

Novel dicyanomethylene compounds from the reaction of 2-aryl-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinoxalines with ethenetetracarbonitrile

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Dedicated to Professor A. T. Balaban at the occasion of his 75th birthday

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Abstract

2-Aryl-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinoxalines **8a-d** react with ethenetetracarbonitrile (TCNE) in aerated benzene with formation of [3-(2-aryl-3-dicyanomethylene-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinoxalin-1-ylidene)-2-aryl-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinoxalin-1-ylidene]propanedinitriles **9a-d** (41-48%), [2-aryl-3-arylimino-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinoxalin-1-ylidene]propanedinitriles **10a-d** (19-22%) as well as quinoxaline-2,3-diol (**11**, 8-11%). Rationales for these transformations are presented.

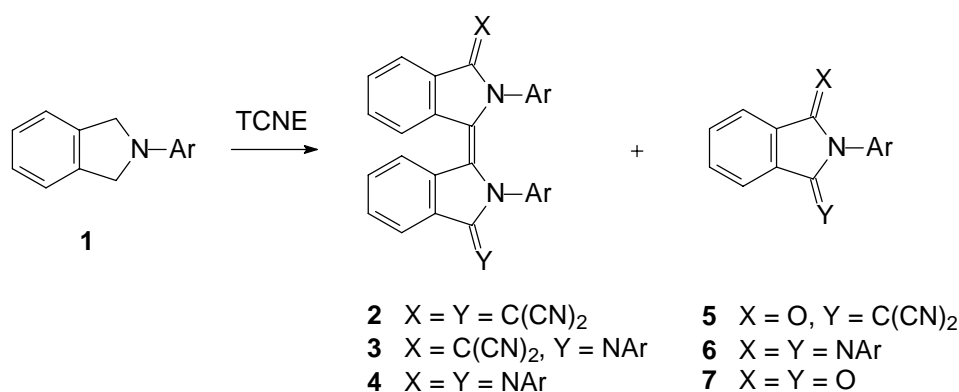
Keywords: Azaisoindoles, dehydrogenation, nitrenes, oxygenation

Introduction

The preparation and reactivity of stable azaisoindoles and benzoanellated analogues thereof have been reported.¹⁻⁶ A π -deficient anellation should make the pyrrole ring more stable towards electrophilic attack.⁵ On the other hand, the successful [4+2]-cycloaddition of electron deficient dienophiles, namely dimethyl ethynedicarboxylate and *N*-methylmaleimide, to 2-*tert*-butylpyrrolo[3,4-*b*]quinoxaline has been reported.^{6,7}

Previously, we have demonstrated that *N*-arylisindolines underwent charge-transfer complexation⁸ as well as deep seated chemical transformations^{9,10} with ethenetetracarbonitrile (TCNE) under initial α -H-atom abstraction to give α -dicyanomethylene derivatives **2** as well as α -oxygenated products **5** and **7** (Scheme 1). The latter two compounds also were obtained from the interaction of 1,4-benzo- or 1,4-naphthoquinones with *N*-arylisindolines.^{11,12} These findings had prompted us to investigate the interaction between another π -acceptor, namely (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile and *N*-arylisindolines in pyridine with admission of air to give products **3**, **4**, **6** and **7** in moderate yields.¹³ 4-Amino-2,7-dinitro-9-fluorenone as

well as (4-amino-2,7-dinitro-9*H*-fluoren-9-ylidene)propanedinitrile also were formed¹³ in this complex process.



Ar = C₆H₄R with R = 2- or 3-OCH₃, 2- or 3- or 4-CH₃, H, 2- or 3-Cl, 4-COCH₃

Scheme 1

This unique reactivity has no precedence and warrants further study. In the present investigation, we undertook the preparation of electron poorer analogues of **1**, namely 2-aryl-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinoxalines **8a-d**, and investigated their behaviour towards **TCNE**.

Results and Discussion

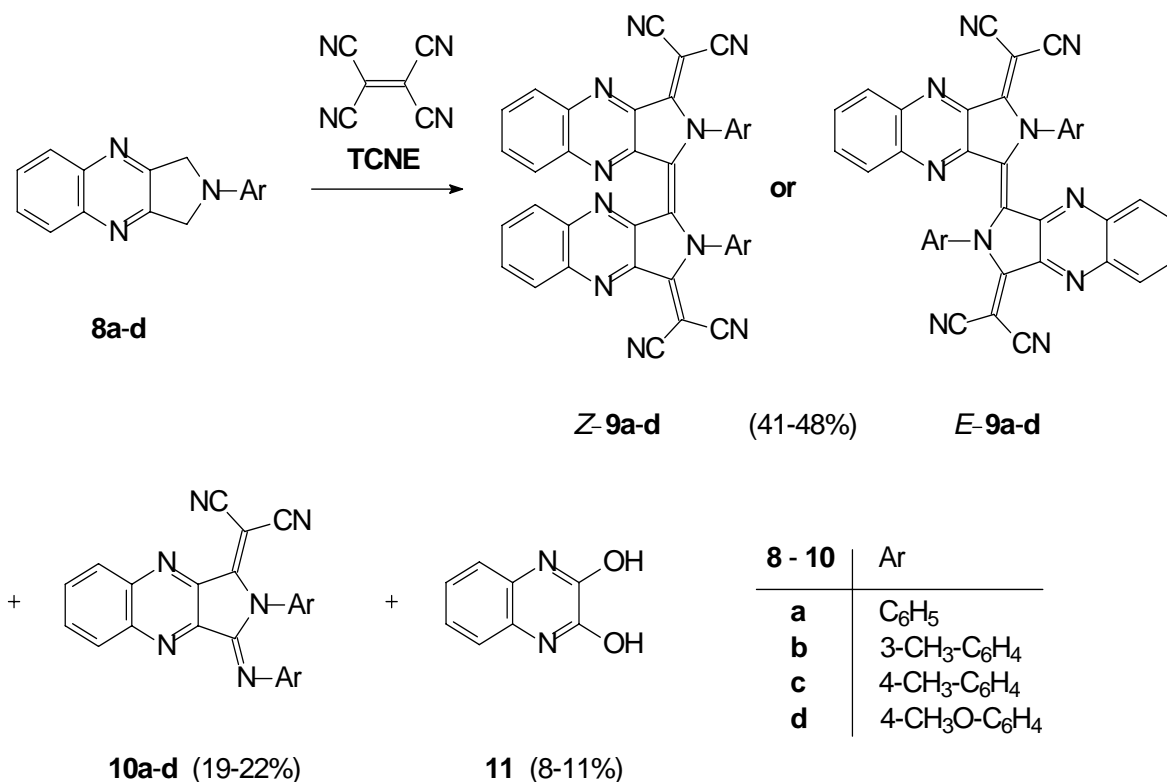
Starting materials **8a-d** were prepared from 2,3-bis(bromomethyl)quinoxaline and anilines. Upon addition of doubled molar amounts of **TCNE** to solutions of **8a-d** in benzene with admission of air, a green colouration is observed which gradually gives way to a brown and finally to a characteristic blue colour. After concentration, the residue was subjected to vacuum sublimation to remove any unreacted **TCNE**. Chromatographic separation of the residue gave some tarry material and numerous coloured zones. From the three most intense zones products **9-11** could be isolated (Scheme 2).

Solutions of compounds **9a-d** show a characteristic deep blue colour, attributable to the local push-pull systems of conjugated double bonds and lone pairs. The λ_{max} values of **9a-d** in the visible spectrum (586-602 nm in acetonitrile solution, log ϵ 4.12-4.45) are very close indicating the same molecular gross structure and configuration. They are also in good agreement with the visible spectra of nine compounds of type **2** (λ_{max} 570-584 nm, log ϵ 4.33-4.84 in acetonitrile) reported earlier.¹⁰

The structures of **9a-d** are further supported by characteristic IR, NMR and mass spectral data. For example, the ¹H-NMR spectrum of **9b** in CDCl₃ clearly shows the absence of

methylene protons but the presence of two isochronous methyl groups located on the two phenyl rings (one singlet only at δ 2.30 ppm for six protons), and phenyl protons. The gross formula $C_{40}H_{22}N_{10}$ for **9b** was confirmed by the mass spectrum which exhibited the molecular ion at m/z 642 (31%). It should also be noted that the mass spectra of compounds **9a-d** show the loss of $C(CN)_2$ from the molecular ions but the correspondent fragment peaks are of relatively low intensity. The IR spectrum of **9b** shows a sharp absorption at 2215 cm^{-1} characteristic for conjugated $C\equiv N$ groups.

The configurational assignment of compounds **9a-d** needs to be addressed. In neither the *Z*- nor the *E*-isomers can the *N*-aryl group be coplanar with the adhering pyrroloquinoxaline unit. Therefore, in the *E*-form the “inner” quinoxaline N-atoms would show an unfavourable interaction with the *N*-aryl π -systems, and the “inner” *peri*-protons would experience the shielding influence of the *N*-aryl ring. No significantly upfield shifted aryl-H signals are detectable, however. Therefore, the *Z* geometry is proposed as most likely for compounds **9a-d** in accordance with their close structural relationship to the clearly cisoid {3-[3-dicyanomethylene-2-(3-methylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(3-methylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (**2**, Ar = 3- CH_3 - C_6H_4), the structure of which had been confirmed unambiguously by a single crystal X-ray structure analysis.¹⁰

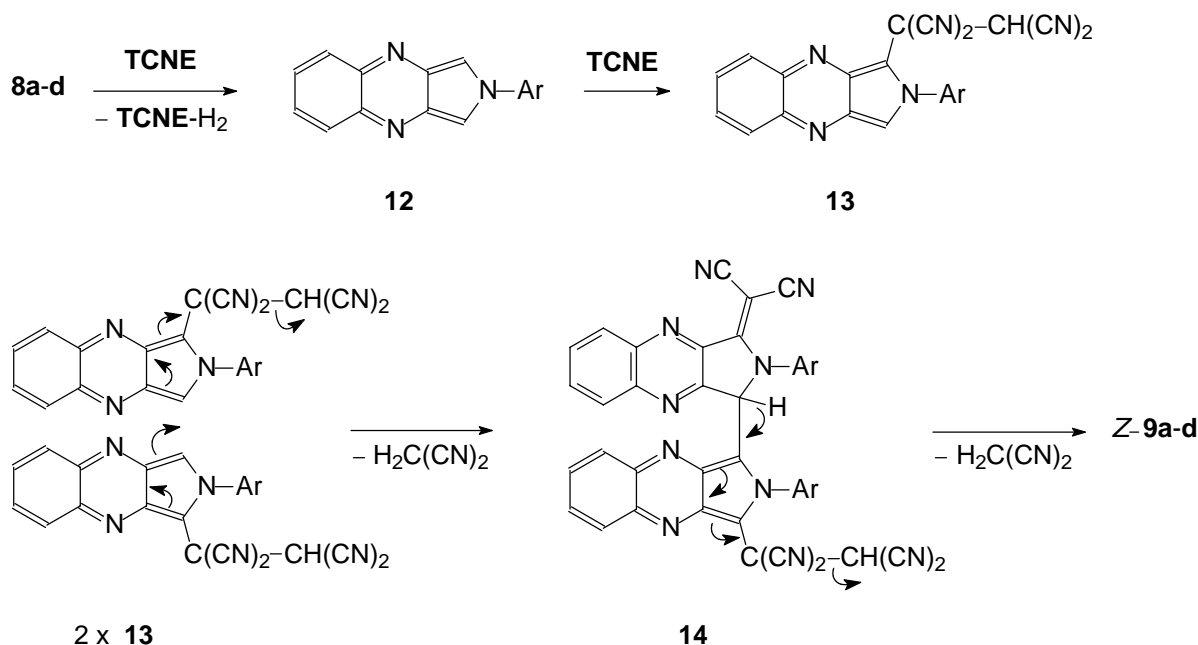


Scheme 2

Similarly, the structures of products **10a-d** are supported by their analytical and spectral data. For example, the elemental analysis of **10b** suggested a gross formula $C_{27}H_{18}N_6$. This was confirmed by the mass spectrum which exhibited a molecular ion at m/z 426 (100%). The IR spectrum showed a strong band at 2214 cm^{-1} due to conjugated cyano groups. The 300 MHz $^1\text{H-NMR}$ spectrum also clearly indicates the absence of any signals at δ 4.83 ppm expected for CH_2 groups of the 1,3-dihydropyrrole ring, but shows two singlets at δ 2.30 and 2.40 ppm with a 1:1 ratio assignable to the two different methyl groups, in addition to the aromatic proton signals.

The structure of quinoxaline-2,3-diol (**11**) was assigned on the basis of its spectroscopic properties (see experimental part) and by comparison of its melting point with the literature value.¹⁴

The reaction conditions provide an overall dehydrogenating and oxygenating environment. For the formation of the main products **9a-d**, an initial didehydrogenation of the starting materials **8a-d** to the fully unsaturated 2*H*-pyrrolo[3,4-*b*]quinoxalines **12** seems to be most logical. This may, by analogy to the reactions of **TCNE** with isoindolines **1** as reported earlier,¹⁰ be effected either by a concerted hydride transfer¹⁵ from C1 of **8** to **TCNE** followed by proton transfer to generate **12** together with 1,1,2,2-tetracyanoethane (**TCNE-H₂**), or by a consecutive (non-concerted) sequence of electron and proton transfers leading to the same products. While the colouration effects observed immediately after combination of the reactant solutions do point to the formation of charge-transfer complexes, they do not allow a clear decision in favour of the non-concerted pathway for didehydrogenation of **8** to **12**. For this reaction to occur via radical ion pairs an additional electronic excitation may be required¹⁶, which is not available under the conditions used in this study.



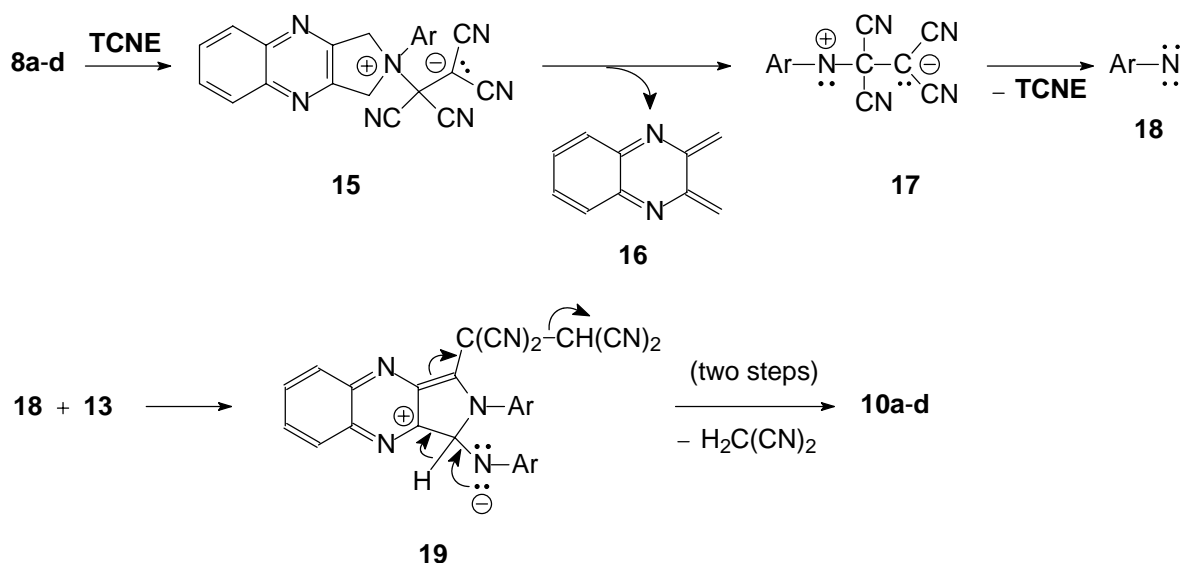
Scheme 3

Intermediates **12** are not isolated and very likely in turn react with **TCNE** to form tetracyanoethylated products **13** (Scheme 3), while there is so far no indication of formation of Diels-Alder type cycloadducts. The conversion **12** → **13** is in fact the first step of a so-called tricyanovinylolation.¹⁷ Instead of expelling one molecule of hydrogen cyanide, however, two molecules of **13** react (in analogy to the case reported before¹⁰) to form **Z-9** via **14** with successive release of two molecules of malononitrile (Scheme 3). This sequence is a dehydrogenative symmetric coupling and at the same time an α -dicyanomethylenation. A closely analogous introduction of a dicyanomethylene group has been observed in the reaction of 1-hydroxy-2-phenylindole with **TCNE** yielding (1-oxido-2-phenyl-3*H*-indol-3-ylidene)propanedinitrile.¹⁸ In contrast to the case reported here, 2-unsubstituted isoindoles (as 1-phenylisoindole) seem to undergo oxidative bimolecular couplings via their radical cations.^{19,20}

The formation of products **10a-d** also clearly involves the conversion of two molecules of starting material **8a-d**, one being dehydrogenated to **12** and further converted into **13**, the other being degraded to provide a source of the (*N*-aryl)imino function. An electrophilic aryl-nitrogen species attacking C3 of **13** would most logically serve this purpose. The nature of this species, however, has not been unraveled yet. An arylnitrene **18**, as proposed in Scheme 4, is just one possibility.

Several reports of either cheletropic or stepwise release of nitrogen species from various types of 1,4-dihydro-1,4-iminonaphthalenes or higher anellated analogues thereof are found in the literature, the prime motive of which is removal of the imino bridge to generate anellated arenes. In all cases, prior to extrusion, the imino nitrogen atom is attached to an electrophilic atom or group, such as oxygen from a peracid,^{21,22} nitrosyl,²³ dichlorocarbene,²⁴ amino (followed by dehydrogenation),^{25,26} but also dimethyl ethyne dicarboxylate²⁷ and benzyne²⁷. It had been suggested^{27,28} that the latter two form zwitterionic adducts from 1,4-iminonaphthalenes by C-N bond heterolysis, and that these zwitterions either release the naphthalene or undergo cyclization to 1,2-heteroanellated naphthalenes.

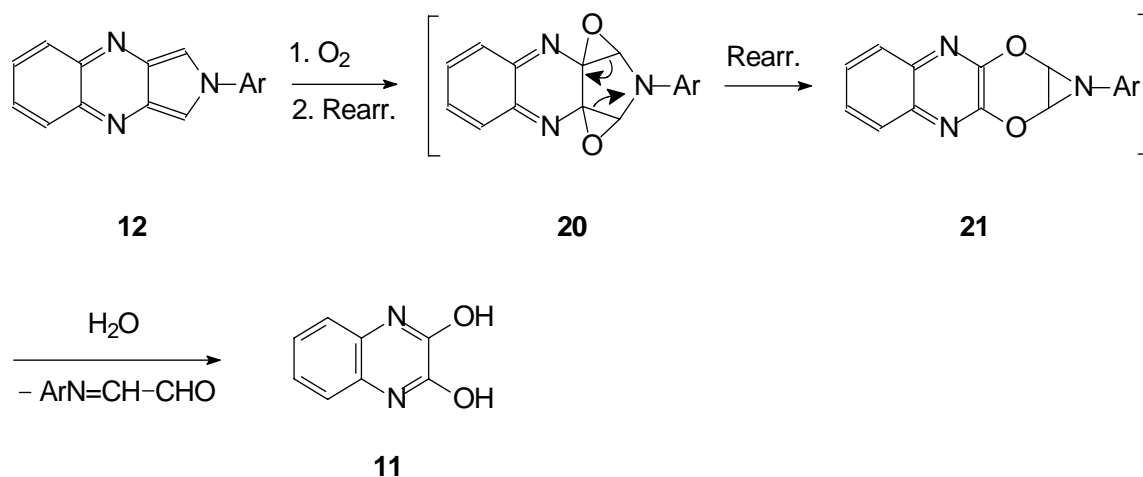
Thus, **TCNE** could, by analogy to the abovementioned behaviour of dimethyl ethylenedicarboxylate,²⁷ add to N2 of **8**, and the resulting zwitterion **15** could release **16** and the betaine **17** (Scheme 4). Either **17** or the nitrene **18** released therefrom could serve as electrophilic agent on **13**. With **18** (in a prototypical sense) intermediate **19** would be formed, which in two steps would afford **10a-d** with release of malononitrile. The betaine **17** could act in the same sense. Also, the radical cation formed from **8** and **TCNE** could, in principle, release the nitrene **18**, and in all cases products **10a-d** would finally be reached. A similar pathway had been proposed earlier for the formation of compounds **3** from isoindolines **1**.¹³ However, no products derived in any way from **16** have been identified so far.



Scheme 4

Last, byproduct **11** is probably formed by a Diels-Alder type addition of oxygen to **12** followed by rearrangement of the primary adduct *via* **20** to **21** (not isolated). The latter compound, being sensitive to water, can generate **11** with the likely release of glyoxal mono-(*N*-aryl)imine (Scheme 5). Isoindoles are sensitive to oxygen,¹⁹ and formation of endo-peroxides which may undergo homolysis to bis-alkoxyl biradicals and further reactions thereof has been reported for a series of *N*-substituted 1,3,4,7-tetramethylisoindoles.²⁹

When evaluating the yields it needs to be considered that the formation of both products **9** and **10** each requires the transformation of two molecules of **8**. Since the reactions occurring involve numerous steps and unidentifiable tarry products are also formed, moderate yields have to be accepted.



Scheme 5

Conclusions

As previously reported for the transformations of isoindolines **1** to products **2** and **3**,^{10,13} dicyanomethylenation and overall dehydrogenative symmetric couplings of the title compounds **8a-d** under the action of ethenetetracarbonitrile (TCNE) have been observed and plausibly rationalized on the basis of relevant findings taken from the literature. The results reported here supplement the rich chemistry of TCNE.¹⁷ Aza-substitution in the starting materials **8a-d** did not lead to decreased reactivity towards TCNE but rather activated their methylene hydrogen atoms.

Experimental Section

General Procedures. The uncorrected melting points were determined with a Reichert Thermovar hot stage microscope. The IR spectra were obtained from KBr disks on either a Shimadzu 408 or a Bruker Vector 22 FT-IR instrument. The 300 MHz ¹H-NMR spectra were recorded on a Bruker WM 300 instrument with tetramethylsilane as internal reference, s = singlet, d = doublet, m = multiplet. The mass spectra (70 eV, electron impact mode) were obtained on an AMD 604 instrument. The visible spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Combustion analyses were run on a Carlo Erba Model 1106 CHN analyser, the results were found to be in good agreement ($\pm 0.2\%$) with the calculated values. Preparative layer chromatography was carried out using air dried 1.0 mm thick layers of slurry applied silica gel Merck PF254 on 48 cm wide and 20 cm high glass plates. Zones were detected by their colour or by quenching of indicator fluorescence upon exposure to 254 nm light.

Preparation of 2-aryl-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalines (8a-d). To a solution of 3.16 g (10 mmol) of 2,3-bis(bromomethyl)quinoxaline in 50 ml of dry toluene, 10 mmol of arylamine and 2.02 g (20 mmol) of triethylamine were added. The mixture was kept under reflux for 3h. After cooling to room temperature, the reaction mixture was filtered and the precipitate was washed thoroughly with chloroform. The washings were shaken with water, dried over anhydrous calcium chloride, and concentrated to give a yellow precipitate, which was crystallized from toluene.

2-Phenyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxaline (8a). Yellow crystals (1.61 g, 65%), mp 246-248 °C. IR (KBr): ν 2967, 2825 (CH₂), 1516 (Ar-C=C) cm⁻¹. ¹H-NMR (CDCl₃): δ 4.82 (s, 4H, 2 CH₂), 6.75-6.90 (m, 3H, Ar-H), 7.25-7.42 (m, 2H, Ar-H), 7.70-7.80 (m, 2H, Ar-H), 8.07-8.15 (m, 2H, Ar-H). MS *m/z* (%): 247 (73) [M⁺], 246 (100), 219 (7), 143 (13), 109 (4), 102 (13), 91 (6), 77 (19). Anal. Calcd. for C₁₆H₁₃N₃ (247.29): C, 77.71; H, 5.30; N, 16.99. Found: C, 77.85; H, 5.23; N, 17.07.

2-(3-Methylphenyl)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxaline (8b). Yellow crystals (1.83g, 70%), mp 233-235 °C. IR (KBr): ν 2992 (CH₃), 2830 (CH₂), 1520 (Ar-C=C) cm⁻¹. ¹H-NMR (CDCl₃): δ 2.35 (s, 3H, CH₃), 4.80 (s, 4H, 2 CH₂), 6.55-6.70 (m, 3H, Ar-H), 7.20-7.28 (m, 1H,

Ar-H), 7.70-7.78 (m, 2H, Ar-H), 8.07-8.13 (m, 2H, Ar-H). MS m/z (%): 261 (73) [M^+], 260 (100), 143 (10), 102 (11), 91 (16), 65 (11), 40 (11). Anal. Calcd. for $C_{17}H_{15}N_3$ (261.31): C, 78.13; H, 5.79; N, 16.08. Found: C, 78.25; H, 5.83; N, 16.17.

2-(4-Methylphenyl)-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxaline (8c). Yellow crystals (1.96g, 75%), mp 281-283 °C. IR (KBr): ν 2916 and 2842 (CH_2), 1610 (Ar-C=C) cm^{-1} . 1H -NMR ($CDCl_3$): δ 2.32 (s, 3H, CH_3), 4.83 (s, 4H, 2 CH_2), 6.70 (d, $J = 6.7$ Hz, 2H, Ar-H), 7.20 (d, $J = 6.7$ Hz, 2H, Ar-H), 7.75-7.86 (m, 2H, Ar-H), 8.10-8.17 (m, 2H, Ar-H). MS m/z (%): 261 (74) [M^+], 260 (100), 245 (5), 233 (3), 218 (5), 143 (12), 131 (4), 116 (9), 102 (10), 91 (15). Anal. Calcd. for $C_{17}H_{15}N_3$ (261.31): C, 78.13; H, 5.79; N, 16.08. Found: C, 78.05; H, 5.89; N, 15.98.

2-(4-Methoxyphenyl)-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxaline (8d). Yellow crystals (1.61g, 58%), mp 228-230 °C. IR (KBr) ν 2927 and 2830 (CH_2), 1519 (Ar-C=C) cm^{-1} . 1H -NMR ($CDCl_3$): δ 3.80 (s, 3H, OCH_3), 4.78 (s, 4H, 2 CH_2), 6.72 (d, $J = 6.8$ Hz, 2H, Ar-H), 6.96 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.70-7.80 (m, 2H, Ar-H), 8.10-8.15 (m, 2H, Ar-H). MS m/z (%): 277 (73) [M^+], 276 (48), 262 (57), 246 (3), 232 (10), 143 (7), 102 (10), 101 (21), 92 (17), 86 (100), 65 (10), 58 (44), 44 (14). Anal. Calcd. for $C_{17}H_{15}N_3O$ (277.31): C, 73.63; H, 5.45; N, 15.15. Found: C, 73.55; H, 5.53; N, 15.27.

Reaction of 2-Aryl-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxalines 8a-d with TCNE. A solution of 2.0 mmol of **8a-d** in 30 ml of dry benzene was added dropwise with stirring to 512 mg (4.0 mmol) of **TCNE** in 40 ml of benzene at room temperature. Stirring was continued for 7 days with admission of air. The colour of the mixture gradually changed from green to brown and finally gave way to a blue colour. The reaction mixture was concentrated to dryness and the residue subjected to sublimation at 80 °C under vacuum to remove all unreacted **TCNE**. The residue was then separated by preparative layer chromatography using cyclohexane/ethyl acetate 3:1 as eluent to give numerous coloured zones, the three most intense of which were removed and extracted with acetone. The concentration residue was rechromatographed with the same eluent to enhance separation. The fastest migrating zone, which quenched all indicator fluorescence upon exposure to 254 nm UV-light, contained quinoxaline-2,3-diol (**11**), the second zone (orange colour) contained compounds **10a-d**, whereas the most slowly migrating zone (which is always characterized by a deep blue colour) contained compounds **9a-d**. The dried extracts were crystallized from suitable solvents.

[3-(3-Dicyanomethylene-2-phenyl)-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxalin-1-ylidene)-2-phenyl-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxalin-1-ylidene]propanedinitrile (9a). Blue-black crystals (0.251g, 41%), mp 312-314 °C (acetonitrile); Vis (acetonitrile): λ_{max} (log ϵ) 586 nm (4.30). IR (KBr): ν 2210 (CN), 1585 (Ar-C=C) cm^{-1} . 1H -NMR ($CDCl_3$): δ 7.16 (m, 6H, Ar-H), 7.59-7.71 (m, 2H, Ar-H), 7.80-8.00 (m, 8H, Ar-H), 8.32 (m, 2H, Ar-H). MS m/z (%): 614 (37) [M^+], 550 (45), 398 (32), 295 (77), 270 (84), 133 (94), 106 (91), 44 (100). Anal. Calcd. for $C_{38}H_{18}N_{10}$ (614.64): C, 74.26; H, 2.95; N, 22.79. Found: C, 74.38; H, 2.83; N, 22.87.

{3-[3-Dicyanomethylene-2-(3-methylphenyl)-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxalin-1-ylidene]-2-(3-methylphenyl)-2,3-dihydro-1H-pyrrolo[3,4-*b*]quinoxalin-1-ylidene}prop-

anedinitrile (9b). Blue-black crystals (0.270g, 42 %), mp 322-324 °C (acetonitrile); Vis (acetonitrile) λ_{\max} (log ϵ) 592 nm (4.32). IR (KBr): ν 2220 (CN), 1595 (Ar-C=C) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ 2.25 (s, 6H, 2 CH_3), 7.24 (m, 4H, Ar-H), 7.63-7.72 (m, 4H, Ar-H), 7.82-8.00 (m, 6H, Ar-H), 8.35 (m, 2H, Ar-H). MS m/z (%): 642 (36) [M^+], 578 (47), 552(12), 460 (16), 426(23), 323 (78), 298 (81), 133 (92), 106 (95), 44 (100). Anal. Calcd. for $\text{C}_{40}\text{H}_{22}\text{N}_{10}$ (642.69): C, 74.75; H, 3.45; N, 21.79. Found: C, 74.66; H, 3.33; N, 21.84.

{3-[3-Dicyanomethylene-2-(4-methylphenyl)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene]-2-(4-methylphenyl)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene}propanedinitrile (9c). Blue-black crystals (0.308g, 48%), mp 343-345 °C (acetonitrile); Vis (acetonitrile): λ_{\max} (log ϵ) 596 nm (4.12). IR (KBr): ν 2215 (CN), 1579 (Ar-C=C) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ 2.30 (s, 6H, 2 CH_3), 7.20 (m, 4H, Ar-H), 7.65-7.75 (m, 2H, Ar-H), 7.85-8.05 (m, 8H, Ar-H), 8.35 (m, 2H, Ar-H). MS m/z (%): 642 (31) [M^+], 578 (45), 552 (14), 460 (14), 426 (22), 323 (76), 298 (87), 133 (96), 106 (95), 44 (100). Anal. Calcd. for $\text{C}_{40}\text{H}_{22}\text{N}_{10}$ (642.69): C, 74.75; H, 3.45; N, 21.79. Found: C, 74.58; H, 3.53; N, 21.62.

{3-[3-(Dicyanomethylene)-2-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene]-2-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene}propanedinitrile (9d). Blue-black crystals (0.276g, 41%), mp 350-352 °C (dec., acetonitrile). Vis (acetonitrile) λ_{\max} (log ϵ) 602 nm (4.45). IR (KBr): ν 2210 (CN), 1590 (Ar-C=C) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3): δ 3.86 (s, 6H, 2 OCH_3), 7.18 (m, 4H, Ar-H), 7.56-7.70 (m, 2H, Ar-H), 7.78-7.96 (m, 8H, Ar-H), 8.30 (m, 2H, Ar-H). MS m/z (%): 674 (41) [M^+], 610 (51), 568 (11), 476 (10), 442 (22), 314 (89), 133 (91), 106 (95), 44 (100). Anal. Calcd. for $\text{C}_{40}\text{H}_{22}\text{N}_{10}\text{O}_2$ (674.69): C, 71.21; H, 3.29; N, 20.76. Found: C, 71.18; H, 3.33; N, 20.85.

[2-Phenyl-3-phenylimino-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene]propanedinitrile (10a). Orange crystals (0.076g, 19%), mp 288-290 °C (ethanol). IR (KBr): 2215 (CN), 1600 (Ar-C=C) cm^{-1} . $^1\text{H-NMR}$ ($\text{DMF-}d_7$): δ 7.10-7.65 (m, 6H, Ar-H), 7.88-8.12 (m, 6H, Ar-H), 8.34 (m, 2H, Ar-H). MS m/z (%): 398 (100) [M^+], 376 (16), 296 (10), 189 (9), 164 (7), 91(32). Anal. Calcd. for $\text{C}_{25}\text{H}_{14}\text{N}_6$ (398.44): C, 75.36; H, 3.54; N, 21.09. Found: C, 75.19; H, 3.43; N, 21.16.

[2-(3-Methylphenyl)-3-(3-methylphenylimino)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene]propanedinitrile (10b). Orange crystals (0.085 g, 20%), mp 296-298 °C (ethanol). IR (KBr): ν 2215 (CN), 1620 (Ar-C=C) cm^{-1} . $^1\text{H-NMR}$ ($\text{DMF-}d_7$): δ 2.28 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 7.00-7.66 (m, 6H, Ar-H), 7.74-8.10 (m, 4H, Ar-H), 8.32 (m, 2H, Ar-H). MS m/z (%): 426 (100) [M^+], 400 (15), 320 (16), 213 (11), 178 (10), 117 (25), 91 (29). Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{N}_6$ (426.49): C, 76.04; H, 4.25; N, 19.71. Found: C, 75.96; H, 4.33; N, 19.56.

[2-(4-Methylphenyl)-3-(4-methylphenylimino)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene]propanedinitrile (10c). Orange crystals (0.094g, 22%), mp 318-320 °C (ethanol). IR (KBr): ν 2214 (CN), 1610 (Ar-C=C) cm^{-1} . $^1\text{H-NMR}$ ($\text{DMF-}d_7$): δ 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 7.20 (d, $J = 6.7$ Hz, 2H, Ar-H), 7.70 (d, $J = 6.5$ Hz, 2H, Ar-H), 7.80-8.15 (m, 6H, Ar-H), 8.35 (m, 2H, Ar-H). MS m/z (%): 426 (100) [M^+], 400 (11), 320 (18), 213 (8), 178 (6), 117 (15),

91 (31). Anal. Calcd. for $C_{27}H_{18}N_6$ (426.49): C, 76.04; H, 4.25; N, 19.71. Found: C, 75.88; H, 4.38; N, 19.58.

[2-(4-Methoxyphenyl)-3-(4-methoxyphenylimino)-2,3-dihydro-1H-pyrrolo[3,4-b]quinoxalin-1-ylidene]propanedinitrile (10d). Orange crystals (0.096g, 21%), mp 324-326 °C (ethanol). IR (KBr) ν 2220 (CN), 1610 (Ar-C=C) cm^{-1} . 1H -NMR ($CDCl_3$): δ 3.85 (s, 3H, OCH₃), 3.89 (s, 3H, OCH₃), 7.17 (d, $J = 6.7$ Hz, 2H, Ar-H), 7.62 (d, $J = 6.7$ Hz, 2H, Ar-H), 7.75-8.10 (m, 6H, Ar-H), 8.35 (m, 2H, Ar-H). MS m/z (%): 458 (100) [M^+], 432 (19), 370 (23), 245 (12), 219 (9), 106 (15), 91 (31). Anal. Calcd. for $C_{27}H_{18}N_6O_2$ (458.49): C, 70.73; H, 3.96; N, 18.33. Found: C, 70.56; H, 4.11; N, 18.26.

Quinoxaline-2,3-diol (11). Colourless crystals (8-11%), mp 287-289 °C (ethanol), (lit.¹⁴ 285 °C). IR (KBr): ν 3466 (OH), 3080 (aryl C-H), 1630 (C=N), 1590 (Ar-C=C) cm^{-1} . 1H -NMR ($CDCl_3$): δ 7.25-7.60 (m, 4H, Ar-H), 9.78 (br, 2H, 2OH). MS m/z (%): 162 (6) [M^+], 160 (27), 134 (100), 106 (12), 77 (31), 51 (19).

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