,f** and nitrile oxide **2a, b**

As Figure 1 shows, the HOMO (dipolarophile)-LUMO (dipole) seems to be the dominant interaction between the reagents. Naphthalene (**1c**) and triphenylene (**1d**) have the highest energetic gaps (ΔE = 8.56 and 8.24 eV for interactions **1c-2a** and **1c-2b**, 8.51 and 8.19 eV for interactions **1d-2a** and **1d-2b**), but these are very near to those of phenanthrene (**1a**) (ΔE = 8.48 and 8.16 eV for interactions **1a-2a** and **1a-2b**) which adds to the nitrile oxide. We think that they do not react with 1,3-dipoles because of the highest cost of resonance energy associated with their cycloadditions.

As regards the site- and regio-selectivity of anthracene, molecular orbital coefficients of **1a** combine very well with the "highest adjacent pair"[13] of this PAH, which corresponds with its *k*-region[13] and account for the formation of the observed monocycloadduct. However, this FMO approximation[14,15] is in disagreement with the experimental orientation of **1b** with anthracene and perylene, which on the contrary follow the same trend as **1a**. A reason for the failure of the FMO treatment can be envisaged in the very small difference in the size of the terminal LUMO coefficient of the dipole. Based on these molecular orbital coefficients of the oxygen and carbon atoms the two regioisomers were to be expected, while we have isolated only **3d,e**. These results are not surprising, however, since other cycloadditions of **2b**[16-18] gave cycloadduct orientations in contrast with the prediction of FMO theory.

Further work is in progress to explore the chemical properties (treatment with bases, oxidation and reduction) of monocycloadducts and will be presented at a later date.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer 281 spectrophotometer using potassium bromide discs, and ^1H and ^{13}C NMR spectra were recorded on a Bruker W P 80 spectrometer using tetramethylsilane as internal standard and deutero-chloroform as solvent. Elemental analyses were performed on a Carlo Erba Elemental Analyser 1106. Thin layer chromatographic separations were performed on Merck silica gel 60-F_{254} precoated aluminum plates. Preparative chromatographic separations were conducted by means of flash chromatography using Merck silica gel 60 with cyclohexane-ethyl acetate mixtures as eluents.

Staring materials. Mesitonitrile oxide[19] and 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide[20] were prepared following literature methods. PAHs were purchased from Aldrich Co. All solvents were dried according to literature methods.[21]

General procedure for cycloaddition reactions. To a solution of the PAH (4 mmol) in dry toluene (30 ml) two equivalents of the 1,3-dipole were added portionwise and the reaction mixture was refluxed for one day. After removing the solvent, the reaction mixture was subjected to flash chromatography to give the cycloadducts, whose physical and spectral data are given below.

3a,11b-Dihydro-3-(3,5-dichloro-2,4,6-trimethylphenyl)phenanthro[9,10-d]isoxazole **3a**. Yield 6.5%; m.p. 211-212 °C from diethyl ether (Found: C, 70.57; H, 4.71; N, 3.49. $C_{24}H_{19}NOCl_2$ requires: C, 70.60; H, 4.69; N, 3.43%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.38 (s, 3H, methyl H), 2.47 (s, 3H, methyl H), 2.48 (s, 3H, methyl H), 4.85 (d, 1H, J = 10.8 Hz, isoxazolinic 4-H), 6.14 (d, 1H, J = 10.8 Hz, isoxazolinic 5-H), 6.60 (m, 1H, aromatic H), 7.04 (m, 1H, aromatic H), 7.30 (m, 1H, aromatic H), 7.43 (m, 2H, aromatic H), 7.82 (m, 3H, aromatic H); δ_C ($CDCl_3$) 17.85, 18.52 and 18.96 (methyl C), 53.69 (isoxazolinic C-4), 78.41 (isoxazolinic C-5), 122.60, 123.16, 126.23, 127.99, 128.51, 128.73, 129.31, 129.58, 131.45, 131.70, 133.19, 133.49,

135.45 and 135.75 (aromatic C), 158.96 (isoxazolinic C-3).

3a,11b-Dihydro-3-(3,5-dichloro-2,4,6-trimethylphenyl)pyreno[4,5-d]isoxazole **3b**. Yield 15.9%; m.p. 245-246 °C from diethyl ether (Found: C, 72.24; H, 4.48; N, 3.28. $C_{26}H_{19}NOCl_2$ requires: C, 72.23; H, 4.43; N, 3.24%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.07 (s, 3H, methyl H), 2.52 (s, 3H, methyl H), 2.57 (s, 3H, methyl H), 5.24 (d, 1H, J = 11.3 Hz, isoxazolinic 4-H), 6.47 (d, 1H, J = 11.3 Hz, isoxazolinic 5-H), 6.79 (m, 1H, aromatic H), 7.34 (m, 2H, aromatic H), 7.79 (m, 3H, aromatic H), 8.00 (m, 2H, aromatic H); δ_C ($CDCl_3$) 17.68, 18.58 and 18.98 (methyl C), 53.45 (isoxazolinic C-4), 78.97 (isoxazolinic C-5), 125.37, 125.63, 126.39, 126.48, 126.74, 126.95, 127.32, 127.48, 127.92, 128.37, 129.82, 130.81, 131.04, 135.21 and 135.50 (aromatic C), 158.59 (isoxazolinic C-3).

3a,11a-Dihydro-3-mesityl-anthraceno[1,2-d]isoxazole **3c**. Yield 15.7%; m.p. 164-167 °C from diethyl ether (Found: C, 85.01; H, 6.23; N, 4.11. $C_{24}H_{21}NO$ requires: C, 84.92; H, 6.24; N, 4.13%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.41 (s, 3H, methyl H), 2.18 (s, 3H, methyl H), 2.43 (s, 3H, methyl H), 4.96 (d, 1H, J = 11.7 Hz, isoxazolinic 4-H), 5.80 (ddd, 1H, J = 11.7, 3.0 and 1.2 Hz, isoxazolinic 5-H), 6.05 (dd, 1H, J = 9.9 and 3.0 Hz, vinylic H), 6.50 (s, 1H, aromatic H), 6.79 (d, 1H, J = 9.9 Hz, vinylic H), 6.91 (m, 2H, aromatic H), 7.35 (m, 3H, aromatic H), 7.51 (s, 1H, aromatic H), 7.73 (m, 1H, aromatic H); δ_C ($CDCl_3$) 18.84, 19.85 and 20.99 (methyl C), 52.51 (isoxazolinic C-4), 77.63 (isoxazolinic C-5), 125.20, 126.06, 126.22, 127.45, 127.62, 128.00, 128.20, 128.84, 129.19, 132.73, 132.79, 135.85, 136.04, 138.09, 138.47 and 138.65 (aromatic C), 159.11 (isoxazolinic C-3).

3a,3b,6a,12b-Tetrahydro-3,6-dimesityl-anthraceno[2,1-d][4,3-d]diisoxazole **4a**. Yield 4.6%; m.p. 210-212 °C from diethyl ether (Found: C, 81.53; H, 6.49; N, 5.63. $C_{34}H_{32}N_2O_2$ requires: C, 81.57; H, 6.44; N, 5.60%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.32 (s, 3H, methyl H), 2.01 (s, 6H, methyl H), 2.24 (s, 3H, methyl H), 2.28 (s, 3H, methyl H), 2.33 (s, 3H, methyl H), 4.53 (dd, 1H, J = 9.0 and 2.4 Hz, isoxazolinic 4-H), 4.67 (d, 1H, J = 10.5 Hz, isoxazolinic 4'-H), 4.97 (dd, 1H, J = 10.5 and 2.4 Hz, isoxazolinic 5'-H), 5.99 (d, 1H, J = 9.0 Hz, isoxazolinic 5-H), 6.61 (s, 1H, aromatic H), 6.90 (m, 3H, aromatic H), 7.42 (m, 4H, aromatic H), 7.86 (m, 1H, aromatic H), 8.27 (s, 1H, aromatic H); δ_C ($CDCl_3$) 18.93, 19.87 and 21.02, (methyl C), 51.40 and 51.50, (isoxazolinic C-4), 74.91 and 75.75 (isoxazolinic C-5), 124.25, 124.50, 125.41, 126.28, 126.53, 126.75, 127.17, 128.02, 128.40, 128.58, 128.89, 130.46, 132.57, 132.91, 135.89, 136.92, 139.00 and 139.27 (aromatic C), 158.72 and 159.42 (isoxazolinic C-3).

3a,11a-Dihydro-3-(3,5-dichloro-2,4,6-trimethylphenyl)anthraceno[1,2-d]isoxazole **3d**. Yield 16.5%; m.p. 211-213 °C from diethyl ether (Found: C, 70.68; H, 4.61; N, 3.49. $C_{24}H_{19}NOCl_2$ requires: C, 70.60; H, 4.69; N, 3.43%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.46 (s, 3H, methyl H), 2.44 (s, 3H, methyl H), 2.49 (s, 3H, methyl H), 4.93 (d, 1H, J = 11.4 Hz, isoxazolinic 4-H), 5.86 (ddd, 1H, J = 11.4, 2.8 and 1.3 Hz, isoxazolinic 5-H), 6.06 (dd, 1H, J = 9.8 and 2.8 Hz, vinylic H), 6.81 (d, 1H, J = 9.8 Hz, vinylic H), 6.91 (s, 1H, aromatic H), 7.44 (m, 4H, aromatic H), 7.74 (m, 1H, aromatic H); δ_C ($CDCl_3$) 17.85, 18.53 and 18.98 (methyl C), 53.13 (isoxazolinic C-4), 77.97 (isoxazolinic C-5), 124.34, 125.01, 126.41, 126.52, 127.38, 127.72, 128.19, 128.97, 129.12, 132.64, 132.90, 135.05 and 135.35 (aromatic C), 158.69 (isoxazolinic C-3).

3a,3b,6a,12b-Tetrahydro-3,6-di-(3,5-dichloro-2,4,6-trimethylphenyl)anthraceno[2,1-d][4,3-d]diisoxazole **4b**. Yield 4.3%; m.p. 258-260 °C from diethyl ether (Found: C, 64.01; H, 4.48; N, 4.33. $C_{34}H_{28}N_2O_2Cl_4$

requires: C, 63.97; H, 4.42; N, 4.39%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.32 (s, 6H, methyl H), 2.42 (s, 6H, methyl H), 2.51 (s, 3H, methyl H), 2.54 (s, 3H, methyl H), 4.44 (dd, 1H, J = 9.2 and 2.4 Hz, isoxazolinic 4-H), 4.65 (d, 1H, J = 10.4 Hz, isoxazolinic 4'-H), 5.00 (dd, 1H, J = 10.4 and 2.4 Hz, isoxazolinic 5'-H), 6.03 (d, 1H, J = 9.2 Hz, isoxazolinic 5-H), 6.88 (s, 1H, aromatic H), 7.48 (m, 3H, aromatic H), 7.88 (m, 1H, aromatic H), 8.28 (s, 1H, aromatic H); δ_C ($CDCl_3$) 17.93, 18.48, 18.70, 18.90, 18.96 and 19.10 (methyl C), 52.10 and 52.24, (isoxazolinic C-4), 75.00 and 76.08 (isoxazolinic C-5), 119.20, 124.33, 125.00, 126.42, 126.84, 126.94, 127.14, 128.13, 129.17, 129.78, 130.02, 132.76, 133.07, 133.54, 133.73, 134.08, 134.80, 136.02 and 136.35 (aromatic C), 158.00 and 158.65 (isoxazolinic C-3).

3a,9a,12a,12b-Tetrahydro-3,10-di-(3,5-dichloro-2,4,6-trimethylphenyl)anthraceno[1,2-a][4,3-d]diisoxazole **5a**. Yield 4.3%; m.p. 281-282 °C from diethyl ether (Found: C, 63.91; H, 4.45; N, 4.41. $C_{34}H_{28}N_2O_2Cl_4$ requires: C, 63.97; H, 4.42; N, 4.39%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1. 26 (s, 6H, methyl H), 2.55 (s, 6H, methyl H), 2.57 (s, 6H, methyl H), 4.90 (d, 2H, J = 8.3 Hz, isoxazolinic 4-H), 5.47 (dd, 2H, J = 8.3 and 3.1 Hz, isoxazolinic 5-H), 6.92 (s, 2H, aromatic H), 7.38 (s, 4H, aromatic H); δ_C ($CDCl_3$) 17.90, 18.76 and 19.10 (methyl C), 51.09 (isoxazolinic C-4), 76.37 (isoxazolinic C-5), 123.75, 126.93, 127.07, 127.69, 127.98, 132.22, 132.91, 133.63, 133.86, 135.04 and 136.11 (aromatic C), 159.98 (isoxazolinic C-3).

3a,13a-Dihydro-3-(3,5-dichloro-2,4,6-trimethylphenyl)peryleno[4,5-d]isoxazole **3e**. Yield 8.5%; m.p. 192-198 °C from diethyl ether (Found: C, 74.65; H, 4.31; N, 2.85. $C_{30}H_{21}NOCl_2$ requires: C, 74.69; H, 4.39; N, 2.90%); ν_{max} (KBr) 1450, 1380 cm^{-1}; δ_H ($CDCl_3$) 1.26 (s, 3H, methyl H), 2.54 (s, 3H, methyl H), 2.59 (s, 3H, methyl H), 4.47 (d, 1H, J = 8.9 Hz, isoxazolinic 4-H), 5.03 (dd, 1H, J = 8.9 and 2.2 Hz, isoxazolinic 5-H), 5.45 (d, 1H, J = 2.2 Hz, vinylic H), 6.45 (m, 1H, aromatic H), 7.27 (m, 1H, aromatic H), 7.73 (m, 2H, aromatic H), 7.99 (m, 3H, aromatic H), 8.16 (m, 1H, aromatic H), 8.34, (m, 1H, aromatic H); δ_C ($CDCl_3$) 17.82, 18.86 and 19.14 (methyl C), 50.92 (isoxazolinic C-4), 75.81 (isoxazolinic C-5), 121.47, 122.31, 124.33, 125.29, 126.02, 126.77, 127.66, 127.91, 129.01, 129.44, 129.67, 131.09, 132.41, 133.49, 133.67, 134.05, 134.80, 135.39 and 135.58 (aromatic C), 159.57 (isoxazolinic C-3).

Reaction of **3d** *with* **2b**. To a refluxing solution of **3d** (30 mg, 0.073 mmol) in dry toluene (10 ml) **2b** (50 mg, 0.22 mmol) was added portionwise and the reaction mixture was left under reflux until the 1,3-dipole was consumed. The ^{1}H-NMR spectrum of the reaction mixture showed the characteristic signals the biscycloadducts **4b** and **5a**.

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