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New reaction of ethenetetracarbonitrile with *N*-arylisoindolines

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Abstract—*N*-Arylisoindolines **1a–i** react with ethenetetracarbonitrile **2** in aerated benzene by formation of [3-(2-aryl-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-ylidene)-2-aryl-2,3-dihydro-1*H*-isoindol-1-ylidene]propanedinitriles **8a–i** (20–36%), *N*-aryl-3-dicyanomethylene-isoindol-2-ones **9a–i** (15–21%) and *N*-arylphthalimides **10a–i** (4–9%) as well as 1,1,2,2-tetracyanoethane **11** (35–55%). The structure of **8d** has been unambiguously confirmed by a single crystal X-ray structure analysis. A rationale for the formation of products **8–11** is presented.

1. Introduction

Ethenetetracarbonitrile (previously referred to as tetracyanoethylene, **2**) shows a great affinity for electrons, and is thus a fairly good dehydrogenating agent towards dihydroaromatic and dihydroheteroaromatic systems.[1] It behaves as a strong electron acceptor towards suitable electron donors.[1–4] It forms molecular complexes by an intermolecular charge-transfer interaction,[1,4–6] and the monoelectronic reduction results in the formation of the fairly long-lived radical anion.[1,6] Tetracyanoethylene reacts with *N*,*N*-dialkylanilines or analogous electron rich arenes (with free *p*-position) to products of *p*-tricyanovinylation.[1,7,8] Indole derivatives would undergo this reaction at—depending on conditions—either C-2 or C-3,[9] primary aromatic amines on nitrogen,[1] whereas the secondary amine 2,2,4-trimethyl-1,2-dihydroquinoline shows that reaction on C-6.[10] Compounds with active methylene groups perform a Michael-type addition, giving rise to α-(1,1,2,2-tetracyanoethyl)-derivatives.[11] This addition may be followed by elimination of malononitrile and formation of dicyanomethylene derivatives.[1,12]

N-Arylisoindolines **1**, featuring reactive benzylic hydrogens in a comparatively rigid five-membered ring, show a different behaviour towards tetracyanoethylene deviating from the behaviour of tertiary arylamines or indole.

We recently reported[13] that *N*-arylisoindolines **1** reacted with (2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedinitrile in pyridine with admission of air via a net α-H-atom abstraction to give 2-arylisoindole-1,3-di-(*N*-arylimines) **3** and isoindigoid products like **4** and **5** as well as **6** as a result of an oxidative condensation. The latter type of products is also obtained from the interaction of 1,4-benzo- or 1,4-naphthoquinones with *N*-arylisoindolines.[14–16] 2′-Arylspiro[1,3-benzodioxole-2′-isoindoline]-3′-ones were observed from the reaction of *N*-arylisoindolines with tetrachloro-1,2-benzoquinone.[17] On the other hand, isoindolines reacted with (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile in aerated pyridine to give 2,2′-(2-arylisoindol-1,3-ylene)-di(1,4-naphthoquinone-3-carbonitriles) **7**[18] (Chart 1).

2. Results and discussion

In the present work we describe the reaction of *N*-arylisoindolines **1a–i** with tetracyanoethylene **2**. Upon addition of doubled molar amounts of **2** to a solution of *N*-arylisoindolines **1a–i** in benzene with admission of air, the green colour of a transient charge-transfer complex[19] is observed which quickly gives way to a brown and finally to a characteristic blue colour, and formation of crude tetracyanoethane as precipitate. The concentration residue of the filtrate was subjected to vacuum sublimation to remove any unreacted **2**. Chromatographic separation of the residue gave numerous coloured zones, from which products **8–11** could be isolated (Chart 2).

Structural assignments of compounds **8–11** are based on spectral data, on combustion analyses and on chemical evidence. Compounds **8a–i** show a characteristic blue

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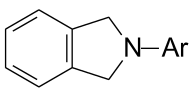
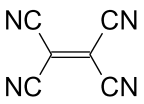


1a-i

a: Ar = 2–$H_3COC_6H_4$
b: Ar = 3–$H_3COC_6H_4$
c: Ar = 2–$H_3CC_6H_4$
d: Ar = 3–$H_3CC_6H_4$
e: Ar = 4–$H_3CC_6H_4$
f: Ar = C_6H_5
g: Ar = 2–ClC_6H_4
h: Ar = 3–ClC_6H_4
i: Ar = 4–$H_3COCC_6H_4$



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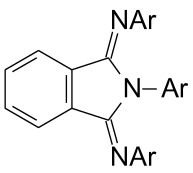

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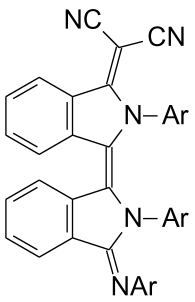

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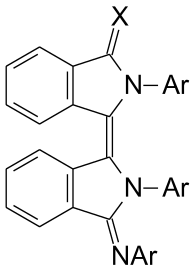

5: X = NR
6: X = O

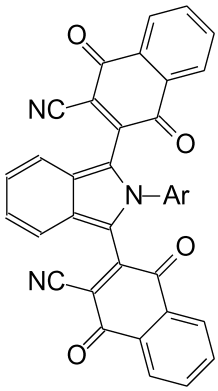

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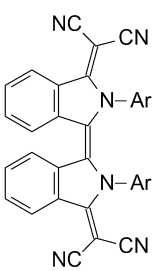
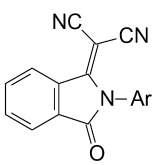
Chart 1.

colour in solution, attributable to the local push–pull systems of conjugated double bonds and lone pairs. The λ_{max} values (584–570 nm) for various substituted compounds **8a–i** are similar due to the same molecular gross structure and configuration. The IR spectrum of (for example) **8b** in KBr shows a sharp absorption characteristic of conjugated C≡N groups at 2210 cm^{-1} and several peaks at 1610 and 1530 for skeletal vibrations of the aryl groups. The ^1H NMR spectra (CD_3NO_2, 300 MHz) of **8a–i** clearly show the absence of methylene protons and the presence of phenyl and (if applicable) methyl protons only. In some cases (**8a–e**,**i**) the substituents (*o*-, *m*-OCH_3; *o*-, *m*-, *p*-CH_3; *p*-$COCH_3$) on the *N*-aryl group give rise to more than one singlet for the CH_3-protons. In the case of **8b** at 303 K, a shoulder at 3.86 ppm and a sharp singlet at 3.78 ppm are present. Upon warming to 333 or 343 K the shoulder is replaced by a second singlet at 3.86 ppm. This behaviour suggests the presence of two very closely related stereoisomers which are not interconvertible at the temperatures applied. Likely a priori possibilities might be atropisomerism with respect to the *N*-aryl bonds (see below) or the coexistence of two conformers with respect to the central double bond, one being twisted, the other one being *anti*-pyramidalized at its termini. Such a situation has been observed recently with bi[1,3-bis(dicyanomethylene)indan-2-ylidene] and in other cases,[20] but does not seem to play a role in the cases reported here (see below). The HPLC-analysis of **8b** using acetonitrile/methanol (9:1 v/v) shows one compound peak only.

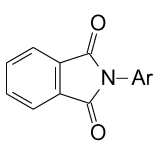
The molecular formulas of compounds **8a–i** are supported by the mass spectra which gave the predicted molecular ion peaks as base peaks. It should also be noted that the mass spectra of compounds **8a–i** are characterized by loss of the $C(CN)_2$ moiety from the molecular ions but the correspondent fragment peaks are of relatively low intensity.



8a-i (20-36%)



9a-i (15-21%)



10a-i (4-9%)

a: Ar = 2–$H_3COC_6H_4$
b: Ar = 3–$H_3COC_6H_4$
c: Ar = 2–$H_3CC_6H_4$
d: Ar = 3–$H_3CC_6H_4$
e: Ar = 4–$H_3CC_6H_4$
f: Ar = C_6H_5
g: Ar = 2–ClC_6H_4
h: Ar = 3–ClC_6H_4
i: Ar = 4–$H_3COCC_6H_4$

$HC(CN)_2$–$C(CN)_2H$

11

Chart 2.

Moreover, the structure of **8d** has been unambiguously confirmed by a single crystal X-ray structure analysis (Figs. 1 and 2, Table 1). The characteristic feature with respect to the C1–C21 double bond (note that the crystallographic numbering does not correspond to the systematic IUPAC numbering rules), showing a bond length of 1.379(2) Å and thus being slightly elongated, is cisoid twisted geometry with a dihedral angle N1–C1–C2–N21 of −33.93(30)°. This value clearly indicates that compounds **8** are sterically crowded due to steric repulsion between the hydrogen atoms at the *peri*-positions C3 and C23 which are in a 3.15 Å distance, and the calculated 3H–23H distance is 2.390(1) Å. Also, compounds **8** are considerably encumbered due to the vicinity of the dicyanomethylene groups and the nearly sandwiched *N*-phenyl-rings. This is documented by the deviation of the C9–C11–N3 and C29–C31–N23 bond angles by 8.4° and 8.6°, respectively, from 180° (Table 1). Also, carbon atoms 1,8,9,21,28, and 29 are planar, since the bond angles surrounding these centres all sum up to 360° within the limits of accuracy, and the sums of bond angles at N1 and N21 are only a few degrees lower than 360°, so the isoindolic N-atoms show very little if any pyramidalization.

It should be noted that the crystal structure of **8d** does show some degree of disorder affecting the *m*-methylphenyl groups attached to N1 and N21. Two conformations, related via a 180° rotation around the N21–C32 bond, are found. The disorder concerning N1 is more complex in so far as two discrete *m*-methylphenyl groups are found in a ratio of 84:16. Thus, **8d** exists as a mixture of two atropisomers (Fig. 1).

Similar typical cisoid arrangements are demonstrated in the X-ray crystal structure analyses of 1-methyl-3-(1-methyl-2-phenylindol-3-yl)-2-phenylindole (with the phenyl groups being nearly sandwiched and the *peri*-hydrogen atoms in close contact),[21a] of a fused biisoindolylidene,[21b] and a biisothianaphtylidene.[21c]

The gross formulas of **9a–i** were confirmed by the elemental analyses and the mass spectra, which exhibited the expected molecular ion peaks in high intensity. The IR-spectra showed absorptions uniformly near 2220 (CN) and between 1745 and 1770 cm^{-1} (CO) (see Section 4). The structures of the *N*-arylphthalimides **10** and of tetracyanoethane (**11**) were confirmed by comparison with authentic samples.

Since the reactions reported very likely require numerous steps, moderate yields (based throughout on the amount of starting materials used, see Section 4) have to be regarded as acceptable.

In order to rationalize the formation of products **8–11**, dehydrogenation of **1** by **2**[1] may be regarded as the initial event, whereby CT-complexes may (but not have to) be intermediate stages, forming tetracyanoethane (**11**) and the corresponding isoindoles **12**, which, however, were not isolated (Scheme 1). Whenever didehydrogenation is unfavourable for structural reasons, e.g. in higher ring homologues of **1**, hydride abstraction is observed followed by cyanation of the cyclic iminium ions.[22]

Compounds with active methylene groups are known to react with **2** by a Michael-type addition followed by release of malononitrile giving rise to dicyanomethylene compounds.[1] Since isoindoles may be seen as vinylogous enamines, a behaviour towards **2** similar to that of methylene active ketones[1] may be expected. Thus, addition of **2** to C1 of **12** may generate **13** which undergoes protonation/deprotonation giving rise to **14** which has two options: (i) release of HCN giving a product (**15**) of tricyanovinylation of **1**; (ii) an 'elimination type of dimerization' (reminescent of the 'oxidative dimerization' typical for isoindoles[23]).

Option (i) does not seem to be the preferred mode of **14** bearing *N*-aryl groups, however, if the aryl group is replaced

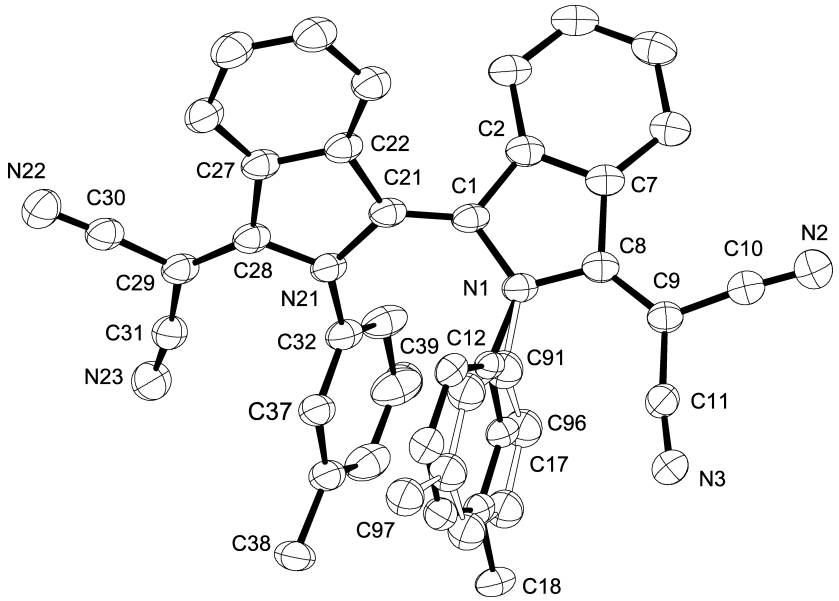


Figure 1. Molecular structure of **8d** in the crystal. The crystallographic numbering does not reflect the systematic IUPAC numbering. Anisotropic displacement parameters are shown at 50% probability level. C39 is the disordered equivalent of C38, C91 to C97 represent a disordered part of the molecule.

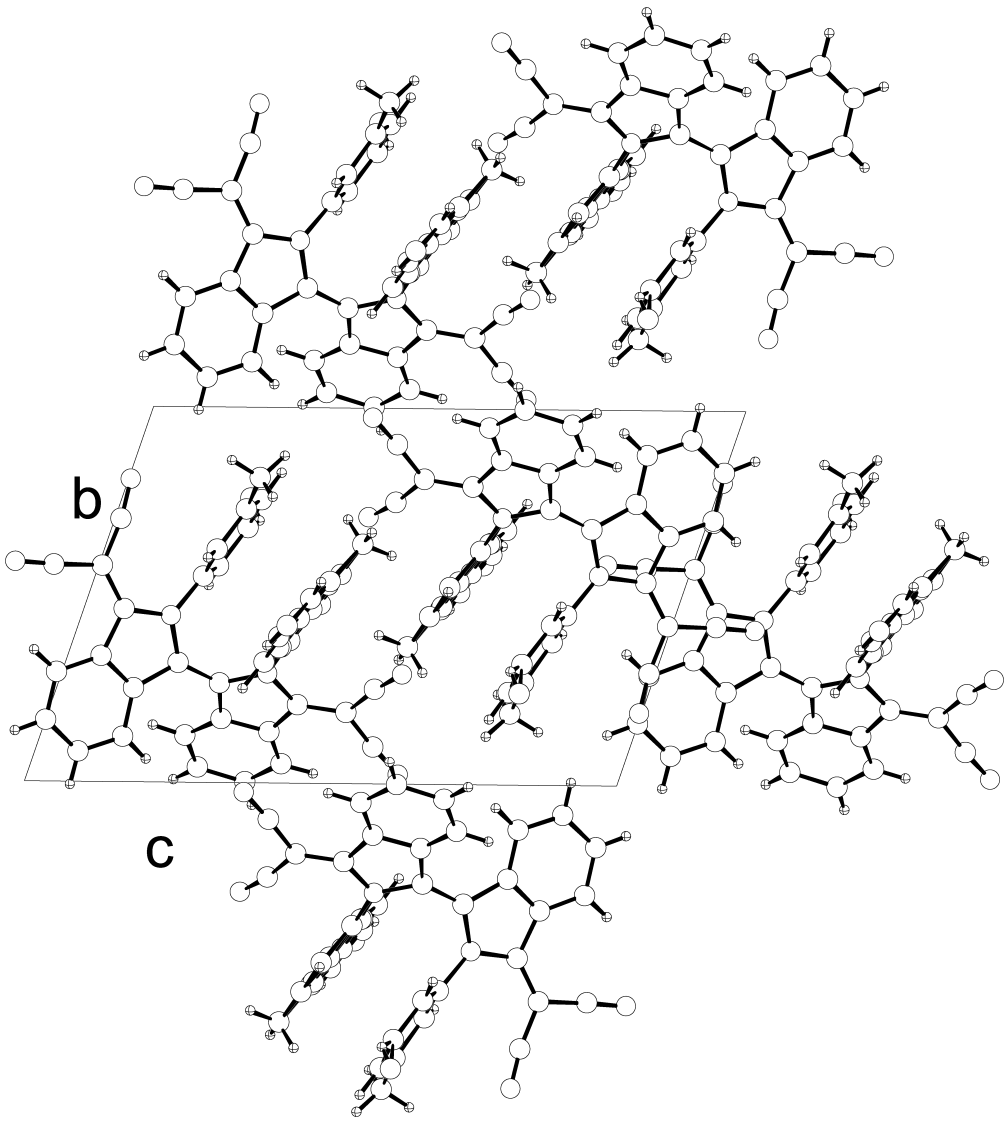


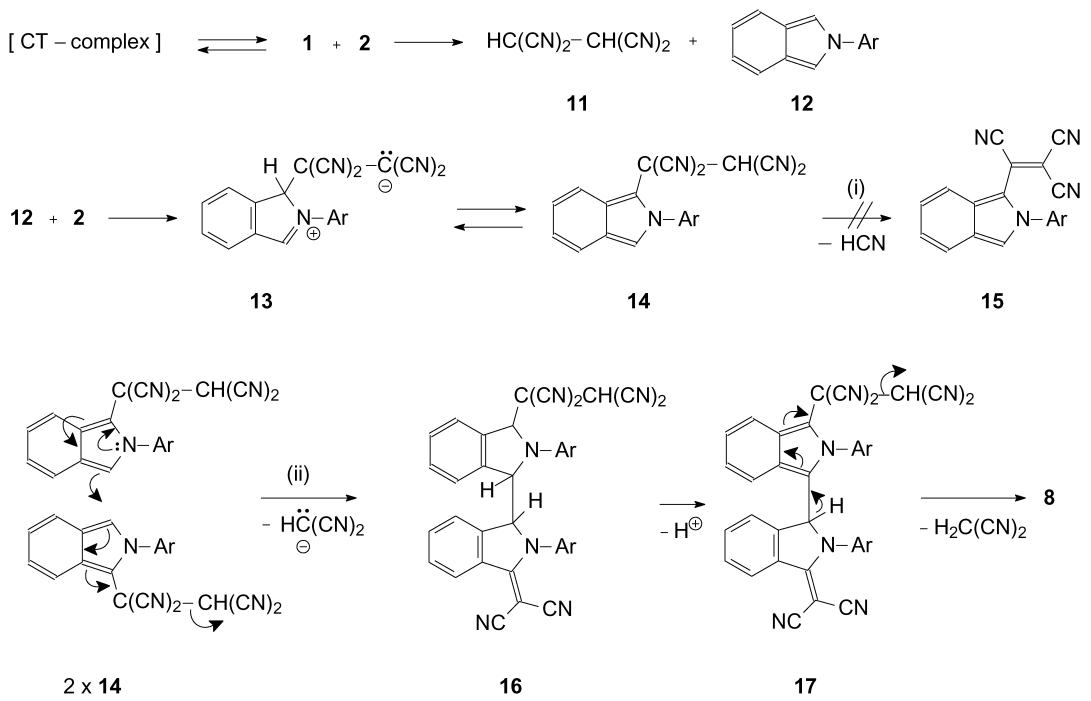
Figure 2. Crystal packing of compound **8d** (view along axis a).

by e.g. *t*-butyl, the corresponding tricyanovinylation product may be isolated.[24] On the other hand, loss of malononitrile from a tetracyanoethyl-substituted indole derivative has been demonstrated earlier.[12]

The formation of **8** via **14** by pathway (ii) thus requires two molecules of **1** and two molecules of **2** and leads to the release of two molecules of malononitrile (Scheme 1). The latter is never isolated as such due to build-up of higher cyanocarbons[25] by reacting with **2**. No attempt has been made to isolate these highly polar materials from the complex mixture of by-products. There is, so far, no indication of a [4+2] cycloaddition of **2** to **1**.

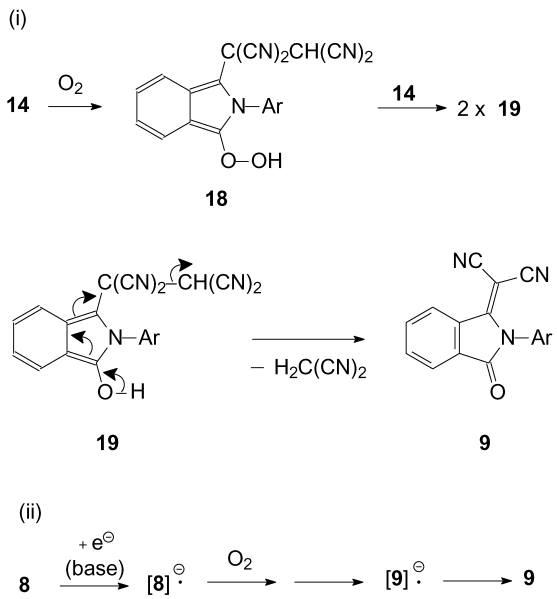
Table 1. Selected bond distances and bond angles of compound **8d** (major atropisomer, the crystallographic numbering does not reflect the systematic IUPAC numbering)

Bond distances (Å)							
C8–C9	1.393(2)	C28–C29	1.388(3)	N1–C8	1.375(2)	N21–C28	1.380(2)
C1–N1	1.413(2)	C21–N21	1.409(2)	C1–C21	1.379(3)		
Bond angles (°)							
C8–C9–C10	121.18(16)	C8–C9–C11	127.81(17)	C10–C9–C11	111.00(16)		
C28–C29–C30	120.01(17)	C28–C29–C31	128.70(18)	C30–C29–C31	111.25(16)		
N1–C8–C7	107.00(15)	N1–C8–C9	126.50(16)	C7–C8–C9	126.32(17)		
N21–C28–C27	106.71(15)	N21–C28–C29	126.32(17)	C27–C28–C29	126.75(17)		
N1–C1–C2	105.69(16)	N1–C1–C21	128.89(16)	C2–C1–C21	125.42(16)		
N21–C21–C22	105.64(16)	N21–C21–C1	129.05(16)	C1–C21–C22	125.23(16)		
C12–N1–C8	123.41(15)	C12–N1–C1	122.12(16)	C1–N1–C8	110.89(14)		
C32–N21–C28	122.55(15)	C32–N21–C21	124.54(15)	C21–N21–C28	111.18(14)		
C9–C10–N2	175.28(19)	C9–C11–N3	171.6(2)	C29–C30–N22	176.7(2)		
C29–C31–N23	171.4(2)						



Scheme 1. For the meaning of Ar, see Charts 1 and 2.

The oxygenated products **9** and **10** may arise from action of air oxygen on either **12** or **14** for which reaction the formation of an intermediate 1,3-endoperoxide has been suggested.[23] Phthalimides as **10** may be formed in this way even when C1 and C3 of the isoindole are alkylated.[23] The build-up of compounds **9**, on the other hand, seems feasible by two routes (Scheme 2): (i) formation of a hydroperoxide **18** which with another molecule of **14** forms **19** which again looses malononitrile to give **9**. It had been reported earlier[26] that the action of *t*-butoxide on a selection of compounds **8** in dry DMSO generates the radical anions of the latter, the ESR signals of which are degraded upon admission of air, giving way to the ESR-signal of the radical anions of the corresponding compounds **9**. This finding requires the breakage of the central double bond and oxygen uptake by either the radical anion of **8** or by any fragments thereof. It is not possible, though, to delineate the exact course of the reaction on the basis of these findings alone.



Scheme 2. For the meaning of Ar, see Charts 1 and 2.

3. Conclusion

In a fairly complex and multistep process two types of dicyanomethylenated products are formed from various *N*-arylisoindolines **1** and ethenetetracarbonitrile (**2**). The latter has a dual functioning role as a dehydrogenating agent and as a source of the dicyanomethylene units. The predominant products **8a–i** have an interesting twisted and strained isoindigoid structure and resemble analogues of the family of heterocyclic tetracyanoquinodimethanes.[27] Tricyanovinylation of the proposed intermediate isoindoles, although certainly feasible, is not observed. While being interpretable by precedence and analogy, the reactions reported add to the very rich chemistry of tetracyanoethylene (**2**) with electron donating organic compounds.

4. Experimental

4.1. General

Mp's were determined with a Reichert Thermovar hot stage microscope and are uncorrected. The UV/Vis spectra were recorded on a Perkin–Elmer 554 spectrophotometer, the IR spectra on Perkin–Elmer 397 and Perkin–Elmer 283 spectrophotometers. The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM 300 instrument, chemical shifts are expressed as δ (ppm) with tetramethylsilane as internal reference, s=singlet, m=multiplet; ^{13}C assignments have been made with the aid

of DEPT 135/90 spectra. The mass spectra (70 eV, electron impact mode) were obtained on a Varian MAT 311 A instrument. Elemental analyses were carried out with a Carlo Erba Mod. 1106 CHN analyzer. The High Pressure Liquid Chromatography was run on a Waters Associates 440 modular equipment using an absorbance detector with 254 nm filter. For preparative layer chromatography 48 cm wide and 20 cm tall glass plates, covered with a 1 mm thick layer of slurry applied and air-dried silica gel Merck PF_{254}, were used. Zones were detected by their colour or by quenching of indicator fluorescence upon exposure to 254 nm light.

4.1.1. Starting materials. 2-Aryl-2,3-dihydro-1*H*-isoindoles **1a**–**i** were prepared according to published procedures.[15,28,29] **1a**: bp 136–138°C/0.13 mb (lit.[28,29] 134–137°C/0.13 mb); **1b**: mp 112–113°C (lit.[28] 112–113°C); **1c**: bp 118–120°C/0.013 mb (lit.[29] 117–120°C/0.013 mb); **1d**: mp 115–116°C (lit.[29] 115–117°C); **1e**: mp 190–192°C (lit.[29] 193°C); **1f**: mp 170–171°C (lit.[29] 172–173°C); **1g**: bp 120–122°C/0.013 mb (lit.[29] 120°C/0.013 mb); **1h**: mp 100–102°C (lit.[29] 101°C), **1i**: mp 182–184°C (lit.[15] 182–184°C). Compounds **1a**,**1c** and **1g** were purified by two consecutive bulb-to-bulb distillations. Ethenetetracarbonitrile (**2**, Merck) was purified by crystallization from chlorobenzene and sublimed, mp 198–199°C.

4.2. Reaction of *N*-arylisoindolines 1a–i with 2

A solution of *N*-arylisoindolines **1a**–**i** (2.56 mmol) in dry benzene (30 mL) was added dropwise with stirring at room temperature to **2** (5.12 mmol) in benzene (40 mL). The reaction colour changed quickly from green to brown which gradually gave way to a blue colour. The stirring was continued for 48 h with admission of air to complete the reaction. The reaction mixture was filtered and the precipitate was washed several times with cold benzene until the washings remained colourless. The filtrate was concentrated to dryness and the residue sublimed at 80°C under vacuum to remove all unreacted **2**. The residue was then separated by preparative layer chromatography (100 mg per plate) using a suitable solvent mixture as eluent (cyclohexane/ethyl acetate 5:1 for the reactions of **2** with **1a**,**1c**,**1g** and **1h**; cyclohexane/ethyl acetate 3:1 for the reactions of **2** with **1b**,**1d**, and **1f**, cyclohexane/ethyl acetate 2:1 for the reactions of **2** with **1e** and **1i**) to give numerous coloured zones, the three intense of which were removed and extracted. The fastest migrating one contained the *N*-arylphthalimides **10a**–**i**, the second zone, which quenched all indicator fluorescence upon exposure to 254 nm UV-light, contained compounds **9a**–**i**, and finally the slowest migrating zone (which is always characterized by deep blue colour) contained the 'dimers' **8a**–**i**. Extraction of the zones with acetone gave a residue, which was rechromatographed to separate the pure compounds. The precipitate was washed several times with cold benzene, dried and sublimed at 135°C under vacuum to give colourless crystals of 1,1,2,2-tetracyanoethane which decomposed at 165–170°C (lit.[30] 165–170°C).

4.2.1. {3-[2-(2-Methoxyphenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylid-ene]-2-(2-methoxyphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedintrile (8a). Blue-black crystals (acetonitrile), mp 323–325°C, (175 mg, 24%); UV/Vis (acetonitrile): λ_{max}=582 nm, log ε=4.67; IR: ν=2210 (CN), 1610 (C=C), 1580 (aryl) cm^{-1}, ^1H NMR (CD_3NO_2): δ=3.85–3.92 (m, 6H, $2OCH_3$), 6.88–7.08 (m, 2H, Ar-H), 7.15–7.75 (m, 12H, Ar-H), 8.46–8.63 (m, 2H, aryl-H); MS: *m*/*z* (%)=570 (M^+, 100), 555 (8), 539 (15), 506 (23), 463 (10), 285 (25), 270 (31), 254 (6), 221 (15), 76 (22). Anal. calcd for $C_{36}H_{22}N_6O_2$ (570.6): C, 75.77; H, 3.88; N, 14.72. Found: C, 75.61; H, 3.76; N, 14.63.

4.2.2. {3-[2-(3-Methoxyphenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(3-methoxyphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8b). Blue-black crystals (acetonitrile), mp 268–270°C, (241 mg, 33%); UV/Vis (acetonitrile): λ_{max}=580 nm, log ε=4.84; IR: ν=2210 (CN), 1610 (C=C), 1530 (aryl) cm^{-1}; ^1H NMR (CD_3NO_2): δ=3.78–3.86 (m, 6H, $2OCH_3$), 6.80–6.90 (m, 4H, Ar-H), 7.00–7.05 (m, 2H, Ar-H), 7.24–7.30 (m, 2H, Ar-H), 7.58–7.65 (m, 4H, Ar-H), 7.94–8.10 (m, 2H, Ar-H), 8.52–8.58 (m, 2H, Ar-H); MS: *m*/*z* (%)=570 (M^+, 100), 555 (14), 539 (10), 506 (21), 463 (7), 285 (10), 270 (3), 254 (7), 221(15), 76 (21). Anal. calcd for $C_{36}H_{22}N_6O_2$ (570.6): C, 75.77; H, 3.88; N, 14.72. Found: C, 75.74; H, 3.83; N, 14.76.

4.2.3. {3-[2-(2-Methylphenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(2-methylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8c). Blue-black crystals (acetonitrile), mp 317–319°C, (193 mg, 28%); UV/Vis (acetonitrile): λ_{max}=580 nm, log ε=4.48; IR: ν=2200 (CN), 1600 (C=C), 1580 (aryl) cm^{-1}; ^1H NMR (CD_3NO_2): δ=2.25–2.40 (m, 6H, $2CH_3$), 6.90–7.55 (m, 10H, Ar-H), 7.70–7.80 (m, 2H, Ar-H), 7.94–8.08 (m, 2H, Ar-H), 8.42–8.62 (m, 2H, Ar-H); MS: *m*/*z* (%)=538 (M^+, 100), 474 (25), 447 (3), 432 (2), 380 (6), 369 (4), 357 (3), 269 (17), 243 (16), 205 (13), 91 (31). Anal. calcd for $C_{36}H_{22}N_6$ (538.6): C, 80.28; H, 4.11; N, 15.60. Found: C, 80.20; H, 4.07; N, 15.50.

4.2.4. {3-[2-(3-Methylphenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(3-methylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8d). Blue-black crystals (acetonitrile), mp 326–328°C, (268 mg, 39%); UV/Vis (acetonitrile): λ_{max}=579 nm, log ε=4.54; IR: ν=2210 (CN), 1615 (C=C), 1530 (Ar-CH) cm^{-1}; ^1H NMR (CD_3NO_2): δ=2.30–2.46 (m, 6H, $2CH_3$), 6.74–7.50 (m, 8H, Ar-H), 7.56–7.60 (m, 4H, Ar-H), 7.84–8.10 (m, 2H, Ar-H), 8.50–8.54 (m, 2H, Ar-H); MS: *m*/*z* (%)=538 (M^+, 100), 474 (31), 447 (4), 380 (7), 369 (5), 357 (2), 269 (21), 243 (7), 91 (46). Anal. calcd for $C_{36}H_{22}N_6$ (538.6): C, 80.28; H, 4.11; N, 15.60. Found: C, 80.37; H, 4.09; N, 15.70.

4.2.5. {3-[2-(4-Methylphenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(4-methylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8e). Blue-black crystals (acetonitrile), dec. 330–332°C, (214 mg, 31%); UV/Vis (acetonitrile): λ_{max}=584 nm, log ε=4.33; IR: ν=2200 (CN), 1600 (C=C), 1550 (aryl) cm^{-1}; ^1H NMR (CD_3NO_2): δ=2.25–2.40 (m, 6H, $2CH_3$), 6.65–6.80 (m, 2H, Ar-H), 6.90–7.84 (m, 12H,

Ar-H), 8.52–8.75 (m, 2H, Ar-H); MS: *m/z* (%)=538 (M^+, 100), 474 (10), 447 (5), 369 (2), 357 (22), 269 (13), 243 (6), 91 (24). Anal. calcd for $C_{36}H_{22}N_6$ (538.6): C, 80.28; H, 4.11; N, 15.60. Found: C, 80.33; H, 4.11; N, 15.67.

4.2.6. [3-(2-Phenyl-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-ylidene)-2-phenyl-2,3-dihydro-1*H*-isoindol-1-ylidene]propanedinitrile (8f). Blue-black crystals (acetonitrile), mp 301–303°C, (189 mg, 29%); UV/Vis (acetonitrile): λ_{max}=578 nm, log ε=4.51; IR: ν=2210 (CN), 1580 (aryl) cm^{-1}; ^1H NMR (CD_3NO_2): δ=6.65–6.70 (m, 2H, Ar-H), 7.45–7.75 (m, 12H, Ar-H), 8.30–8.70 (m, 4H, Ar-H); MS: *m/z* (%)=510 (M^+, 100), 446 (5), 433 (5), 255 (22), 229 (11), 77 (44). Anal. calcd for $C_{34}H_{18}N_6$ (510.6) C, 79.98; H, 3.55; N, 16.46. Found: C, 79.75; H, 3.46; N, 16.41.

4.2.7. {3-[2-(2-Chlorophenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(2-chlorophenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8g). Blue-black crystals (acetonitrile), mp 254–256°C, (148 mg, 20%); UV/Vis (acetonitrile): λ_{max}=570 nm, log ε=4.40; IR: ν=2200 (CN), 1525 (aryl) cm^{-1}; ^1H NMR (CD_3NO_2): δ=6.55–6.70 (m, 2H, Ar-H), 6.95–7.95 (m, 12H, Ar-H), 8.45–8.60 (m, 2H, Ar-H); MS: *m/z* (%)=583 (18), 581 (36), 579 (M^+, 100), 543 (52), 508 (15), 482 (9), 467 (9), 289 (15), 254 (24), 76 (15). Anal. calcd for $C_{34}H_{16}N_6Cl_2$ (579.4): C, 70.47; H, 2.78; N, 14.50. Found: 70.31; H, 2.82; N, 14.44.

4.2.8. {3-[2-(3-Chlorophenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylidene]-2-(3-chlorophenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8h). Blue-black crystals (acetonitrile), mp 323–325°C, (267 mg, 36%); UV/Vis (acetonitrile): λ_{max}=574 nm, log ε=4.48; IR: ν=2210 (CN), 1610 (C=C), 1540 (aryl) cm^{-1}; ^1H NMR (CD_3NO_2): δ=6.75–7.05 (m, 2H, Ar-H), 7.35–8.07 (m, 10H, Ar-H), 8.45–8.62 (m, 4H, Ar-H); MS: *m/z* (%)=583 (20), 581 (39), 579 (M^+, 100), 553 (2),543 (9), 515 (7), 467 (10), 453 (3), 289 (34), 263 (15), 254 (12), 225 (14), 76 (21). Anal. calcd for $C_{34}H_{16}N_6Cl_2$ (579.4): C, 70.47; H, 2.78; N, 14.50. Found: C, 70.36; H, 2.84; N, 14.49.

4.2.9. {3-[2-(4-Acetylphenyl)-3-(dicyanomethylene)-2,3-dihydro-1*H*-isoindol-1-ylid-ene]-2-(4-acetylphenyl)-2,3-dihydro-1*H*-isoindol-1-ylidene}propanedinitrile (8i). Blue-black crystals (acetonitrile), mp 274–276°C, (266 mg, 35%); UV/Vis (acetonitrile): λ_{max}=576 nm, log ε=4.38; IR: ν=2200 (CN), 1600 (C=C), 1685(CO) cm^{-1}; ^1H NMR (CD_3NO_2): δ=2.60–2.70 (s, 6H, Ar-H), 6.95–7.00 (m, 2H, Ar-H), 7.50–8.22 (m, 12H, Ar-H), 8.46–8.64 (m, 2H, Ar-H); MS: *m/z* (%)=594 (M^+, 100), 579 (12), 553 (9), 479 (10), 297 (60), 282 (10), 254 (20), 233 (15), 119 (30). Anal. calcd for $C_{38}H_{22}N_6O_2$ (594.6): C, 76.75; H, 3.72; N, 14.13. Found: C, 76.59; H, 3.61; N, 14.19.

4.2.10. *N*-(2-Methoxyphenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9a). Yellow crystals (acetonitrile), mp 182–183°C, (116 mg, 15%); IR: ν=2220 (CN), 1770–1750 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.85 (s, 3H, OCH_3), 7.00–8.08 (m, 7H, Ar-H), 8.55–8.70 (m, 1H, Ar-H); MS: *m/z* (%)=301 (M^+, 100), 286 (4), 270 (23), 258 (13), 242 (10), 232 (13), 206 (30), 152 (25), 104 (33), 76 (27). Anal. calcd for $C_{18}H_{11}N_3O_2$ (301.3): C, 71.75; H, 3.67; N, 13.94. Found: C, 71.79; H, 3.58; N, 14.02.

4.2.11. *N*-(3-Methoxyphenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9b). Yellow crystals (ethanol), mp 224–226°C, (154 mg, 20%); IR: ν=2220 (CN), 1745 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=3.85 (s, 3H, OCH_3), 6.85–7.68 (m, 4H, Ar-H), 7.78–8.10 (m, 3H, Ar-H), 8.56–8.70 (m, 1H, Ar-H); ^{13}C NMR ($CDCl_3$): δ=55.62 (OCH_3), 61.48 [*C*$(CN)_2$], 109.98 (CN), 113.81 (CN); 115.09, 116.89, 121.37, 125.42, 125.49, 130.55, 134.35, 135.01 (8 aryl CH); 127.53, 132.54, 132.90, 160.59 (4 quaternary C), 158.05 (C-3), 165.81 (C=O); MS: *m/z* (%)=301 (M^+, 100), 286 (6), 270 (28), 258 (10), 242 (9), 232 (10), 206 (3), 152 (5), 104 (20), 76 (15). Anal. calcd for $C_{18}H_{11}N_3O_2$ (301.3): C, 71.75; H, 3.67; N, 13.94. Found: C, 71.62; H, 3.46; N, 13.84.

4.2.12. *N*-(2-Methylphenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9c). Yellow crystals (benzene/pentane), mp 175–177°C, (131 mg, 18%); IR: ν=2210 (CN), 1750 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.25 (s, 3H, CH_3), 7.15–7.55 (m, 4H, Ar-H), 7.80–8.10 (m, 3H, Ar-H), 8.60–8.75 (m, 1H, Ar-H); MS: *m/z* (%)=285 (M^+, 100), 270 (11), 259 (74), 231 (6), 205 (2), 166 (11), 152 (6), 104 (7), 76 (24). Anal. calcd for $C_{18}H_{11}N_3O$ (285.3): C, 75.77; H, 3.88; N, 14.72. Found: C, 75.62; H, 3.70; N, 14.61.

4.2.13. *N*-(3-Methylphenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9d). Yellow crystals (cyclohexane), mp 217–218°C, (153 mg, 21%); IR: ν=2200 (CN), 1745–1770 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.45 (s, 3H, CH_3), 7.10–7.50 (m, 4H, Ar-H), 7.78–8.10 (m, 3H, Ar-H), 8.55–8.70 (m, 1H, Ar-H); ^{13}C NMR ($CDCl_3$): δ=21.37 (CH_3), 61.37 [*C*$(CN)_2$], 109.97 (CN), 113.83 (CN); 125.37, 125.46, 126.23, 129.58, 129.67, 132.07, 134.30, 134.95 (8 aryl-CH); 127.56, 131.49, 132.90, 140.09 (4 quaternary C); 158.18 (C-3), 165.94 (C=O); MS: *m/z* (%)=285 (M^+, 100), 270 (33), 259 (37), 231 (8), 205 (2), 166 (27), 152 (17), 104 (2), 76 (53). Anal. calcd for $C_{18}H_{11}N_3O$ (285.3): C, 75.77; H, 3.88; N, 14.72. Found: C, 75.61; H, 3.72; N, 14.50.

4.2.14. *N*-(4-Methylphenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9e). Colourless crystals (ethanol), mp 238–240°C, (133 mg, 18%); IR: ν=2220 (CN), 1750–1780 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=2.47 (s, 3H, CH_3), 7.15–7.45 (m, 4H, Ar-H), 7.75–8.10 (m, 3H, Ar-H), 8.58–8.70 (m, 1H, Ar-H); ^{13}C NMR ($CDCl_3$): δ=21.50 (CH_3), 61.29 [*C*$(CN)_2$], 110.06 (CN), 113.87 (CN); 125.35, 125.45, 128.92 (2C), 130.49 (2C), 134.28, 134.92 (8 aryl-CH); 127.52, 132.91, 141.65 (3 of 4 quaternary C, one signal not detectable); 158.33 (C-3), 166.02 (C=O); MS: *m/z* (%)=285 (M^+, 100), 270 (17), 259 (11), 231 (2), 205 (1), 166 (5), 152 (2), 129 (14), 104 (21), 76 (11). Anal. calcd for $C_{18}H_{11}N_3O$ (285.3): C, 75.77; H, 3.88; N, 14.72. Found: C, 75.63; H, 3.90; N, 14.63.

4.2.15. *N*-Phenyl-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9f). Colourless crystals (acetonitrile), mp 274–276°C, (139 mg, 20%); IR: ν=2220 (CN), 1750–1770 (CO) cm^{-1}; ^1H NMR (CD_3NO_2): δ=7.38–7.70 (m, 5H,

Ar-H), 7.85–8.10 (m, 3H, Ar-H), 8.52–8.70 (m, 1H, Ar-H); MS: *m/z* (%)=271 (M^+, 100), 245 (89), 217 (8), 191 (2), 179 (24), 163 (4), 152 (17), 131 (54), 104 (41), 76 (46). Anal. calcd for $C_{17}H_9N_3O$ (271.3): C, 75.26; H, 3.34; N, 15.48. Found: C, 75.53; H, 3.30; N, 15.31.

4.2.16. *N*-(2-Chlorophenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9g). Pale yellow crystals (ethanol), mp 158–159°C, (113 mg, 13%); IR: ν=2220 (CN), 1750–1770 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=7.35–7.70 (m, 4H, Ar-H), 7.75–8.10 (m, 3H, Ar-H), 8.60–8.75 (m, 1H, Ar-H); MS: *m/z* (%)=307 (13), 305 (M^+, 70), 270 (100), 244 (11), 216 (14), 201 (18), 190 (5), 125 (14), 104 (9), 76 (77). Anal. calcd for $C_{17}H_8N_3OCl$ (305.7): C, 66.78; H, 2.63; N, 13.74. Found: C, 66.57; H, 2.59; N, 13.78.

4.2.17. *N*-(3-Chlorophenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9h). Colourless crystals (ethanol), mp 228–230°C, (149 mg, 19%); IR: ν=2220 (CN), 1750 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ=7.35–7.60 (m, 4H, Ar-H), 7.70–8.12 (m, 3H, Ar-H), 8.60–8.75 (m, 1H, Ar-H); MS: *m/z* (%)=307 (11), 305 (M^+, 100), 270 (50), 244 (23), 216 (18), 201 (2), 190 (13), 125 (8), 104 (7), 76 (76). Anal. calcd for $C_{17}H_8N_3OCl$ (305.7): C, 66.78; H, 2.63; N, 13.74. Found: C 66.68; H, 2.55; N, 13.66.

4.2.18. *N*-(4-Acetylphenyl)-3-dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-one (9i). Pale yellow crystals (acetonitrile), mp 223–224°C, (136 mg, 17%); IR: ν=2220 (CN), 1660–1680, 1700, 1750–1770 (CO) cm^{-1}; ^1H NMR (DMSO-d_6): δ=2.65 (s, 3H, $COCH_3$), 7.65–8.20 (m, 7H, Ar-H), 8.45–8.55 (m, 1H, Ar-H); MS: *m/z* (%)=313 (M^+, 33), 298 (100), 270 (17), 244 (5), 216 (8), 209 (25), 181 (12), 119 (30), 104 (28), 76 (50). Anal. calcd for $C_{19}H_{11}N_3O_2$ (313.3): C, 72.83; H, 3.53; N, 13.41. Found: C, 72.92; H, 3.46; N, 13.22.

4.2.19. Phthalimides 10a–i. *Compound* **10a**. *N*-(2-Methoxyphenyl)-, mp 156–157°C (lit.[31] 158°C), 26 mg (4%).

Compound **10b**. *N*-(3-Methoxyphenyl)-, mp 124–125°C (lit.[31] 126°C), 32 mg (5%).

Compound **10c**. *N*-(2-Methylphenyl)-, mp 184–186°C (lit.[31] 185°C), 30 mg (5%).

Compound **10d**. *N*-(3-Methylphenyl)-, mp 176–178°C (lit.[31] 175°C), 49 mg (8%).

Compound **10e**. *N*-(4-Methylphenyl)-, mp 204–206°C (lit.[32] 205°C), 30 mg (5%).

Compound **10f**. *N*-Phenyl-, mp 209–210°C (lit.[31] 212°C), 40 mg (7%).

Compound **10g**. *N*-(2-Chlorophenyl)-, mp 144°C (lit.[32] 144°C), 33 mg (5%).

Compound **10h**. *N*-(3-Chlorophenyl)-, 162–164°C (lit.[32] 165°C), 60 mg (9%).

Compound **10i**. *N*-(4-Acetylphenyl)-, mp 248–250°C (lit.[15] 248–250°C), 55 mg (8%).

4.3. Single crystal X-ray structure determination of 8d

Suitable crystals were obtained by recrystallization from acetonitrile. Data were recorded using an Enraf-Nonius Kappa CCD diffractometer with graphite-monochromated Mo K_α-radiation (λ=0.71073 Å). The crystal was mounted in a stream of cold nitrogen gas. The structure was solved by direct methods (*SHELXS-97*[33]) and refined by full matrix least squares techniques against F^2 (*SHELXL-97*[34]). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program.

Crystal and intensity data. $C_{36}H_{22}N_6$, M_r=538.60 g mol^{-1}, blue-black, crystal size 0.35×0.21×0.12 mm, triclinic, $P\bar{1}$ [No. 2], a=7.77510(10), b=11.0928(2), c=16.5963(3) Å, α=108.4270(10), β=92.7020(10), γ=90.7120(10)°, V=13.55.93(4) $Å^3$, Z=2, D_{calc}=1.319 Mg m^{-3}, μ=0.080 mm^{-1}, T=100 K, 33170 reflections collected, 6207 independent reflections, 4795 reflections with $I>2\sigma(I)$, θ_{max}=27.50°, 394 refined parameters, R=0.058, R_w=0.154, S=1.021, largest diff. peak and hole=0.6/−0.6 e $Å^3$.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 190218. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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