Synthetic Exploitation of the Ring-Opening of 3,4-Dinitrothiophene, IX[‡]

Pyrrolidines, Pyrrolines and Pyrroles from 1,4-Diaryl-2,3-dinitro-1,3-butadienes via a 5-*endo-trig* Cyclization

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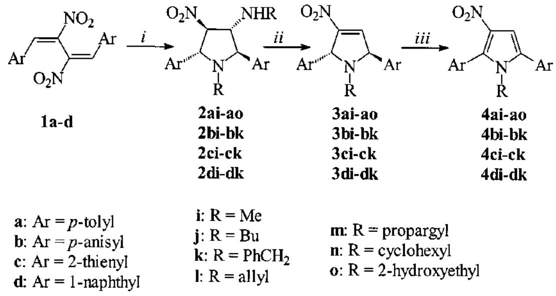
Keywords: 3,4-Dinitrothiophene / Ring-opening / Dinitrobutadienes / Pyrrolidines / Pyrroles

The reactions between 1,4-diaryl-2,3-dinitro-1,3-butadienes **1a**–**d** and primary alkylamines gave high yields of *N*-alkyl-2,5-diaryl-3-alkylamino-4-nitropyrrolidines **2** as pure all-*trans* diastereomers *via* an unusually favoured 5-*endo-trig* ring closure. The stereochemistry of compounds **2** has been attributed through an X-ray crystal structure analysis of the acetyl derivative **5** of **2ai**. Amine elimination from **2** gave the *N*-alkyl-2,5-diaryl-3-nitro-3-pyrrolines **3** which could be easily aromatized to the corresponding pyrroles **4**.

Introduction

In the frame of our studies on the synthetic exploitation of the ring-opening reactions of 3,4-dinitrothiophene and in particular of the ensuing 1,4-diaryl-2,3-dinitro-1,3-butadienes **1**, we have shown that the two conjugated nitrovinyl moieties of **1** can be properly modified to furnish aliphatic and heterocyclic targets which are normally difficult to synthesise.[1]

In the present paper we report on the reactions of dinitrobutadienes **1** with some representative primary amines, a process leading to interesting pyrrolidine derivatives amenable to further transformations, e.g., into pyrrolines **3** and pyrroles **4** (Scheme 1).



Scheme 1. i) RNH_2 (3.3 mol equiv.), CH_2Cl_2/MeOH (1:1); room temp.; ii) PPTS (1.1 mol equiv.), CH_2Cl_2; room temp.; iii) DDQ (1.1 mol equiv.), PhMe; reflux

Results and Discussion

Treatment of 1,4-diaryl-2,3-dinitro-1,3-butadienes **1** with 3.3 molar equivalents of a primary alkylamine, in a dichloromethane/methanol (1:1) mixture and at room temperature, gave generally almost quantitative yields (Table 1) of the corresponding *N*-alkyl-3-alkylamino-2,5-diaryl-4-nitropyrrolidines **2** as single diastereomers. Functionalized amines such as allylamine, propargylamine and ethanolamine have also been successfully employed, while less nucleophilic ones such as arylamines and *tert*-butylamine proved to be unreactive.

In the reactions with the 1-naphthyl derivative **1d** the remarkable drop in the yield of **2** on going from methylamine to the bulkier butyl- or benzylamine indicates that steric factors may play an unfavourable role in the overall transformation of **1** into **2**.

It is worth stressing that the process leading to pyrrolidines **2** proved effective only for 1,4-diaryl-substituted dinitrobutadienes: attempts to extend the same procedure to 2,3-dinitro-1,3-butadienes 1,4-disubstituted with primary alkyl groups were unsuccessful and only complex final mixtures were obtained. For 1,4-dialkyldinitrobutadienes under basic conditions, this is not unprecedented[2] and it is likely that the presence of strongly acidic nitroallylic hydrogens in such substrates triggers (by means of the relevant conjugate bases) undesired competing reactions whose nature is unclear at the moment.

Structure Determination of Pyrrolidines 2

The assignment of the *N*-alkyl-3-alkylamino-2,5-diaryl-4-nitropyrrolidine structure **2** to the isolated compounds relies on their ^1H and ^{13}C NMR spectra and microanalytical data. As regards the stereochemical outcome of the studied

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1434−193X/00/0306−0903 $ 17.50+.50/0

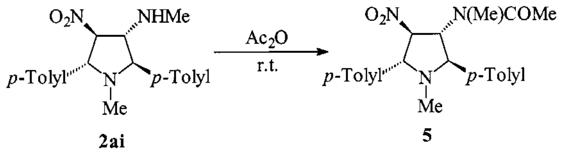
Table 1. Results of the reactions of dinitrobutadienes **1a–d** with primary alkylamines and of the subsequent transformations into pyrrolines **3** and pyrroles **4**; for reagents and conditions see Scheme 1

Ar	R	**2** Yield (%)[a]	**3** Yield (%)[a,b]	**4** Yield (%)[a,b]
1a: *p*-Tolyl	**i**: Methyl	**2ai**, 98	**3ai**, 61	**4ai**, 83
1a	**j**: Butyl	**2aj**, 98	**3aj**, 74	**4aj**, 86
1a	**k**: CH_2Ph	**2ak**, 98	**3ak**, 63	**4ak**, 98
1a	**l**: $CH_2CH{=}CH_2$	**2al**, 98	**3al**, 55	**4al**, 60
1a	**m**: $CH_2C{\equiv}CH$	**2am**, 98	**3am**, 32	**4am**, 98
1a	**n**: Cyclohexyl	**2an**, 98	**3an**, 20	**4an**, 62
1a	**o**: CH_2CH_2OH	**2ao**, 98	**3ao**, 35	**4ao**, 92
1b: *p*-Anisyl	**i**: Methyl	**2bi**, 98	**3bi**, 50	**4bi**, 98
1b	**j**: Butyl	**2bj**, 90	**3bj**, 41	**4bj**, 61
1b	**k**: CH_2Ph	**2bk**, 98	**3bk**, 36	**4bk**, 73
1c: 2-Thienyl	**i**: Methyl	**2ci**, 98	**3ci**, 35	**4ci**, 85
1c	**j**: Butyl	**2cj**, 98	**3cj**, 35	**4cj**, 80
1c	**k**: CH_2Ph	**2ck**, 98	**3ck**, 60	**4ck**, 60
1d: 1-Naphthyl	**i**: Methyl	**2di**, 85	**3di**, 77	**4di**, 77
1d	**j**: Butyl	**2dj**, 42	**3dj**, 72	**4dj**, 70
1d	**k**: CH_2Ph	**2dk**, 45	**3dk**, 54	**4dk**, 80

[a] Yields of isolated products. – [b] Yields refer to a single step from the relevant precursors, after chromatographic purification.

transformations of dinitrobutadienes **1** into pyrrolidines **2**, it is necessary to stress that, within the limits of the ^1H NMR analysis of the crude products, the reactions appeared to generally furnish a single diastereomer of **2**. Moreover, the similarity of the ^1H NMR spectroscopic data (chemical shift values, ^1H-^1H coupling constants) of the four ring hydrogens showed, in all cases, an identical relative stereochemistry of the four contiguous stereogenic centres. Such data, however, did not appear sufficient[3,4] for an unequivocal attribution of configuration. The only hint on this regard came from the analysis of the benzyl derivatives **2ak**, **2bk**, **2ck** and **2dk** which showed two magnetically nonequivalent protons (AB system, J 14 Hz) for the benzylic methylenes: an outcome which is in agreement[4] with a *trans*-2,5-disubstituted pyrrolidine ring.

For a definitive stereochemical characterization of pyrrolidines **2** an X-ray crystal structure analysis was essential; however, we were unable to obtain suitable crystals from any compound **2**. The problem was solved when pyrrolidine **2ai** was transformed (Scheme 2) into the corresponding *N*-acetyl derivative **5** which furnished suitable crystals from a dilute solution in EtOH.



Scheme 2

The crystal structure determination of compound **5** thus allowed us to define unambiguously its relative stereochemistry (see Figure 1). In particular, the ring substituents on C(2), C(3), C(4) and C(5) are all *trans* to each other. According to the asymmetry parameters calculated following Duax,[6] the pyrrolidine ring is in a distorted envelope conformation, the atoms N(1), C(2), C(3), C(4) being coplanar within 0.046(2) Å, while C(5) lies at a distance of 0.650(2) Å from the mean plane above. In the Cambridge Structural Database V5.18,[7] this conformation of *N*-methyl pyrrolidines is more frequent than that of the half chair type. The amide moiety is planar within 0.048(4) Å.

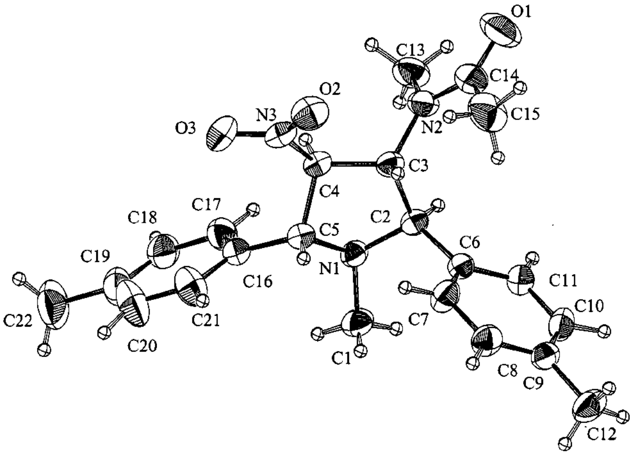


Figure 1. ORTEP[5] drawing of the structure of compound **5**, with numbering of atoms. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms, treated as isotropic, are on an arbitrary scale. Atom H22B is hidden by atom C22.

Selected bond lengths, bond angles and torsion angles between heavier atoms are reported in Table 2. For the whole molecule, the corresponding standard deviations are in the ranges 0.002–0.005 Å, 0.1–0.3° and 0.1–0.4°, respectively. In the crystal structure there are no intermolecular contacts shorter than 0.14 Å with respect to the sum of the van der Waals radii involved.[8]

All geometry calculations were done using PARST.[9] Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.[10] In conclusion, on the grounds of the above outcomes relevant to **5**, and on the reasonable assumption that no stereomutation occurred in the derivatization of Scheme 2, an all-*trans* stereochemistry can be confidently assumed for pyrrolidine **2ai**. The same all-*trans* configuration was finally assigned also to the other pyrroli-

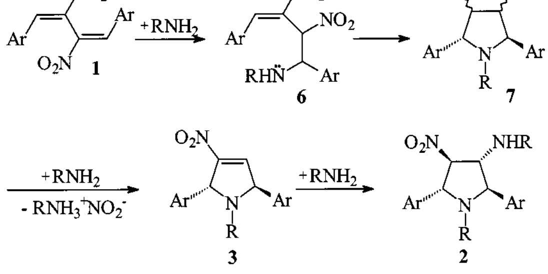
Table 2. Selected geometrical parameters [Å, °] for **5**

C(2)–N(1)	1.479(2)	C(6)–C(2)–C(3)–N(2)	100.4(2)
C(2)–C(3)	1.550(2)	N(1)–C(2)–C(3)–C(4)	–7.3(2)
C(3)–C(4)	1.522(2)	N(2)–C(3)–C(4)–N(3)	–81.2(2)
C(4)–C(5)	1.538(2)	C(2)–C(3)–C(4)–C(5)	32.1(2)
C(5)–N(1)	1.464(2)	C(3)–C(4)–C(5)–N(1)	–44.1(2)
N(1)–C(2)–C(3)	103.5(1)	N(3)–C(4)–C(5)–C(16)	74.2(2)
C(4)–C(3)–C(2)	104.2(1)	C(16)–C(5)–N(1)–C(1)	–60.7(2)
C(3)–C(4)–C(5)	103.4(1)	C(4)–C(5)–N(1)–C(2)	41.3(2)
N(1)–C(5)–C(4)	98.6(1)	C(6)–C(2)–N(1)–C(1)	–30.7(2)
C(5)–N(1)–C(2)	109.7(1)	C(3)–C(2)–N(1)–C(5)	–22.1(2)

dines **2** based on the already mentioned analogies in the NMR spectra.

Mechanistic Considerations

According to the ascertained stoichiometry of the reaction, that requires three mol of amine per mol of dinitrobutadiene **1**, the most likely path to **2** involves (Scheme 3) an initial Michael addition of the amine to one of the two nitrovinyl moieties of **1**, followed by a second, intramolecular, conjugate addition to the remaining nitrovinyl through a "disfavoured"[11,12] 5-*endo*-*trig* ring closure. In the presence of free amine, the ensuing pyrrolidine **7** should undergo a fast base-induced elimination of nitrous acid to give the nitropyrroline **3**, which is not isolable under the present reaction conditions because its nitrovinyl system evidently adds another amine molecule to furnish the isolated pyrrolidine **2**. By amine elimination from the latter (see next section) we were able to isolate authentic samples of the corresponding *trans*-2,5-diaryl-3-nitro-3-pyrrolines **3**. Thus, a control experiment could be performed by reacting the dinitrobutadiene **1a** with one molar equivalent of both benzylamine and triethylamine. The observed formation of **3ak** as the sole product after very short reaction times (TLC) and of both **3ak** and **2ak** in the final mixture (as the minor and the major product, respectively, along with unchanged **1a**, ^{1}H NMR spectroscopy) was in agreement with the mechanism of Scheme 3 and with comparable rates for the formation of **3** and for its evolution to **2**.



Scheme 3

To confirm definitively the intermediacy of **3** along the pathway to **2**, the pyrroline **3dj** was shown to add a butylamine molecule, under conditions similar to those used for **1**, to provide good yields of the relevant pyrrolidine **2dj**. On account of the ascertained 2,5-*trans* configuration of both **2** and **3**, this outcome indicates that the amine addition to **3** proceeds *syn*-stereospecifically at the nitrovinyl moiety.[13]

Since the **7** to **3** transformation (removal of nitrous acid) involves only C(3) and C(4), a 2,5-*trans* configuration can be confidently assigned also to the never-isolated pyrrolidine **7** and should arise at the very moment of the cyclization, when the open-chain precursor **6**, in a suitable conformation, "closes" the ring.

Conformational searches by molecular mechanics using the MMFF94 force field[14a,14b] showed, among the conformers of **6** suitable for cyclization, two couples of low-lying energy: **6A,A'** and **6B,B'** of Scheme 4. Their structure was optimized with ab initio quantum-mechanical calculations at the HF/6–31G* level.[14a,14c] The **6A,A'** couple originates from a kinetically controlled[15] *anti*-addition of an amine molecule to **1**, while the **6B,B'** couple accounts for a possible equilibration to the more stable *syn*-addition product preceding the cyclization. Within each couple, one conformer (**6A** or **6B**) cyclizes to a 2,5-*trans* pyrrolidine, and the other (**6A'** or **6B'**) to a 2,5-*cis* pyrrolidine.

In conformer **6A**, the distance calculated between the two reactive centres involved in the cyclization (3.32 Å) is close to the sum of the van der Waals radii for C and N (3.20 Å).[8] Conversely, in conformer **6A'** (precursor of a 2,5-*cis* pyrrolidine) the above distance is estimated to be 3.56 Å. In the light of the sensitivity of 5-*endo*-*trig* cyclizations to geometric factors[11] such ab initio results can furnish a rationale for the noteworthy diastereoselectivity of the process.

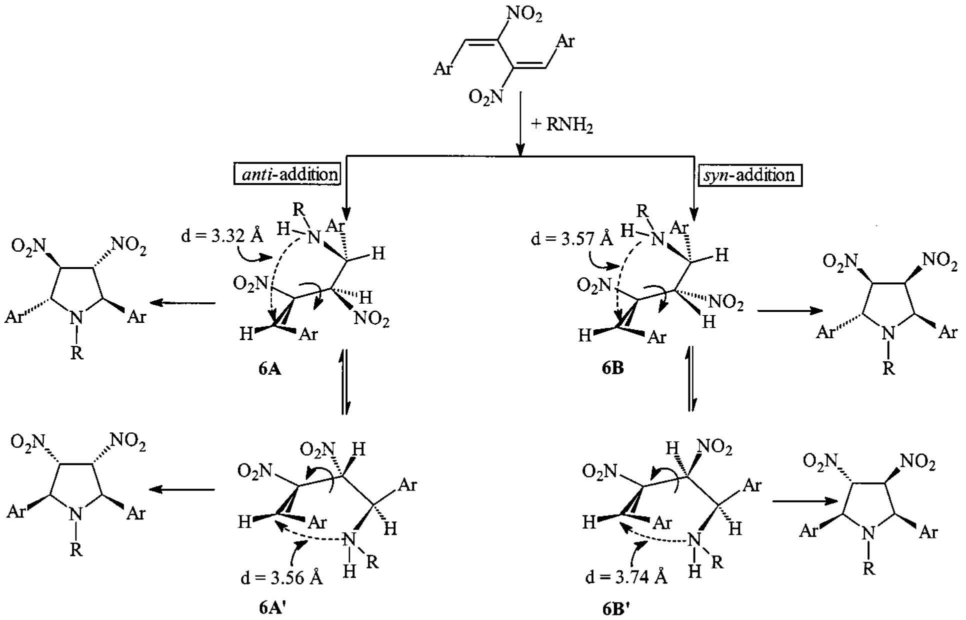
Likewise, within the couple of conformers **6B** and **6B'**, the former, leading to a 2,5-*trans* pyrrolidine, is characterized by a more favourable calculated C···N distance: 3.57 Å vs. 3.74 Å for **6B'**.

In conclusion, the performed quantum-mechanical calculations agree with the experimental outcome and, moreover, indicate that, whatever the configuration at C(3) and C(4), the formation of a 2,5-*trans*-disubstituted pyrrolidine ring from **6** should be favoured by geometrical factors.

Finally, it is important to underline that in no experiment performed on dinitrobutadienes **1** were products detected deriving from a possible competitive addition of a second molecule of amine to the remaining nitrovinyl moiety of **6**. This fact shows that, in spite of its geometric requirements, the 5-*endo*-*trig* cyclization herein is particularly favourite.

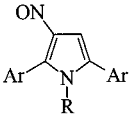
Transformation of Pyrrolidines 2 into Nitropyrrolines 3 and Pyrroles 4

Within the frame of a study aimed at exploiting the easily available pyrrolidines **2**, the possibility of eliminating an amine molecule in order to obtain the corresponding pyrrolines **3** was first investigated. A number of methods were tried with poor results,[16] mainly because of some instability of pyrrolines **3** in the reaction medium and/or during



Scheme 4. Low-energy conformers **6A,A'** and **6B,B'** and relevant distances between the reactive centres

the necessary workup. The method of choice was found to be the treatment of **2** with 1.1 molar equivalents of PPTS in dry dichloromethane at room temperature. As can be seen from the yields reported in Table 1, even under these very mild conditions some decomposition of **3** was observed mainly due to the relatively long reaction times required. Furthermore, to lower the yields of **3**, the competitive formation of *N*-alkyl-2,5-diaryl-3-nitrosopyrroles **8** was always observed: the latter compounds were in some cases isolated although never quantified (see Experimental Section).



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A further, obvious utilization of pyrrolines **3** was their transformation, generally in more than satisfactory yields (Table 1), into the *N*-alkyl-2,5-diaryl-3-nitropyrroles **4** by oxidative aromatization with DDQ in toluene.

Conclusions

In conclusion, in this paper we have reported an easy access, through an unusual *5-endo-trig* cyclization, to highly substituted, diastereochemically pure pyrrolidines, which can be transformed into pyrroline and pyrrole systems. Five membered aza-heterocycles, whose importance is especially due to their wide diffusion among biologically and pharmacologically active compounds,[17] have recently found new applications as powerful catalysts in numerous asymmetric reactions,[17a,18] and are the subject of an increasing number of reports in the recent literature.

Experimental Section

General: Melting points were determined with a Büchi 535 apparatus and are uncorrected. – ^{1}H NMR and ^{13}C NMR spectra were recorded using $CDCl_3$ solution (unless otherwise stated) at 200 and 50 MHz, respectively, with a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as δ values (ppm).

Materials: Petroleum ether and light petroleum refer to the fractions with b.p. 40–60 °C and 80–100 °C, respectively. Methylene chloride and toluene were dried by distillation over phosphorus pentoxide and kept over molecular sieves (4Å). Dry methanol was commercial. – 1,4-Diaryl- and 1,4-dialkyl-2,3-dinitro-1,3-butadienes were synthesized according to a procedure previously reported.[19] Commercial methylamine (2.0 M solution in methanol) was used as received; other primary amines were commercial samples distilled before use and kept over KOH drops or molecular sieves (4Å). Pyridinium *p*-toluenesulfonate (PPTS) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were commercial samples, crystallized before use; PPTS was then dried over P_2O_5 and stored under argon. Column (or preparative plate, PTLC) chromatographies were performed on silica gel using petroleum ether and gradients (or appropriate mixtures) with CH_2Cl_2, Et_2O or AcOEt as eluents, the solvents being distilled before use.

Reactions of 1,4-Diaryl-2,3-dinitro-1,3-butadienes with Primary Alkyl Amines: In an Erlenmeyer flask, the appropriate 2,3-dinitro-1,3-butadiene (1 mmol) was dissolved in a CH_2Cl_2/MeOH 1:1 mixture (80 mL) and the amine (3.3 mmol) was added by syringe under magnetic stirring. The pale yellow solution turned red and after a few seconds the colour disappeared. The reaction was followed by TLC and at the end poured into a saturated aqueous NH_4Cl solution. The organic phase was separated and the aqueous one extracted with dichloromethane. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and evaporated under vacuum. The ^{1}H NMR spectrum of the residue generally showed the signals of a clean, diastereochemically pure compound. In a few cases the crude pyrrolidine was purified by column chromatography over silica gel (petroleum ether/dichloromethane gradients as eluent); relevant yields of **2** are collected in Table 1.

***N*-Methyl-3-methylamino-2,5-bis(4-methylphenyl)-4-nitropyrrolidine (2ai):** Orange oil. – ^{1}H NMR: δ = 1.77 (s, 3 H), 2.36 (s, 6 H), 2.41 (s, 3 H), 3.87 (m, 2 H), 4.73 (d, *J* = 5.0 Hz, 1 H), 4.97 (app. t, 1 H) and 7.25 (m, 8 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 21.16, 34.73, 71.48, 73.14, 96.41, 128.41, 128.48, 129.43, 134.58, 136.79, 137.96, 138.19. – $C_{20}H_{25}N_3O_2$ (339.4): calcd. C 70.8, H 7.4, N 12.4; found C 70.6, H 7.6, N 12.3.

***N*-Butyl-3-butylamino-2,5-bis(4-methylphenyl)-4-nitropyrrolidine (2aj):** Yellow oil. – ^{1}H NMR: δ = 0.71 (t, *J* = 6.6 Hz, 3 H), 0.83 (t, *J* = 6.9 Hz, 3 H), 1.25 (m, 8 H), 2.04 (m, 2 H), 2.36 (s, 6 H), 2.55 (m, 2 H), 3.87 (app. t, 1 H), 4.02 (d, *J* = 6.0 Hz, 1 H), 4.86 (m, 2 H), 7.18 (two partly overlapping AA' of AA'BB', *J* = 8.0 Hz, 4 H), 7.30 (two partly overlapping BB' of AA'BB', 4 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 13.83, 13.92, 20.03, 20.22, 21.14, 29.62, 32.16, 45.39, 47.65, 69.51, 71.65, 72.09, 97.27, 128.50, 129.32, 129.38, 135.49, 137.64, 137.73, 137.95. – $C_{26}H_{37}N_3O_2$ (423.6): calcd. C 73.7, H 8.8, N 9.9; found C 73.8, H 8.7, N 9.9.

***N*-Benzyl-3-benzylamino-2,5-bis(4-methylphenyl)-4-nitropyrrolidine (2ak)**: Yellow oil. – ^{1}H NMR: δ = 2.34 and 2.35 (two partly overlapped s, 6 H in all), 2.90 and 3.44 (AB, *J* = 14.7 Hz, 1 H each), 3.77 (AB, *J* = 13.2 Hz, 2 H), 4.02 (m, 2 H), 4.82 (d, *J* = 3.8 Hz, 1 H), 5.06 (app. t, 1 H), 7.22 (m, 18 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 21.14, 49.78, 52.23, 68.15, 71.32, 71.68, 96.39, 126.71, 127.17, 127.92, 127.98, 128.18, 128.40, 128.47, 128.98, 129.21, 129.42, 133.89, 136.59, 138.06, 138.36, 139.23. – $C_{32}H_{33}N_3O_2$ (491.6): calcd. C 78.2, H 6.8, N 8.6; found C 78.1, H 6.9, N 8.6.

***N*-Allyl-3-allylamino-2,5-bis(4-methylphenyl)-4-nitropyrrolidine (2al):** Yellow oil. – ^{1}H NMR: δ = 2.36 (s, 6 H), 2.48 (dd, *J* = 7.0 and 15.4 Hz, 1 H), 2.83 (ddt, *J* = 2.2, 3.7 and 15.4 Hz, 1 H), 3.21 (m, 2 H), 3.94 (dd, *J* = 5.1 and 6.3 Hz, 1 H), 4.03 (d, *J* = 6.3 Hz, 1 H), 4.97 (m, 6 H), 5.54 (dddd, *J* = 3.7, 7.0, 9.8 and 17.9 Hz, 1 H), 5.74 (ddt, *J* = 6.0, 9.8 and 17.6 Hz, 1 H), 7.18 and 7.32 (two AA'BB', *J* = 8.1 Hz, 8 H in all) (the N*H* signal was not detected). – ^{13}C NMR: δ = 21.12, 48.12, 50.40, 68.83, 70.53, 71.59, 96.84, 116.44, 116.62, 128.47, 128.61, 129.30, 129.34, 134.47, 134.65, 135.63, 136.27, 137.88, 138.24. – $C_{24}H_{29}N_3O_2$ (391.5): calcd. C 73.6, H 7.5, N 10.7; found C 73.4, H 7.6, N 10.5.

2,5-Bis(4-methylphenyl)-4-nitro-*N*-propargyl-3-propargylaminopyrrolidine (2am): Orange oil. – ^{1}H NMR: δ = 2.07 (t, *J* = 2.4 Hz, 1 H), 2.12 (t, *J* = 2.5 Hz, 1 H), 2.36 (s, 6 H), 2.58 (dd, *J* = 2.4 and 16.6 Hz, 1 H), 3.01 (dd, *J* = 2.5 and 16.6 Hz, 1 H), 3.44 (d, *J* = 2.4 Hz 2 H), 4.01 (d, *J* = 6.5 Hz, 1 H), 4.13 (m, 1 H), 5.02 (m, 2 H), 7.20 (two partly overlapping AA' of AA'BB', 4 H), 7.36 (two partly overlapping BB' of AA'BB', *J* = 8.1 Hz, 4 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 21.20, 35.94, 37.06, 68.84, 69.56, 70.86, 72.06, 72.26, 79.84, 80.84, 95.87, 128.71, 129.02, 129.48, 129.59, 133.43, 135.14, 138.45, 138.50. – $C_{24}H_{25}N_3O_2$ (387.5): calcd. C 74.4, H 6.5, N 10.8; found C 74.3, H 6.6, N 10.6.

***N*-Cyclohexyl-3-cyclohexylamino-2,5-bis(4-methylphenyl)-4-nitropyrrolidine (2an):** Orange oil. – ^{1}H NMR: δ = 1.40 (m, 22 H), 2.35 (s, 3 H), 2.36 (s, 3 H), 3.99 (app. t, 1 H), 4.24 (d, *J* = 5.7 Hz, 1 H), 4.79 (app. t, 1 H), 5.01 (d, *J* = 4.4 Hz, 1 H), 7.20 (m, 8 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 21.24, 25.85, 25.93, 25.98, 26.40, 34.14, 34.46, 54.68, 56.05, 68.68, 69.09, 70.94, 98.77, 128.34, 128.51, 129.24, 129.38, 137.34, 137.73, 138.64, 139.46. – $C_{30}H_{41}N_3O_2$ (475.7): calcd. C 75.8, H 8.7, N 8.8; found C 75.5, H 8.8, N 8.7.

***N*-(2-Hydroxyethyl)-3-(2-hydroxyethylamino)-2,5-bis(4-methylphenyl)-4-nitropyrrolidine (2ao):** Yellowish solid, m.p. 49.8–51.7 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 2.36 (two overlapped s, 6 H), 2.79 (app. td, 2 H), 3.17 (m, 2 H), 3.50 (m, 2 H), 3.62 (t, *J* = 4.9 Hz, 2 H), 4.02 (app. t, 1 H), 4.22 (d, *J* = 6.2 Hz, 1 H), 4.89 (d, *J* = 5.1 Hz, 1 H), 5.04 (app. t, 1 H), 7.20 (two overlapped AA' of AA'BB', 4 H), 7.31 (two partly overlapping BB' of AA'BB', *J* = 8.1 and 8.3 Hz, 4 H) (the N*H* and O*H* signals were not detected). – ^{13}C NMR: δ = 21.17, 47.37, 49.39, 58.79, 61.35, 68.99, 71.46, 72.08, 96.52, 128.46, 128.60, 129.77, 129.82, 134.23, 136.41, 138.48, 138.63. – $C_{22}H_{29}N_3O_4$ (399.5): calcd. C 66.1, H 7.3, N 10.5; found C 65.8, H 7.5, N 10.2.

2,5-Bis(4-methoxyphenyl)-*N*-methyl-3-methylamino-4-nitropyrrolidine (2bi): Orange oil. – ^{1}H NMR: δ = 1.76 (s, 3 H), 2.42 (s, 3 H), 3.82 (m, 8 H), 4.71 (d, *J* = 4.9 Hz, 1 H), 4.93 (m, 1 H), 6.92 (two partly overlapping AA' of AA'BB', *J* = 8.6 and 8.7 Hz, 4 H), 7.32 (two partly overlapping BB' of AA'BB', 4 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 34.67, 34.81, 55.26, 71.13, 72.78, 73.06, 96.42, 114.05, 114.09, 129.60, 129.74, 130.45, 131.74, 159.54, 159.62. – $C_{20}H_{25}N_3O_4$ (371.4): calcd. C 64.7, H 6.8, N 11.3; found C 64.6, H 6.9, N 11.2.

***N*-Butyl-3-butylamino-2,5-bis(4-methoxyphenyl)-4-nitropyrrolidine (2bj):** Yellow oil. – ^{1}H NMR: δ = 0.70 (t, *J* = 6.8 Hz, 3 H), 0.84 (t, *J* = 7.1 Hz, 3 H), 1.26 (m, 8 H), 2.01 (m, 2 H), 2.54 (m, 2 H) 3.83 [partly overlapping two s (δ = 3.82 and 3.83) and m, 7 H in all], 3.98 (d, *J* = 5.9 Hz, 1 H), 4.84 (m, 2 H), 6.91 (two partly overlapping AA' of AA'BB', *J* = 8.6 Hz, 4 H), 7.34 (two partly overlapping BB' of AA'BB', *J* = 8.6 Hz, 4 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 13.85, 13.92, 20.01, 20.20, 29.53, 32.10, 45.22, 47.68, 55.21, 69.11, 71.56, 97.19, 113.98, 129.65, 129.74, 130.31, 132.64, 159.33, 159.46. – $C_{26}H_{37}N_3O_4$ (455.6): calcd. C 68.5, H 8.2, N 9.2; found C 68.6, H 8.2, N 9.1.

***N*-Benzyl-3-benzylamino-2,5-bis(4-methoxyphenyl)-4-nitropyrrolidine (2bk):** Yellow oil. – ^{1}H NMR: δ = 2.86 and 3.45 (AB, *J* = 14.5 Hz, 2 H in all), 3.80 [two partly overlapping s (δ = 3.81 and 3.82) and AB (*J* = 13.2 Hz), 8 H in all], 3.98 (m, 2 H), 4.20 (d, *J* = 3.6 Hz, 1 H), 5.05 (m, 1 H), 6.88 (d, *J* = 8.7 Hz, 4 H), 7.30 (m, 14 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 49.79, 52.24, 55.28, 67.89, 71.18, 71.32, 96.48, 113.87, 114.12, 126.75, 126.86, 127.12, 127.22, 127.92, 127.98, 128.23, 128.44, 129.69, 130.26, 138.40, 139.21, 159.54, 159.63. – $C_{32}H_{33}N_3O_4$ (532.6): calcd. C 73.4, H 6.4, N 8.0; found C 73.3, H 6.5, N 7.8.

***N*-Methyl-3-methylamino-4-nitro-2,5-bis(2-thienyl)pyrrolidine (2ci):** Brown oil. – ^{1}H NMR: δ = 1.97 (s, 3 H), 2.48 (s, 3 H), 3.86 (app. t, 1 H), 4.24 (d, *J* = 5.8 Hz, 1 H), 4.89 (app. t, 1 H), 5.08 (d, *J* = 4.5 Hz, 1 H), 7.01 (m, 2 H), 7.09 (m, 2 H), 7.34 (m, 2 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 34.52, 34.72, 66.14, 68.11, 73.33, 96.02, 125.86, 126.20, 126.75, 126.97, 127.06, 128.07, 140.14, 142.90. – $C_{14}H_{17}N_3O_2S_2$ (323.4): calcd. C 52.0, H 5.3, N 13.0; found C 51.7, H 5.4, N 12.8.

***N*-Butyl-3-butylamino-4-nitro-2,5-bis(2-thienyl)pyrrolidine (2cj):** Brown oil. – ^{1}H NMR: δ = 0.82 and 0.87 (two partly overlapping t, *J* = 7.1 Hz, 6 H in all), 1.35 (m, 8 H), 2.02 (m, 1 H), 2.32 (m, 1 H), 2.65 (m, 2 H), 3.90 (app. t, 1 H), 4.31 (d, *J* = 5.4 Hz, 1 H), 4.84 (app. t, 1 H), 5.18 (d, *J* = 4.4 Hz, 1 H), 7.00 (m, 2 H), 7.07 (dd, *J* = 1.1 and 3.4 Hz, 1 H), 7.11 (dd, *J* = 1.1 and 3.4 Hz, 1 H), 7.32 (m, 2 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 13.88, 14.00, 20.03, 20.24, 29.69, 32.05, 45.73, 47.47, 63.92, 66.92, 71.68, 96.46, 125.70, 126.07, 126.57, 126.86, 128.03, 140.52, 142.90. – $C_{20}H_{29}N_3O_2S_2$ (407.6): calcd. C 58.9, H 7.2, N 10.3; found C 58.7, H 7.3, N 10.2.

***N*-Benzyl-3-benzylamino-4-nitro-2,5-bis(2-thienyl)pyrrolidine (2ck):** Brown oil. – ^{1}H NMR: δ = 3.04 and 3.69 (AB, *J* = 14.1 Hz, 1 H each), 3.81 and 3.91 (AB, *J* = 13.3 Hz, 1 H each), 4.01 (dd, *J* = 4.6 and 5.9 Hz, 1 H), 4.40 (d, *J* = 5.9 Hz, 1 H), 4.98 (app. t, 1 H), 5.16 (d, *J* = 3.7 Hz, 1 H), 6.97 (m, 4 H), 7.28 (m, 12 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 50.02, 52.04, 64.55, 66.99, 71.59, 96.19, 126.20, 126.44, 126.67, 127.00, 127.11, 127.36, 127.45, 128.00, 128.13, 128.25, 128.40, 128.58, 137.93, 139.21, 139.37, 143.31. – $C_{26}H_{25}N_3O_2S_2$ (475.6): calcd. C 65.7, H 5.3, N 8.8; found C 65.8, H 5.3, N 8.8.

***N*-Methyl-3-methylamino-2,5-bis(1-naphthyl)-4-nitropyrrolidine (2di):** Yellowish solid, m.p. 118.8–119.5 °C (petroleum ether). – ^{1}H NMR: δ = 1.93 (s, 3 H), 2.39 (s, 3 H), 4.17 (dd, *J* = 4.8 and 6.6 Hz, 1 H), 4.95 (d, *J* = 6.6 Hz, 1 H), 5.28 (app. t, 1 H), 6.01 (d, *J* = 4.1 Hz, 1 H), 7.56 (m, 6 H), 7.86 (m, 6 H), 8.36 (d, *J* = 8.1 Hz, 1 H), 8.60 (d, *J* = 8.3 Hz, 1 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 34.77, 34.92, 66.53, 70.29, 73.39, 96.13, 123.12, 123.42, 125.28, 125.59, 125.83, 125.98, 126.39, 126.46, 126.55, 126.78, 128.83, 129.06, 129.13, 129.25, 132.28, 132.36, 133.41, 134.09, 134.20, 135.07. – $C_{26}H_{25}N_3O_2$ (411.5): calcd. C 75.9, H 6.1, N 10.2; found C 75.9, H 6.2, N 10.2.

***N*-Butyl-3-butylamino-2,5-bis(1-naphthyl)-4-nitropyrrolidine (2dj):** Glassy yellow solid. – ^{1}H NMR: δ = 0.50 (t, *J* = 7.1 Hz, 3 H), 0.71 (t, *J* = 7.1 Hz, 3 H), 1.11 (m, 8 H), 2.46 (m, 4 H), 4.15 (app. t, 1 H), 5.08 (app. t, 1 H), 5.28 (d, *J* = 5.9 Hz, 1 H), 6.15 (d, *J* = 4.0 Hz, 1 H), 7.56 (m, 6 H), 7.86 (m, 6 H), 8.30 (d, *J* = 8.0 Hz, 1 H), 8.58 (d, *J* = 8.1 Hz, 1 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 13.67, 13.95, 20.00, 20.05, 30.41, 31.89, 46.29, 47.30, 69.33, 71.87, 95.97, 122.88, 123.59, 125.12, 125.48, 125.64, 125.97, 126.15, 126.79, 128.33, 128.81, 128.99, 129.20, 131.67, 132.17, 134.13, 134.25, 134.77, 136.42. – $C_{32}H_{37}N_3O_2$ (495.7): calcd. C 75.5, H 7.5, N 8.5; found C 75.4, H 7.6, N 8.4.

***N*-Benzyl-3-benzylamino-2,5-bis(1-naphthyl)-4-nitropyrrolidine (2dk)**: Glassy orange solid. – ^{1}H NMR: δ = 3.26 and 3.56 (AB, *J* = 14.4 Hz, 1 H each), 3.66 and 3.76 (AB, *J* = 13.3 Hz, 1 H each), 4.35 (app. t, 1 H), 5.29 (m, 2 H), 6.03 (d, *J* = 3.4 Hz, 1 H), 6.6–8.4 (m, 24 H) (the N*H* signal was not detected). – ^{13}C NMR: δ = 50.62, 52.07, 63.68, 71.22, 96.83, 123.12, 123.27, 125.12, 125.58, 125.73, 125.86, 126.27, 126.40, 126.69, 127.16, 127.69, 127.92, 128.07, 128.34, 128.84, 129.00, 129.07, 129.18, 132.05, 132.37, 133.97, 134.13, 135.25, 138.52, 139.08. – $C_{38}H_{33}N_3O_2$ (563.7): calcd. C 81.0, H 5.9, N 7.5; found C 81.1, H 6.0, N 7.5.

Synthesis of Pyrrolidine 5 from 2ai: In a flask, compound **2ai** (1 mmol) was dissolved in acetic anhydride (2.5 mL). After ca. one hour, the reaction mixture was poured into water and the pH adjusted to neutrality with a saturated Na_2CO_3 aqueous solution. After extraction with diethyl ether, the organic phase was washed with a $NaHCO_3$ aqueous solution, then with water and finally dried over Na_2SO_4. After evaporation of ether under reduced pressure, the crude residue was purified by column chromatography to give the product **5** as a white solid (62% yield). Single crystals of **5**, suitable for X-ray crystallography (see below) were grown by slow crystallization from ethanol.

3-(*N'*-Acetyl-*N'*-methylamino)-*N*-methyl--2,5-bis(4-methylphenyl)-4-nitropyrrolidine (5): Colourless crystals, m.p. 114.1–114.5 °C (petroleum ether). – The ^{1}H NMR spectrum showed absorptions attributable to two conformers (A and B, in a ca. 3:2 ratio) due to the presence of the acetamido group. ^{1}H NMR: δ = 1.71 [s, 3 H(B)], 1.78 [s, 3 H(A)], 1.88 [s, 3 H(B)], 2.10 [s, 3 H(A)], 2.36 and 2.37 [two partly overlapping s, 6 H(A) + 6 H(B)], 2.86 [s, 3 H(A)], 3.09 [s, 3 H(B)], 4.29 [d, *J* = 6.2 Hz, 1 H(B)], 4.68 [m, 3 H(A) + 1 H(B)], 5.05 [app. t, 1 H(B)], 5.21 [dd, *J* = 6.2 and 8.1 Hz, 1 H(B)], 5.75 [dd, *J* = 6.2 and 7.4 Hz, 1 H(A)], 7.24 [m, 6 H(A) + 8 H(B)], 7.43 [AA' of AA'BB', *J* = 8.1 Hz, 2 H(A)]. – $C_{22}H_{27}N_3O_3$ (381.5): calcd. C 69.3, H 7.1, N 11.0; found C 69.2, H 7.2, N 11.0.

Reactions of Pyrrolidines 2 with PPTS: To a solution of pyrrolidine **2** (0.6 mmol) in anhydrous dichloromethane (30 mL) at room temperature PPTS (0.66 mmol) was added all at once under magnetic stirring. The progress of the reaction was checked by TLC, the end being judged by the disappearance of the substrate (≥ 10 h). Dichloromethane (30 mL) was then added and the solution washed with saturated aqueous NaCl solution, dried (Na_2SO_4), filtered and evaporated under vacuum. Pure products **3** were obtained by column chromatography on silica gel (see Table 1 for relevant yields) together with minor quantities of nitrosopyrroles **8**. Generally, the pyrrolines **3** were immediately submitted to ^{1}H NMR analysis and to further chemical transformation; their structure was confirmed through the corresponding aromatized compounds **4**.

***N*-Methyl-2,5-bis(4-methylphenyl)-3-nitro-3-pyrroline (3ai):** Yellow oil. – ^{1}H NMR: δ = 2.00 (s, 3 H), 2.35 (s, 3 H), 2.36 (s, 3 H), 4.98 (dd, *J* = 2.0 and 6.3 Hz, 1 H), 5.33 (dd, *J* = 1.0 and 6.3 Hz, 1 H), 7.20 (m, 9 H).

***N*-Butyl-2,5-bis(4-methylphenyl)-3-nitro-3-pyrroline (3aj):** Yellow oil. – ^{1}H NMR: δ = 0.64 (t, *J* = 6.8 Hz, 3 H), 1.10 (m, 6 H), 2.35 (s, 3 H), 2.36 (s, 3 H), 5.13 (dd, *J* = 2.2 and 6.4 Hz, 1 H), 5.42 (dd, *J* = 1.0 and 6.4 Hz, 1 H), 6.99 (dd, *J* = 1.0 and 2.2 Hz, 1 H), 7.21 (m, 8 H).

***N*-Benzyl-2,5-bis(4-methylphenyl)-3-nitro-3-pyrroline (3ak):** Yellow needles, m.p. 111.5–112.6 °C (petroleum ether). – ^{1}H NMR: δ = 2.35 (s, 3 H), 2.37 (s, 3 H), 3.25 and 3.66 (AB, *J* = 14.0 Hz, 1 H each), 5.15 (dd, *J* = 2.0 and 6.2 Hz, 1 H), 5.30 (d, *J* = 6.2 Hz, 1 H), 7.11 (m, 14 H). – ^{13}C NMR: δ = 21.20, 51.04, 67.81, 70.62, 125.96, 127.23, 128.13, 128.49, 128.61, 129.29, 129.56, 136.68, 138.53, 138.75, 152.35.

***N*-Allyl-2,5-bis(4-methylphenyl)-3-nitro-3-pyrroline (3al):** Yellow oil. – ^{1}H NMR: δ = 2.35 (s, 3 H), 2.36 (s, 3 H), 2.85 (dd, *J* = 7.1 and 14.8 Hz, 1 H), 3.04 (ddt, *J* = 1.9, 4.4 and 14.8 Hz, 1 H), 4.91 (m, 2 H), 5.17 (dd, *J* = 1.8 and 6.4 Hz, 1 H), 5.46 [partly overlapping d (*J* = 6.4 Hz) and m, 2 H in all], 7.02 (dd, *J* = 1.1 and 1.8 Hz, 1 H), 7.21 (m, 8 H).

2,5-Bis(4-methylphenyl)-3-nitro-*N*-propargyl-3-pyrroline (3am): Yellow oil. – ^{1}H NMR: δ = 2.04 (X of ABX, J_{AX} = J_{BX} = 2.4 Hz, 1 H), 2.35 (s, 3 H), 2.36 (s, 3 H), 2.99 and 3.21 (AB of ABX, J_{AX} = J_{BX} = 2.4 and *J* =$_{AB}$ = 16.7 Hz, 1 H each), 5.16 (dd, *J* = 1.9 and 6.1 Hz, 1 H), 5.53 (d, *J* = 6.1 Hz, 1 H), 7.05 (app. t, 1 H), 7.19 (two partly overlapping AA' of AA'BB', *J* = 8.1 and 8.3 Hz, 4 H), 7.27 (two partly overlapping BB' of AA'BB', 4 H).

***N*-Cyclohexyl-2,5-bis(4-methylphenyl)-3-nitro-3-pyrroline (3an)**: Yellow oil. – ^{1}H NMR: δ = 1.30 (m, 11 H), 2.34 (s, 3 H), 2.36 (s, 3 H), 5.50 (dd, *J* = 1.9 and 7.1 Hz, 1 H), 5.63 (d, *J* = 7.1 Hz, 1 H), 6.82 (app. t, 1 H), 7.20 (m, 8 H).

***N*-(2-Hydroxyethyl)-2,5-bis(4-methylphenyl)-3-nitro-3-pyrroline (3ao):** Yellow oil. – ^{1}H NMR: δ = 2.35 (s, 3 H), 2.36 (s, 3 H), 2.54 (m, 2 H), 3.14 (m, 1 H), 3.33 (m, 1 H), 5.18 (dd, *J* = 1.7 and 6.3 Hz, 1 H), 5.44 (dd, *J* = 0.9 and 6.3 Hz, 1 H), 7.04 (app. s, 1 H), 7.21 (app. s, 8 H) (the O*H* signal was not detected).

2,5-Bis(4-methoxyphenyl)-*N*-methyl-3-nitro-3-pyrroline (3bi): Yellow needles, m.p. 129.8–130.4 °C (taken up with petroleum ether). –

^{1}H NMR: δ = 2.00 (s, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 4.96 (dd, *J* = 2.0 and 6.2 Hz, 1 H), 5.30 (dd, *J* = 1.0 and 6.2 Hz, 1 H), 6.91 (two partly overlapping AA' of AA'BB', *J* = 8.7 Hz, 4 H), 7.04 (br s, 1 H), 7.25 (two partly overlapping BB' of AA'BB', 4 H).

_N_-Butyl-2,5-bis(4-methoxyphenyl)-3-nitro-3-pyrroline (3bj): Yellow oil. – ^{1}H NMR: δ = 0.65 (t, *J* = 7.0 Hz, 3 H), 1.13 (m, 4 H), 2.31 (t, *J* = 7.4 Hz, 2 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 5.11 (dd, *J* = 1.9 and 6.3 Hz, 1 H), 5.39 (d, *J* = 6.3 Hz, 1 H), 6.90 (two partly overlapping AA' of AA'BB', *J* = 8.7 Hz, 4 H), 6.97 (app. s, 1 H), 7.27 (two partly overlapping BB' of AA'BB', *J* = 8.7 Hz, 4 H).

_N_-Benzyl-2,5-bis(4-methoxyphenyl)-3-nitro-3-pyrroline (3bk): Orange oil. – ^{1}H NMR: δ = 3.25 and 3.67 (AB, *J* = 13.8 Hz, 1 H each), 3.81 and 3.82 (two partly overlapping s, 6 H in all), 5.13 (d, *J* = 5.9 Hz, 1 H), 5.29 (d, *J* = 5.9 Hz, 1 H), 6.95 (m, 8 H), 7.24 (m, 6 H).

_N_-Methyl-3-nitro-2,5-bis(2-thienyl)-3-pyrroline (3ci): Orange oil. – ^{1}H NMR: δ = 2.16 (s, 3 H), 5.29 (dd, *J* = 1.9 and 5.4 Hz, 1 H), 5.61 (d, *J* = 5.4 Hz, 1 H), 7.05 (m, 4 H), 7.30 (m, 3 H).

_N_-Butyl-3-nitro-2,5-bis(2-thienyl)-3-pyrroline (3cj): Brown oil. – ^{1}H NMR: δ = 0.75 (t, *J* = 7.1 Hz, 3 H), 1.25 (m, 4 H), 2.35 (m, 2 H), 5.38 (dd, *J* = 1.9 and 5.4 Hz, 1 H), 5.71 (d, *J* = 5.4 Hz, 1 H), 7.02 (m, 4 H), 7.10 (dd, *J* = 1.2 and 3.5 Hz, 1 H), 7.31 (m, 2 H).

_N_-Benzyl-3-nitro-2,5-bis(2-thienyl)-3-pyrroline (3ck): Yellow oil. – ^{1}H NMR: δ = 3.31 and 3.86 (AB, *J* = 13.9 Hz, 1 H each), 5.47 (dd, *J* = 1.5 and 5.3 Hz, 1 H), 5.62 (d, *J* = 5.3 Hz, 1 H), 6.79 (d, *J* = 3.6 Hz, 1 H), 6.98 (m, 3 H), 7.05 (br s, 1 H), 7.27 (m, 7 H).

_N_-Methyl-2,5-bis(1-naphthyl)-3-nitro-3-pyrroline (3di): Yellow solid, m.p. 126.7–127.5 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 2.02 (s, 3 H), 5.83 (dd, *J* = 1.4 and 6.4 Hz, 1 H), 6.58 (d, *J* = 6.4 Hz, 1 H), 7.39 (app. t, 1 H), 7.60 (m, 7 H), 7.89 (m, 5 H), 8.23 (d, *J* = 8.1 Hz, 1 H), 8.44 (d, *J* = 8.4 Hz, 1 H).

_N_-Butyl-2,5-bis(1-naphthyl)-3-nitro-3-pyrroline (3dj): Yellow oil. – ^{1}H NMR: δ = 0.41 (t, *J* = 6.9 Hz, 3 H), 0.95 (m, 4 H), 2.39 (t, *J* = 6.8 Hz, 2 H), 6.12 (dd, *J* = 1.1 and 6.6 Hz, 1 H), 6.65 (d, *J* = 6.6 Hz, 1 H), 7.28 (m, 1 H), 7.57 (m, 7 H), 7.91 (m, 5 H), 8.27 (d, *J* = 8.1 Hz, 1 H), 8.47 (d, *J* = 8.4 Hz, 1 H).

_N_-Benzyl-2,5-bis(1-naphthyl)-3-nitro-3-pyrroline (3dk): Glassy yellowish compound. – ^{1}H NMR: δ = 3.32 and 3.72 (AB, *J* = 13.7 Hz, 1 H each), 6.14 (d, *J* = 6.5 Hz, 1 H), 6.49 (d, *J* = 6.5 Hz, 1 H), 6.63 (app. d, 2 H), 7.05 (m, 4 H), 7.39 (m, 2 H), 7.57 (m, 6 H), 7.88 (m, 5 H), 8.20 (m, 1 H).

_N_-Methyl-2,5-bis(4-methylphenyl)-3-nitrosopyrrole (8ai): Greenish solid, m.p. 146.6–147.8 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 2.41 (s, 3 H), 2.46 (s, 3 H), 3.64 (s, 3 H), 5.95 (s, 1 H), 7.26, 7.35 and 7.73 (two AA'BB' systems, *J* = 8.1 Hz, 2 H, 4 H and 2 H respectively). – ^{13}C NMR: δ = 21.28, 21.45, 34.32, 91.59, 126.16, 128.24, 129.11, 129.29, 129.49, 131.49, 138.03, 138.71, 139.98, 149.96, 164.14. – $C_{19}H_{18}N_2O$ (290.4): calcd. C 78.6, H 6.3, N 9.7; found C 78.7, H 6.1, N 9.8.

_N_-Butyl-2,5-bis(4-methylphenyl)-3-nitrosopyrrole (8aj): Greenish solid, m.p. 85.6–86.3 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 0.60 (t, *J* = 7.2 Hz, 3 H), 0.94 (app. sext., 2 H), 1.29 (app. quint., 2 H), 2.41 (s, 3 H), 2.46 (s, 3 H), 4.11 (t, *J* = 7.3 Hz, 2 H), 5.90 (s, 1 H), 7.25 and 7.31 (AA'BB', *J* = 8.5 Hz, 2 H each), 7.37 and 7.68 (AA'BB', *J* = 8.1 Hz, 2 H each). – ^{13}C NMR: δ = 13.25, 19.39, 21.29, 21.46, 32.16, 45.27, 92.60, 126.61, 128.85, 129.20, 129.30, 129.47, 131.30, 137.41, 138.63, 139.75, 149.94, 164.55. – $C_{22}H_{24}N_2O$ (332.4): calcd. C 79.5, H 7.3, N 8.4; found C 79.5, H 7.4, N 8.1.

_N_-Benzyl-2,5-bis(4-methylphenyl)-3-nitrosopyrrole (8ak): Green oil. – ^{1}H NMR: δ = 2.35 (s, 3 H), 2.41 (s, 3 H), 5.31 (s, 2 H), 6.05 (s, 1 H), 6.74 (m, 2 H), 7.15 (m, 7 H), 7.27 and 7.62 (AA'BB', *J* = 8.1 Hz, 2 H each). – ^{13}C NMR: δ = 21.25, 21.43, 48.90, 92.78, 126.08, 127.54, 128.17, 128.65, 129.28, 131.34, 137.05, 137.89, 138.69, 139.95, 150.35, 164.44. – $C_{25}H_{22}N_2O$ (366.5): calcd. C 81.9, H 6.1, N 7.6; found C 81.6, H 6.2, N 7.4.

_N_-Allyl-2,5-bis(4-methylphenyl)-3-nitrosopyrrole (8al): Green oil. – ^{1}H NMR: δ = 2.39 (s, 3 H), 2.45 (s, 3 H), 4.64 (m, 2 H), 4.82 (dd, *J* = 1.0 and 17.1 Hz, 1 H), 5.14 (dd, *J* = 1.0 and 10.4 Hz, 1 H), 5.73 (m, 1 H), 5.95 (s, 1 H), 7.29 (m, 6 H), 7.70 (AA' of AA'BB', *J* = 8.1 Hz, 2 H). – ^{13}C NMR: δ = 21.28, 21.46, 47.39, 92.42, 117.42, 126.08, 127.29, 129.18, 129.29, 129.39, 131.28, 133.36, 137.51, 138.79, 139.96, 149.95, 164.38. – $C_{21}H_{20}N_2O$ (316.4): calcd. C 79.7, H 6.4, N 8.9; found C 79.6, H 6.5, N 8.9.

_N_-Butyl-2,5-bis(4-methoxyphenyl)-3-nitrosopyrrole (8bj): Green oil. – ^{1}H NMR: δ = 0.62 (t, *J* = 7.2 Hz, 3 H), 0.89 (m, 2 H), 1.26 (m, 2 H), 3.86 (s, 3 H), 3.90 (s, 3 H), 5.89 (s, 1 H), 4.09 (t, *J* = 7.4 Hz, 2 H), 6.97 and 7.72 (AA'BB', *J* = 8.9 Hz, 2 H each), 7.08 and 7.33 (AA'BB', *J* = 8.8 Hz, 2 H each). – ^{13}C NMR: δ = 13.41, 19.48, 32.17, 45.31, 55.45, 92.60, 114.28, 114.33, 121.70, 124.03, 130.68, 132.82, 137.34, 150.02, 160.05, 160.92, 164.60. – $C_{22}H_{24}N_2O_3$ (364.4): calcd. C 72.5, H 6.6, N 7.7; found C 72.5, H 6.7, N 7.8.

_N_-Benzyl-2,5-bis(4-methoxyphenyl)-3-nitrosopyrrole (8bk): Greenish solid, m.p. 139.2–140.1 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 3.80 (s, 3 H), 3.85 (s, 3 H), 5.26 (s, 2 H), 5.97 (s, 1 H), 6.80 (m, 4 H), 6.98 (half AA'BB' system, *J* = 8.6 Hz, 2 H), 7.18 (m, 5 H), 7.65 (half AA'BB' system, *J* = 8.8 Hz, 2 H). – ^{13}C NMR: δ = 48.88, 55.37, 92.71, 114.02, 114.13, 121.17, 123.35, 126.04, 127.59, 128.74, 130.77, 132.85, 137.11, 137.69, 150.19, 159.94, 160.91, 164.45. – $C_{25}H_{22}N_2O_3$ (398.5): calcd. C 75.4, H 5.6, N 7.0; found C 75.3, H 5.5, N 7.0.

_N_-Methyl-3-nitroso-2,5-bis(2-thienyl)pyrrole (8ci): Green oil. – ^{1}H NMR: δ = 3.86 (s, 3 H), 5.99 (s, 1 H), 7.13 and 7.17 (two partly overlapping dd, respectively: *J* = 3.6 and 4.9 Hz, *J* = 1.4 and 3.6 Hz, 2 H in all), 7.28 (dd, *J* = 3.7 and 4.9 Hz, 1 H), 7.42 (dd, *J* = 1.3 and 4.9 Hz, 1 H), 7.67 (m, 2 H). – ^{13}C NMR: δ = 34.45, 92.68, 127.21, 127.75, 128.06, 128.73, 130.64, 131.18, 131.57, 131.73, 142.81, 163.20. – $C_{13}H_{10}N_2OS_2$ (274.4): calcd. C 56.9, H 3.7, N 10.2; found C 56.6, H 3.8, N 10.0.

_N_-Butyl-3-nitroso-2,5-bis(2-thienyl)pyrrole (8cj): Green oil. – ^{1}H NMR: δ = 0.80 (t, *J* = 7.2 Hz, 3 H), 1.25 (m, 2 H), 1.65 (m, 2 H), 4.27 (t, *J* = 7.9 Hz, 2 H), 5.99 (s, 1 H), 7.11 and 7.15 (two partly overlapping dd, respectively: *J* = 3.6 and 5.0 Hz, *J* = 1.4 and 3.6 Hz, 2 H in all), 7.26 (dd, *J* = 3.7 and 5.0 Hz, 1 H), 7.43 (dd, *J* = 1.4 and 5.1 Hz, 1 H), 7.66 (m, 2 H). – ^{13}C NMR: δ = 13.44, 19.64, 32.71, 45.67, 93.83, 127.35, 127.63, 127.79, 128.36, 128.54, 130.01, 130.32, 131.75, 132.17, 142.21, 163.77. – $C_{16}H_{16}N_2OS_2$ (316.4): calcd. C 60.7, H 5.1, N 8.9; found C 60.5, H 5.2, N 8.8.

Reactions of Pyrrolines 3 with DDQ: In a two-neck flask equipped with a reflux condenser with an argon inlet, a rubber septum and a magnetic stirring bar, 0.66 mmol of DDQ was added to a solution of **3** (0.6 mmol) in 15 mL of dry toluene. The reaction mixture was deaerated with three freeze-pump-thaw cycles, and then heated at reflux (generally 1 h, the end of reaction being judged by TLC analysis). After cooling, the precipitate was filtered off and the solution was diluted with 15 mL of diethyl ether, washed with a saturated aqueous solution of Na_2CO_3, with water and then dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure furnished a residue which was usually purified by chromatography on preparative plate.

***N*-Methyl-2,5-bis(4-methylphenyl)-3-nitropyrrole (4ai):** Yellow oil. – ^{1}H NMR: δ = 2.41 and 2.43 (two partly overlapping s, 6 H in all), 3.35 (s, 3 H), 6.85 (s, 1 H), 7.26 (AA' of AA'BB', *J* = 8.4 Hz, 2 H), 7.33 (m, 6 H). – ^{13}C NMR: δ = 21.24, 21.45, 33.73, 105.26, 127.01, 128.47, 129.21, 129.35, 129.47, 130.30, 133.97, 134.43, 135.11, 138.48, 139.36. – $C_{19}H_{18}N_2O_2$ (306.4): calcd. C 74.5, H 5.9, N 9.1; found C 74.6, H 6.0, N 9.1.

***N*-Butyl-2,5-bis(4-methylphenyl)-3-nitropyrrole (4aj):** Pale-yellow solid, m.p. 71.9–72.5 °C (petroleum ether). – ^{1}H NMR: δ = 0.56 (t, *J* = 7.2 Hz, 3 H), 0.88 (sext, *J* = 7.3 Hz, 2 H), 1.21 (quint, *J* = 7.3 Hz, 2 H), 2.41 and 2.44 (two partly overlapping s, 6 H in all), 3.78 (t, *J* = 7.6 Hz, 2 H), 6.80 (s, 1 H), 7.28 (m, 8 H). – ^{13}C NMR: δ = 13.21, 19.34, 21.27, 21.46, 32.38, 45.04, 105.81, 127.10, 128.83, 129.29, 129.42, 130.22, 133.92, 134.03, 134.75, 138.42, 139.15. – $C_{22}H_{24}N_2O_2$ (348.4): calcd. C 75.8, H 6.9, N 8.0; found C 76.0, H 7.0, N 8.1.

***N*-Benzyl-2,5-bis(4-methylphenyl)-3-nitropyrrole (4ak):** Yellow oil. – ^{1}H NMR: δ = 2.35 and 2.36 (two partly overlapping s, 6 H in all), 4.99 (s, 2 H), 6.63 (m, 2 H), 6.91 (s, 1 H), 7.18 (m, 11 H). – ^{13}C NMR: δ = 21.21, 21.40, 48.80, 106.02, 126.03, 126.78, 127.42, 128.49, 129.16, 129.36, 129.47, 130.27, 134.65, 135.17, 137.34, 138.56, 139.24. – $C_{25}H_{22}N_2O_2$ (382.5): calcd. C 78.5, H 5.8, N 7.3; found C 78.3, H 5.9, N 7.2.

***N*-Allyl-2,5-bis(4-methylphenyl)-3-nitropyrrole (4al):** Yellow oil. – ^{1}H NMR: δ = 2.40 and 2.42 (two partly overlapping s, 6 H in all), 4.35 (m, 2 H), 4.67 (dd, *J* = 0.9 and 17.1 Hz, 1 H), 5.05 (dd, *J* = 0.9 and 10.0 Hz, 1 H), 5.57 (ddt, *J* = 4.5, 10.0 and 17.1 Hz, 1 H), 6.86 (s, 1 H), 7.22 and 7.32 (AA'BB', *J* = 8.0 Hz, 2 H each), 7.27 (s, 4 H). – ^{13}C NMR: δ = 21.26, 21.45, 47.35, 105.71, 117.15, 126.88, 128.49, 129.18, 129.33, 129.47, 130.28, 133.51, 134.21, 134.32, 134.82, 138.61, 139.35. – $C_{21}H_{20}N_2O_2$ (332.4): calcd. C 75.9, H 6.1, N 8.4; found C 75.6, H 6.2, N 8.3.

2,5-Bis(4-methylphenyl)-3-nitro-*N*-propargylpyrrole (4am): Pale-yellow solid, m.p. 79.5–80.5 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 2.40, 2.42 and 2.44 [one t (*J* = 2.5 Hz) and two partly overlapped s, 7 H in all], 4.35 (d, *J* = 2.5 Hz, 2 H), 6.87 (s, 1 H), 7.30 (two partly overlapping AA' of AA'BB', 4 H), 7.44 (BB' of AA'BB', *J* = 8.4 Hz, 2 H), 7.49 (BB' of AA'BB', *J* = 8.1 Hz, 2 H). – ^{13}C NMR: δ = 21.29, 21.50, 35.71, 73.81, 79.20, 105.69, 126.24, 127.97, 129.36, 129.43, 129.56, 130.54, 134.29, 134.49, 134.87, 138.84, 139.69. – $C_{21}H_{18}N_2O_2$ (330.4): calcd. C 76.3, H 5.5, N 8.5; found C 76.4, H 5.6, N 8.4.

***N*-Cyclohexyl-2,5-bis(4-methylphenyl)-3-nitropyrrole (4an):** Pale-yellow solid, m.p. 188.7–190.7 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 0.71 (m, 3 H), 1.53 (m, 5 H), 1.75 (m, 2 H), 2.43 and 2.45 (two partly overlapping s, 6 H in all), 3.86 (tt, *J* = 12.2 Hz, 1 H), 6.72 (s, 1 H), 7.26 (m, 8 H). – ^{13}C NMR: δ = 21.34, 21.54, 24.99, 26.22, 33.72, 59.58, 106.52, 128.02, 129.02, 129.81, 130.51, 130.69, 134.00, 134.23, 134.40, 138.57, 139.09. – $C_{24}H_{26}N_2O_2$ (374.5): calcd. C 77.0, H 7.0, N 7.5; found C 77.1, H 7.0, N 7.4.

***N*-(2-Hydroxyethyl)-2,5-bis(4-methylphenyl)-3-nitropyrrole (4ao):** Yellow oil. – ^{1}H NMR: δ = 2.40 and 2.43 (two partly overlapping s, 6 H in all), 3.35 (t, *J* = 6.1 Hz, 2 H), 3.99 (t, *J* = 6.1 Hz, 2 H), 6.82 (s, 1 H), 7.30 (two partly overlapping AA'BB', 8 H) (the OH signal was not observed). – ^{13}C NMR: δ = 21.27, 21.46, 46.91, 61.31, 106.12, 126.98, 128.64, 129.47, 129.53, 129.61, 130.40, 134.25, 134.42, 135.10, 138.73, 139.44. – $C_{20}H_{20}N_2O_3$ (336.4): calcd. C 71.4, H 6.0, N 8.3; found C 71.1, H 6.1, N 8.0.

2,5-Bis(4-methoxyphenyl)-*N*-methyl-3-nitropyrrole (4bi): Yellow oil. – ^{1}H NMR: δ = 3.34 (s, 3 H), 3.86 and 3.88 (two partly overlapping s, 6 H in all), 6.82 (s, 1 H), 7.01 (two partly overlapping AA' of AA'BB', 4 H), 7.34 (two partly overlapping BB' of AA'BB', *J* = 8.8 and 8.9 Hz, 4 H). – ^{13}C NMR: δ = 33.67, 55.39, 105.09, 114.17, 114.31, 122.02, 123.77, 130.65, 131.84, 134.11, 134.78, 159.94, 160.43. – $C_{19}H_{18}N_2O_4$ (338.4): calcd. C 67.5, H 5.4, N 8.3; found C 67.5, H 5.5, N 8.4.

***N*-Butyl-2,5-bis(4-methoxyphenyl)-3-nitropyrrole (4bj):** Yellow oil. – ^{1}H NMR: δ = 0.58 (t, *J* = 7.2 Hz, 3 H), 0.88 (m, 2 H), 1.22 (m, 2 H), 3.76 (t, *J* = 7.5 Hz, 2 H), 3.87 and 3.88 (two partly overlapping s, 6 H in all), 6.78 (s, 1 H), 7.00 (two partly overlapping AA' of AA'BB', 4 H), 7.34 (two partly overlapping BB' of AA'BB', 4 H). – ^{13}C NMR: δ = 13.30, 19.44, 32.45, 45.02, 55.39, 105.74, 114.13, 114.24, 122.20, 124.15, 130.81, 131.78, 133.63, 134.06, 134.41, 159.89, 160.28. – $C_{22}H_{24}N_2O_4$ (380.4): calcd. C 69.5, H 6.4, N 7.4; found C 69.3, H 6.5, N 7.3.

***N*-Benzyl-2,5-bis(4-methoxyphenyl)-3-nitropyrrole (4bk):** Yellow oil. – ^{1}H NMR: δ = 3.81 and 3.82 (two partly overlapping s, 6 H in all), 4.97 (s, 2 H), 6.40 (m, 2 H), 6.87 (m, 5 H), 7.20 (m, 7 H). – ^{13}C NMR: δ = 48.71, 55.34, 105.86, 113.99, 114.15, 121.79, 123.67, 125.98, 127.44, 128.54, 130.89, 131.74, 134.30, 134.50, 134.80, 137.37, 159.97, 160.33. – $C_{25}H_{22}N_2O_4$ (414.5): calcd. C 72.5, H 5.4, N 6.8; found C 72.4, H 5.5, N 6.9.

***N*-Methyl-3-nitro-2,5-bis(2-thienyl)pyrrole (4ci):** Pale-yellow solid, m.p. 74.1–75.1 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 3.52 (s, 3 H), 6.99 (s, 1 H), 7.17 (m, 4 H), 7.42 (dd, *J* = 1.5 and 4.8 Hz, 1 H), 7.59 (dd, *J* = 1.5 and 4.8 Hz, 1 H). – ^{13}C NMR: δ = 33.68, 107.15, 127.05, 127.37, 127.72, 127.91, 127.97, 128.89, 129.10, 130.89, 131.02, 131.83, 135.48. – $C_{13}H_{10}N_2O_2S_2$ (290.4): calcd. C 53.8, H 3.5, N 9.7; found C 53.7, H 3.5, N 9.6.

***N*-Butyl-3-nitro-2,5-bis(2-thienyl)pyrrole (4cj):** Yellow oil. – ^{1}H NMR: δ = 0.71 (t, *J* = 7.2 Hz, 3 H), 1.09 (sext, *J* = 7.7 Hz, 2 H), 1.52 (m, 2 H), 3.91 (t, *J* = 7.9 Hz, 2 H), 6.97 (s, 1 H), 7.16 (m, 4 H), 7.43 (dd, *J* = 1.5 and 4.8 Hz, 1 H), 7.58 (dd, *J* = 2.1 and 4.2 Hz, 1 H). – ^{13}C NMR: δ = 13.32, 19.60, 33.10, 45.53, 107.80, 126.67, 127.07, 127.25, 127.55, 128.11, 128.82, 128.93, 130.86, 131.77, 135.55. – $C_{16}H_{16}N_2O_2S_2$ (332.4): calcd. C 57.8, H 4.9, N 8.4; found C 57.5, H 5.0, N 8.1.

***N*-Benzyl-3-nitro-2,5-bis(2-thienyl)pyrrole (4ck):** Yellow oil. – ^{1}H NMR: δ = 5.14 (s, 2 H), 6.83 (m, 2 H), 6.90 (dd, *J* = 1.2 and 3.6 Hz, 1 H), 6.98 (m, 2 H), 7.03 (dd, *J* = 3.6 and 5.1 Hz, 1 H), 7.09 (s, 1 H), 7.26 [partly overlapping m and dd (*J* = 1.2 and 5.1 Hz), 4 H in all], 7.47 (dd, *J* = 1.2 and 5.0 Hz, 1 H). – ^{13}C NMR: δ = 49.03, 107.85, 125.64, 127.06, 127.15, 127.32, 127.53, 127.66, 127.89, 127.95, 128.33, 128.82, 129.10, 130.88, 131.37, 135.86, 137.21. – $C_{19}H_{14}N_2O_2S_2$ (366.4): calcd. C 62.3, H 3.9, N 7.6; found C 62.1, H 4.0, N 7.4.

***N*-Methyl-2,5-bis(1-naphthyl)-3-nitropyrrole (4di):** Pale-yellow solid, m.p. 213.0–213.8 °C (taken up with petroleum ether). – ^{1}H NMR: δ = 2.99 (s, 3 H), 7.10 (s, 1 H), 7.59 (m, 9 H), 7.77 (m, 1 H), 7.99 (m, 4 H). – ^{13}C NMR: δ = 32.85, 106.82, 124.56, 125.20, 125.29, 125.40, 126.42, 127.20, 127.29, 127.79, 128.66, 128.80, 128.91, 129.44, 129.79, 130.05, 132.33, 132.47, 132.85, 132.93, 133.76, 135.16. – $C_{25}H_{18}N_2O_2$ (378.4): calcd. C 79.4, H 4.8, N 7.4; found C 79.5, H 4.8, N 7.5.

***N*-Butyl-2,5-bis(1-naphthyl)-3-nitropyrrole (4dj):** Glassy pale-yellow solid. – ^{1}H NMR ([D$_6$]DMSO): δ = 0.06 (t, *J* = 7.3 Hz, 3 H), 0.54 (sext, *J* = 7.2 Hz, 2 H), 0.89 (m, 2 H), 3.19 and 3.68 (br AB, 1 H each), 7.08 (s, 1 H), 7.74 (m, 10 H), 8.10 (m, 4 H). – ^{13}C NMR: δ = 12.79, 19.16, 32.82, 45.66, 107.37, 124.73, 125.25, 126.41, 127.13, 127.20, 127.90, 128.61, 128.75, 129.02, 129.49, 129.73, 130.03, 131.84, 132.46, 132.75, 133.07, 133.77, 135.37. –

$C_{28}H_{24}N_2O_2$ (420.5): calcd. C 80.0, H 5.8, N 6.7; found C 79.9, H 5.9, N 6.6.

***N*-Benzyl-2,5-bis(1-naphthyl)-3-nitropyrrole (4dk):** Pale-yellow solid, m.p. 187.3–188.8 °C (taken up with petroleum ether). – ^{1}H NMR ([D$_6$]DMSO): δ = 4.75 (m, 2 H), 6.38 (br s, 2 H), 6.89 (m, 3 H), 7.19 (s, 1 H), 7.59 (m, 9 H), 7.87 (m, 1 H), 8.05 (m, 4 H). – ^{13}C NMR: δ = 49.59, 107.52, 124.56 (br), 125.05, 125.16, 126.27, 126.49 (br), 127.14, 127.28, 128.07, 128.59, 129.71, 129.78, 130.04, 132.51, 132.93, 133.64, 135.67. – $C_{31}H_{22}N_2O_2$ (454.5): calcd. C 81.9, H 4.9, N 6.2; found C 81.9, H 4.9, N 6.1.

X-ray Crystallographic Study of Compound 5: Transparent, colourless single crystals were grown from ethanol. After preliminary Laue photographs, X-ray data were recorded on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo-K_α (λ = 0.7107 Å) radiation. Cell constants were determined by least-squares refinement of diffractometer angles for 25 automatically centred reflections. During the data collection the centring of six reflections was repeated periodically to test the crystal orientation, and two reflections were monitored every two hours to check the crystal stability. No significant crystal decay was observed.

Crystal Data: $C_{22}H_{27}N_3O_3$, M = 381.5 g/mol. Triclinic, a = 7.499(2), b = 12.474(3), c = 12.489(4) Å, α = 109.53(2), β = 103.64(2), γ = 99.14(2)°, V = 1033.3(5) Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.226 g cm^{-3}, $F(000)$ = 408. Crystal dimensions 0.22 × 0.33 × 0.40 mm, μ = 0.082 mm^{-1}; ω/θ scan mode, scan width 1.35°, scan speed 1.0–16.5° min^{-1}; 4712 unique reflections measured ($2.5 \leq \theta \leq 27.5°$).

Structure Solution and Refinement: The structure was solved by direct methods using the SIR97 program[20] and refined by full-matrix least-squares techniques,[21] including the whole data set of 4712 F_o^2 in the calculations. In the final refinement all heavier atoms were treated as anisotropic. For most hydrogen atoms the positional parameters (obtained from difference Fourier syntheses) as well as the isotropic displacement parameters could be refined; to all the methyl hydrogens an U_{iso} value equal to 1.2 times the U_{iso} of the bonded carbon atom was assigned. The hydrogens bonded to C(12) and C(22) were localized by circular difference syntheses and refined as belonging to idealized rigid groups. Convergence was reached with a maximum shift-to-e.s.d. ratio equal to 0.12. Final reliability factors are R_1 = 0.051 on 3279 $F_o \geq 4\sigma(F_o)$, wR_2 = 0.144 for all 4712 F_o^2 and 330 parameters, with a goodness of fit S = 1.024. At the end of the refinement the difference Fourier map was essentially flat, the electron density ranging between 0.17 and –0.18 eÅ^{-3}.

Acknowledgments

We thank Miss P. Franceschini for skilful contributions with the experimental work. Financial support from the University of Genoa and from C. N. R. (Rome) is gratefully aknowledged.

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Received June 2, 1999
[O99325]