Dicyanomethylene Compounds as Cyanation Reagents [1]*

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Dedicated to Professor W. S. Veeman on the occasion of his 60th birthday

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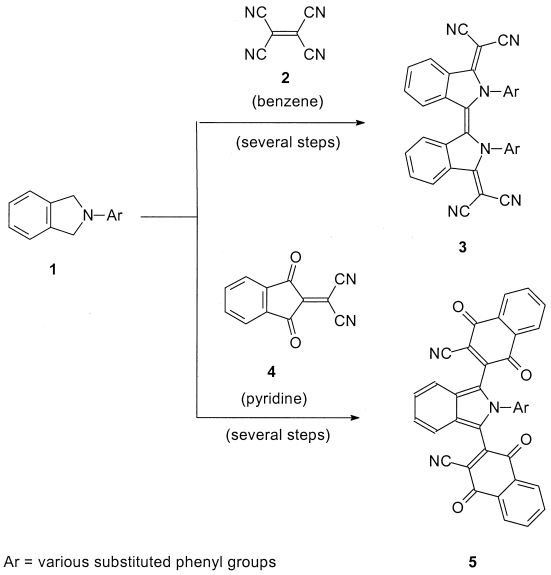
Dihydroisoquinolines, Bridged Functional Biphenyls, Cyclic Iminium Ions

Ethenetetracarbonitrile (**2**, in benzene solution) and 1,3-dioxoindan-2-ylidene propanedinitrile (**4**, in ethanol or acetonitrile solution) act on *N*-aryl-2,3-dihydro-1*H*-benz[*d,e*]isoquinolines **6a-d** and *N*-aryl-6,7-dihydro-5*H*-dibenz[*c,e*]azepines **11a-d** *via* hydride abstraction followed by addition of cyanide to the iminium carbon atom forming the corresponding 1- and 5-carbonitriles **9a-d** and **13a-d**, respectively, in moderate to medium yields. Additionally, the known 1,3-dihydroxy-2*H*-inden-2-ylidenepropanedinitrile **15** and a novel dispirocyclopropane (**17**) are formed from **4** in the reaction with **6** in acetonitrile and ethanol, respectively. The structures of **17** and 6-(4-methylphenyl)-6,7-dihydro-5*H*-dibenz[*c,e*]azepine-5-carbonitrile have been unambiguously confirmed by single-crystal X-ray crystallography.

Introduction

N,N-Dialkylanilines undergo a *para*-tricyanovinylation (TCV) reaction when exposed to ethenetetracarbonitrile (**2**)[2]. *N*-Phenylisoindoline (**1**, Ar = Ph) or other N-phenylisoindolines even with free *para*-position on the phenyl group do not show significant *para*-tricyanovinylation with **2**, instead, a complex sequence of steps ultimately leading to **3** is observed [3]. This behaviour is most likely due to the sensitivity of positions 1 and 3 in **1** to formal (stepwise or concerted) hydride abstraction or C-H homolyses [3]. In contrast, 1,3-dioxoindan-2-ylidene propanedinitrile (**4**) does show a TCV-analogous reaction with the above-mentioned isoindolines and at the same time a multistep-sequence of events ultimately leading to substitution of 1-H and 3-H of the isoindole derived from **1** by 2-cyano-1,4-naphthoquinon-1-yl [3], a residue accessible by electron-transfer mediated rearrangement [4] of **4**. The structures of products **3** and **5** have been confirmed for **3** (Ar = 3-$CH_3C_6H_4$)) and **5** (Ar = 4-$H_3COC_6H_4$) by single crystal structural analyses [3, 5].



Scheme 1.

These intriguing transformations led us to investigate the reactions of dihydro-benz[*d,e*]isoquinolines **6** and dihydrodibenz[*c,e*]azepines (**11**) bearing a selection of *N*-aryl substituents with the acceptor systems **2** and **4**. Both donor systems (**6**, **11**) feature benzylic activation of the α-carbon

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atoms as in **1** and should therefore be reactive at these positions towards **2** and **4**.

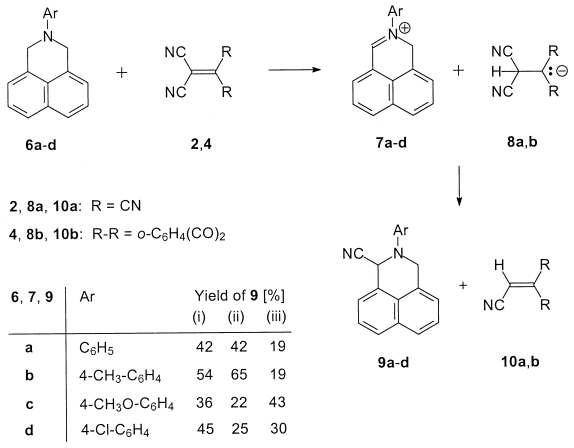
Results and Discussion

The heterocyclic donors **6a-d** [6] and **11a-d** [7] were prepared according to published procedures.

Treatment of **6a** with three molar equivalents of ethenetetracarbonitrile (**2**) in benzene as solvent at room temperature resulted in a green colouration of the solution which later became dark brown. While a yellow colour of the CT complex from **2** and the solvent was persistent and detectable at all times (λ_{max} = 384 nm, [8]), monitoring of the reaction by visible spectroscopy failed since at lower concentrations no significant colour changes were observed any more. Concentration of the preparative runs resulted in formation of a precipitate which by washing with ethyl acetate yielded a dark-blue solid which did not melt below 300 °C, showed CN absorptions at 2216 and 2254 cm^{-1}, was insoluble in all common solvents and was not characterized further. The formation of polymers from **2** in the presence of alcohols, phenols and amines has been observed [9] and most of the nitrile groups seem to be involved in the polymerization [10, 11].

The remaining soluble materials were subjected to preparative layer chromatography. From the one significant zone and by crystallization from ethanol, the α-aminonitrile **9a** (see below for characterization) was obtained in 7% yield. It was found to be air-sensitive, thus in all further cases the work-up was carried out as quickly as possible to minimize losses. Since 1-H is activated by its benzyl-like position and any C-1 centered radical would be highly stabilized including a captodative [12] contribution, this sensitivity is quite plausible. While an increase in reaction temperature to 50 °C did not lead to any improvement, by keeping the temperature as close as possible to the freezing point of the mixture by external ice/water cooling, the yield of **9a** could be raised to 54%. Similar results were obtained for the analogous compounds **9b-d** from **6b-d** (see Scheme 2). All yields given in this study refer to converted starting material.

The structures of **9a-d** were delineated from their spectroscopic properties (see Experimental Section). The salient feature is the change in the



2, **8a**, **10a**: R = CN

4, **8b**, **10b**: R-R = *o*-$C_6H_4(CO)_2$

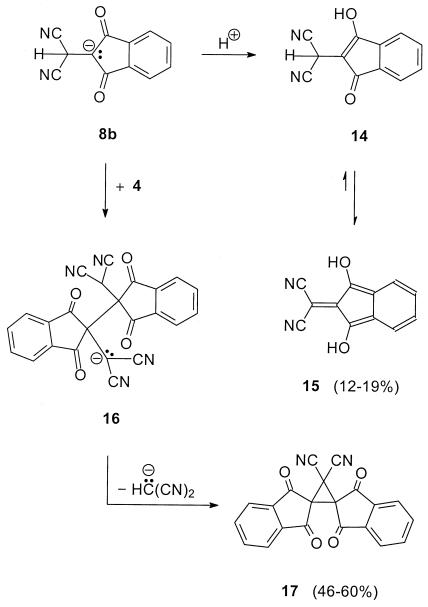
6, **7**, **9**	Ar	Yield of **9** [%] (i)	(ii)	(iii)
a	C_6H_5	42	42	19
b	4-CH_3-C_6H_4	54	65	19
c	4-CH_3O-C_6H_4	36	22	43
d	4-Cl-C_6H_4	45	25	30

(i): **6** : **2** = 1 : 3, benzene, 5°C → 20 °C, 18 h
(ii): **6** : **4** = 1 : 2, ethanol, 20 °C, 68 h
(iii): **6** : **4** = 1 : 2, acetonitrile, 20 °C, 3 h

Scheme 2.

CH_2-resonances in going from **6** to **9**: Due to the introduction of a stereogenic centre at C-1, the C-3 methylene protons now show an AB pattern while 1-H gives rise to a singlet.

A plausible rationale for the introduction of a cyano group at C-1 is depicted in Scheme 2. A net hydride abstraction [2, 13] by **2** from **6** forms the cyclic iminium ion **7** and tetracyanoethanide **8a**.



Scheme 3.

The latter may deliver a cyanide ion to **7** directly within the ion pair, since release of CN^- into the non-anionstabilizing solvent seems less likely. The fate of **10a** is not clear at present, formation of intractable polymers is a likely possibility, since it is more reactive towards bases than **2**, water (for example during work-up and chromatography) initiates HCN-elimination and produces hitherto unidentified materials [14]. Products derived from **6** with higher molecular weight, structurally analogous to **3**, may be present in the reaction mixtures in very small amounts as indicated from MS investigation of minor zones, but certainly not in quantities sufficient for full characterization.

The weaker acceptor **4,** being easily accessible [15] from indane-1,2,3-trione, was expected to react similarly to **2** with the heterocyclic donors **6a-d**. Due to insufficient solubility of **4** in benzene, the reaction was carried out both in dry ethanol and in acetonitrile at room temperature. In the former solvent, nearly three days were required to achieve conversions of 85–90% for **6a-c** and 53% for **6d** and low to medium yields of compounds **9a-d** (see Scheme 2). In acetonitrile, nearly quanti-

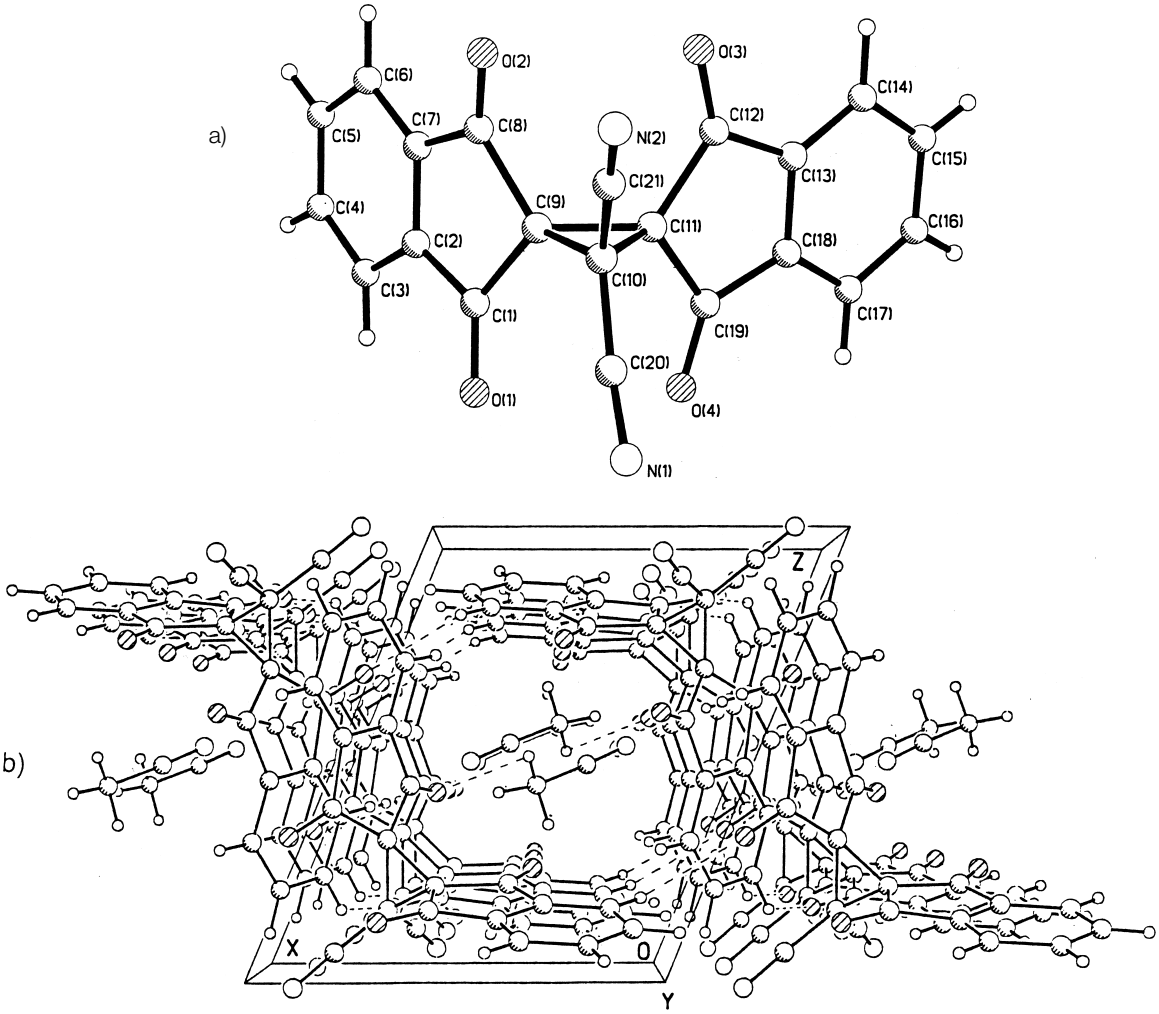


Fig. 1. a) Structure of compound **17** in the crystal. The crystallographic numbering does not match the systematic numbering. Selected bond lengths [Å]: C(9)-C(10) 1.517(3), C(9)-C(11) 1.533(3), C(10)-C(11) 1.539(3), C(10)-C(21) = C(10)-C(20) = 1.460(3); selected angles [°]: C(20)-C(10)-C(21) 111.9(2), C(12)-C(11)-C(19) 105.8(1), C(1)-C(9)-C(8) 104.4(1); b) detail of crystal structure of **17**·MeCN viewed along the *y*-axis.

tative conversions were achieved already after three hours, but yields of **9a-d** tended to be low or moderate. In addition, 1,3-dihydroxyindan-2-ylidenepropanedinitrile (**15**) was formed in yields varying between 12 and 19%. A rationale for the formation of this known [16] byproduct is abstraction of a proton by the carbanion **8b** resulting from hydride abstraction, see Scheme 3.

In ethanol solution, on the other hand, **15** is not a significant byproduct, although protonation of any **8b** formed should be favourable. Instead, a new compound was regularly detected and identified as the cyclopropane **17**. Aside of the simple ^{1}H and ^{13}C NMR spectra demonstrating the presence of two equivalent dioxoindanylidene units and two equivalent CN groups, the structure of **17** was unambiguously corroborated by a single crystal structure determination of its 1:1 stoichiometric solvate with acetonitrile (Figs 1 and 2). This compound, being the formal 1,3-dioxoindan-2-ylidene adduct to the C=C double bond of **4** may be formed from the carbanion **8b** by conjugate addition to **4**, followed by intramolecular displacement of malodinitrile anion (Scheme 3). For a review on the formation of polycyano cyclopropanes, see ref. [17].

The C_{2v}- symmetry of **17** in solution is reduced to C_1 in the crystal (see Fig. 2). The C(9)-C(21) bond (1.517 Å) is significantly shorter (by 0.002 Å) than the two other C-C bonds of the three-membered ring. In the crystal lattice of **17**·MeCN the solvent molecules reside in tubes formed by stacking the indanylidene units (Fig. 1b).

1,3-Dihydrobenz[*c*,*e*]azepines **11a-d** may be regarded as 1,2-phenylene homologues of isoindolines **1** and are thus expected to show a reactivity towards **2** and **4** similar to that of **1**. To our surprise, however, again solely α-cyanation forming carbonitriles **13a-d** was observed when **11a-d** was allowed to react with either **2** in benzene or its analogue **4** in ethanol.

The structural assignment rests largely on the ^{1}H and ^{13}C NMR spectra: Due to the creation of a stereogenic centre at C-5, the 4H singlets for the methylene protons in **11a-d** give way to a 1H singlet for 5-H and an AB-quartet for 7-CH_2. Also, these spectra in total reflect the reduction of symmetry in **13** with respect to **11** (see Experimental Section). Rigorous structure proof comes from the single crystal X-ray structural analysis of **13b** (see Fig. 3 and Table 1).

The central seven-membered ring is confined into a twist-form, and the planes of the two phenyl rings in the biphenyl moiety form a twist angle of ± 42.7°. The (relative) configuration of **13b** is *rel*-(5*R*, a*S*), the unit cell consists of two molecules each of the (5*R*, a*S*)- and (5*S*, a*R*)-enantiomers.

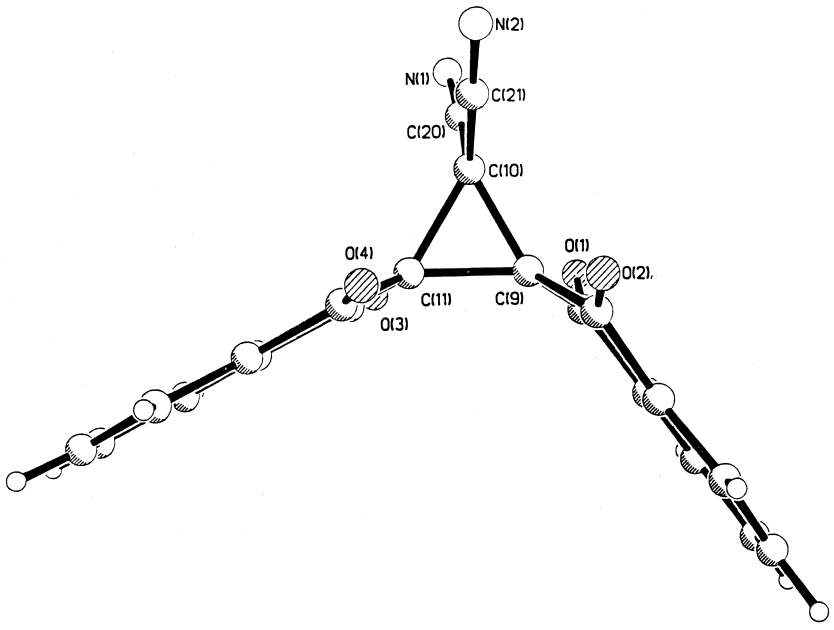


Fig. 2. Structure of **17** in the crystal. View perpendicular to the plane of the three-membered ring

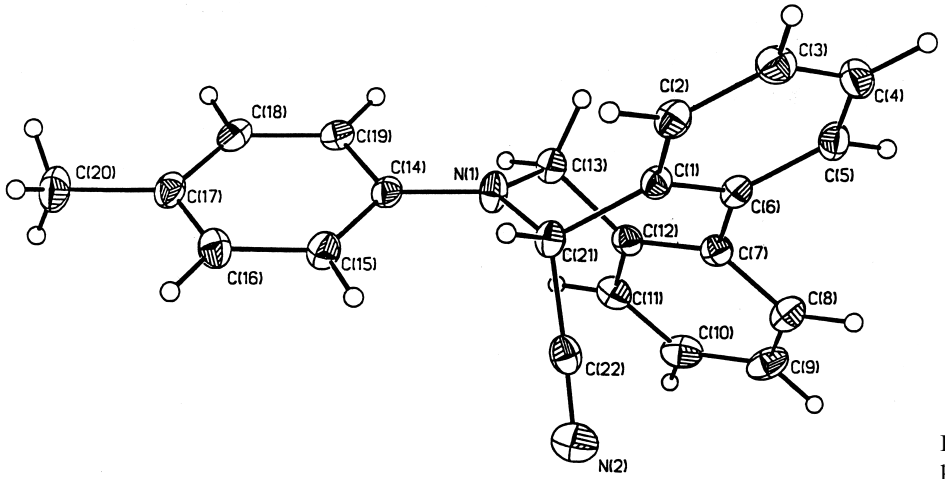
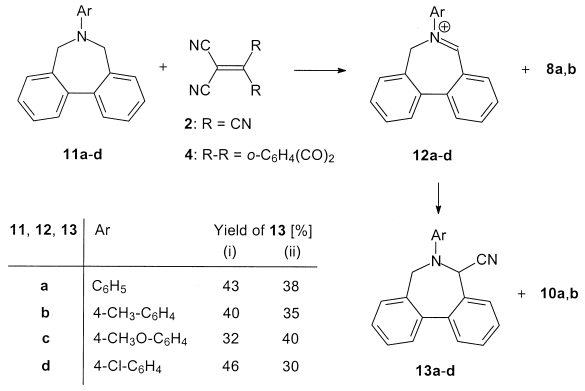


Fig. 3. Structure of compound **13b** in the crystal.

Table 1. Selected bond lengths [Å] and angles [°] of compound **13b** ($C_{22}H_{18}N_2$) in the crystal. The crystallographic numbering does not correspond to systematic numbering.

Bond lengths [Å]		Bond angles [°]	
C(1)–C(6)	1.406(2)	C(1)–C(6)–C(7)	120.3(1)
C(6)–C(7)	1.485(2)	C(6)–C(7)–C(12)	120.0(1)
C(7)–C(12)	1.405(2)	C(7)–C(12)–C(13)	120.8(1)
C(12)–C(13)	1.512(2)	C(12)–C(13)–N(1)	114.0(1)
C(13)–N(1)	1.473(2)	C(13)–N(1)–C(21)	116.3(1)
N(1)–C(21)	1.452(2)	N(1)–C(21)–C(1)	112.6(1)
C(21)–C(1)	1.522(2)	C(6)–C(1)–C(21)	121.4(1)
C(21)–C(22)	1.501(2)	N(1)–C(21)–C(22)	111.5(1)
C(22)–N(2)	1.145(2)	C(1)–C(21)–C(22)	110.9(1)
		C(13)–N(1)–C(14)	122.0(1)
		C(14)–N(1)–C(21)	120.6(1)

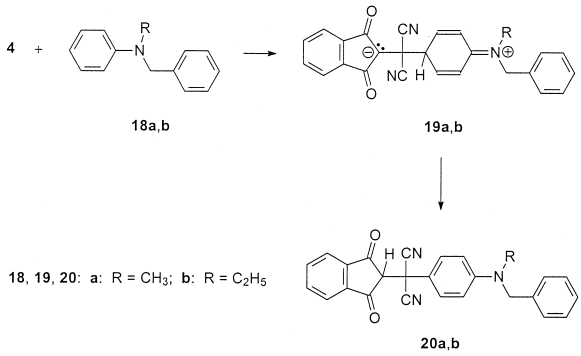


11, 12, 13	Ar	Yield of 13 [%] (i)	(ii)
a	C_6H_5	43	38
b	4-CH_3-C_6H_4	40	35
c	4-CH_3O-C_6H_4	32	40
d	4-Cl-C_6H_4	46	30

(i): **11** : **2** = 1 : 2, benzene, 20 °C, 48 h; (ii): **11** : **4** = 1 : 2, ethanol, 20 °C, 96 h

Scheme 4.

Since the cyclic benzofused substrates **6** and **11** might be especially favourable for α-hydride abstraction, and the *N*-phenyl derivatives **6a** and **11a** did not show much of *para*-tricyanovinylation with **2** or an analogous reaction with **4**, the question was addressed whether such a reaction would take place on 4-unsubstituted *N*-benzylanilines at all. Using substrates **18a,b** attack of **4** at the free *para*-position took place; however, the primary 1:1 adducts **19a,b** only underwent prototropy to form **20a,b**. Subsequent coloration and HCN elimination took place upon melting. Any products of α-cyanation at the benzylic carbon atom could not be detected.



Scheme 5.

Conclusion

Under favourable conditions, as with compounds **6** and **11** bearing activated α-positions, eth-

enetetracarbonitrile (**2**) and 1,3-dioxo-2-indanylidene propanedinitrile (**4**) react by net cyanation, most likely by initial hydride abstraction and subsequent transfer of a cyanide ion to the amine-derived iminium ion. Scope and limitations of this process have not been explored yet, and no optimization has so far been attempted. Nevertheless this reaction sequence may be developed into another method of α-cyanation of tertiary amines.

This ought to be seen in the context that α-aminonitriles may be regarded as stabilized iminium ions [18]. Several related α-cyanations using trimethylsilylcyanide as a cyanide source for iminium ions generated by photooxidation [19–22], or action of other oxidants [18] on tertiary amines to generate iminium ions which are then reacted with cyanide ions [18] have been reported. Sodium borohydride reduction of pyridinium ions in the presence of sodium cyanide to generate 1,2,3,6-tetrahydropyridine 2-carbonitriles is a complementary technique of α-cyanation [23]. In the examples presented in this study, the same reagent is functioning as dehydrogenating agent and as cyanide ion source.

Experimental Section

M.p.'s have been determined on a Kofler hot stage microscope. – IR-spectra were recorded on Perkin Elmer 283 and 983 instruments. Weak (strong) bands have been indicated by w (s) after the wavenumber. – A Bruker WM 300 instrument has been used to determine ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra. Assignment of carbon resonances has been supported by DEPT experiments. Abbreaviations indicating signal multiplicity: s singlet, d doublet, t triplet, m multiplet. – Mass spectra have been obtained with a Varian MAT 311 doubly focussing instrument using electron impact ionization (70 eV). – Elemental analyses have been determined on a Carlo Erba Model 1106 Elemental Analyzer. Analytical thin-layer chromatography: Al-sheets coated with Merck silica gel 60 F_{254}. – Preparative layer chromatography (plc): Glass plates 48 × 20 cm covered with slurry applied and air dried layers of Merck silica gel PF_{254}. Detection of zones by fluorescence quenching after 254 nm excitation. Zones were removed from the plates and extracted with cold acetone.

Starting materials

Ethenetetracarbonitrile (**2**), Merck, was sublimed prior to use, m. p. 198–200 °C (lit. [2a] 200–202 °C).

(1.3-Dioxoindan-2-ylidene)propanedinitrile (**4**) was prepared according to Chatterjee [15b], m.p. 279–282 °C (lit. [15b] 280–285 °C).

1,8-Bis(hydroxymethyl)naphthalene was prepared according to Boekelheide and Vick [24] in 51% yield, m.p. 158–160 °C (lit. [24] 157–158 °C). – This material was converted [25] into 1,8-bis(bromomethyl)-naphthalene, m. p. 129–133 °C (lit. [25] 131–133 °C).

This compound (instead of the corresponding bis(chloromethyl) analogue) was used to prepare the 2-aryl-2,3-dihydro-1*H*-benz[*d*,*e*]isoquinolines **6a-d**: Samples of 100 mg (3.2 mmol) and equimolar amounts of the corresponding aniline were refluxed in 10 ml of toluene in the presence of 0.47 g (8.0 mmol) of triethylamine. Thereafter the mixture was treated with 2 M NaOH and extracted with $CHCl_3$. After drying and concentration the residue was crystallized from methanol (**6a**) or ethanol (**6b-d**).

*2-Phenyl-2,3-dihydro-1H-benz[d,e]isoquinoline (**6a**):* Yield 0.52 g (66%), m. p. 58–59 °C (lit.[6] 57–59 °C).

*2-(4-Methylphenyl)-2,3-dihydro-1H-benz[d,e]-isoquinoline (**6b**):* Yield 0.57 g (69%) m. p. 148–150 °C (lit. [6] 146–148 °C).

*2-(4-Methoxyphenyl)-2,3-dihydro-1H-benz[d,e]-isoquinoline (**6c**):* Yield 0.54 g (61%), m. p. 107–108 °C (lit. [6] 106–107 °C).

*2-(4-Chlorophenyl)-2,3-dihydro-1H-benz[d,e]-isoquinoline (**6d**):* Yield 0.51 g (57%), m. p. 116–118 °C (lit. [6] 117–119 °C).

2,2′-Bis(hydroxymethyl)biphenyl, prepared according to Rieche, Höft and Schultze [7], had m. p. 113 °C (lit. [7] 112 °C). This was converted into *2,2′-bis(bromomethyl)-biphenyl* by treating with a doubled molar amount of phosphorus tribromide at 20 °C, followed by hydrolysis. Crystallization from petroleum ether gave a 78% yield as colourless crystals, m. p. 88–90 °C (lit. [26] 89–92 °C). To prepare [7] compounds **11**, samples of 340 mg (1.0 mmol) of the dibromide and 1.0 mmol of the corresponding aniline were heated to reflux in 10 ml of toluene containing 0.2 ml of triethylamine for 2 h. The mixture was treated with 2 M NaOH and the organic layer was dried and concentrated. The residues were crystallized from ethanol to give 2.2 g (81%) **11a**, 1.4 g (49%) **11b**, 2.63 g (87%) **11c**, and 1.53 g (50%) of **11d**.

*6-Phenyl-6,7-dihydro-5H-dibenz[c,e]azepine (**11a**):* M.p. 84–86 °C (lit. [7] 89.5–90.0 °C). – IR (KBr pellet): ν = 2939, 2834 (CH_2), 1591, 1564, 1492 s, 1469, 1379, 1210, 821s, 757s cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 4.12 (s, 4H, 2 × CH_2), 6.79 (m, 1H, 4′-H), 6.79 (m, 2H, 2′-, 6′-H); 7.22–7.35 (m, 6H), 7.42 (m, 2H), 7.52 (m, 2H) (all aryl-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.13 (2 × *C*H_2), 118.17 (4′-C); 114.93, 127.66, 128.04, 128.23, 129.14, 129.57 (2 aryl-*C*H each); 134.84, 140.68 C-4a, C-7a, C-11a, C-11b), 149.47 (1′-C). – MS (EI, 70 eV): *m/z* (%) = 271 (95) [M^+], 270 (100) [M^+-1], 194 (5) [M^+-C_6H_5], 178 (24), 165 (33), 152 (8) [biphenylylene$^+$] 135.5 (7) [M^{++}], 104 (43), 77 (35). – $C_{20}H_{17}N$ (271.3): calcd. C 88.52, H 6.32, N 5.16; found: C 88.51, H 6.35, N 5.11.

*6-(4-Methylphenyl)-6,7-dihydro-5H-dibenz[c,e]-azepine (**11b**):* M.p. 110–111 °C (lit. [7] 104–105 °C). – IR (KBr pellet): 2909, 2855 (CH_2), 1614, 1516 s, 804 s, 756 s cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.26 (s, 3H, CH_3), 4.06 (s, 4H, 2 × CH_2), 6.89 (m, 2H, 3′-, 5′-H), 7.06 (m, 2H, 2′-, 6′-H), 7.30 (m, 4H), 7.40 (m, 2H), 7.51 (m, 2H) (all biphenylylene-H). – ^{13}C NMR (75.47 MHz), $CDCl_3$): δ = 20.35 (*C*H_3), 52.49 (2× *C*H_2); 115.35, 127.59, 127.98, 128.14, 129.55, 129.64 (all aryl-*C*H each); 134.88, 140.69 (C-4a, C-7a, C-11a, C-11b), 147.46 (1′-C). – MS (EI, 70 eV): *m/z* (%) = 285 (98) [M^+], 284 (100)[M^+-1], 178 (22), 165 (27), 118 (29), 91 (29) [$C_7H_7^+$]. – $C_{21}H_{13}N$ (285.4): calcd. C 88.38, H 6.71, N 4.91; found C 88.28, H 6.76, N 4.94.

*6-(4-Methoxyphenyl)-6,7-dihydro-5H-dibenz-[c,e]azepine (**11c**):* M.p. 148–149 °C (lit. [7] 148–149 °C). – IR (KBr pellet): ν = 2935, 2385 (CH_2), 1511 s, 1249, 1036, 822, 770 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.74 (s, 3H, O*C*H_3), 4.02 (s, 4H, 2 × C*H*$_2$), 6.84 (m, 2H, 2′-, 6′-H), 6.94 (m, 2H, 3′-, 5′-H); 7.30 (m, 4H), 7.41 (m, 2H), 7.50 (m, 2H) (all biphenylylene-H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 53.36 (2 × CH_2), 55.58 (O*C*H_3); 114.50, 117.40, 127.57, 127.99, 128.16, 129.55 (2 aryl-CH each); 134.81, 140.74 (C-4a, C-7a, C-11a, C-11b), 144.23 (1′-C), 152.93 (4′-C). – MS (EI, 70 eV): *m/z* (%) = 301 (100) [M^+], 300 (74) [M^+-1]; 286 (14) [M^+-CH_3] 179 (26), 178 (21), 134 (18), 120 (15). – $C_{21}H_{19}NO$ (301.4): calcd. C 83.69, H 6.35, N 4.65; found C 83.66, H 6.32, N 4.58.

*6-(4-Chlorophenyl)-6,7-dihydro-5H-dibenz[c,e]-azepine (**11d**):* M.p. 146–147 °C (lit. [7] 147–149 °C). – IR (KBr pellet): ν = 2939, 2834 (CH_2), 1591, 1564, 1492s, 1460, 1379, 1210s, 821, 757s cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 4.06 (s, 4H, 2 × CH_2), 6.88 (m, 2H, 2′-, 6′-H), 7.20 (m, 2H, 3′-, 5′-H), 7.31 (m, 4H), 7.43 (m, 2H), 7.53 (m, 2H) (all biphenylylene-H). – ^{13}C (75.47 MHz, $CDCl_3$): δ = 52.27 (2× *C*H_2); 116.07, 127.74, 128.10, 128.39, 128.95, 129.49 (all 2 aryl-*C*H each); 122.94 (4′-C); 134.46 and 140.57 (C-4a, C-7a, C-11a, C-11b); 148.02 (C-1′). – MS (EI, 70 eV): *m/z* (%) = 305 (100) [M^+], 304 (98) [M^+-H], 178 (32), 166 (42), 165 (42), 140 (21), 138 (40), 111 (21) [$ClC_6H_4^+$]. $C_{20}H_{16}ClN$ (305.8): calcd. C 78.55, H 5.28, N 4.58; found: C 78.50, H 5.31, N 4.63.

Reactions of *2-aryl-2,3-dihydro-1H-benz[d,e]-isoquinolines (**6a,d**) with ethenetetracarbonitrile (**2**)*, general procedure: To a chilled solution of 384 mg (3.0 mmol) of **2** in 10 ml of benzene a precooled solution of **6a-d** in 10 ml of was added dropwise, which caused a spontaneous change of colour from yellow to dark green. The mixture was stirred for 18 h and allowed to warm up to room temp. After concentration, the residue was separated from a not identified deep blue solid by extraction with ethyl acetate. The extract was concentrated to a few ml and subjected to plc using cyclohexane/ethyl acetate 5:1. The fastest moving zones (R_f values given) were removed while still moist, extracted with ethyl acetate and the extracts were concentrated. Crystallization from ethanol gave colourless crystals, 114 mg (42%) of **9a**, R_f = 0.36; 153 mg (54%) of **9b**, R_f = 0.43; 108 mg (36%) of **9c**, R_f = 0,16; 137 mg (45%) of **9d**, R_f = 0.29.

*2-Phenyl-2,3-dihydro-1H-benz[d,e]isoquinoline-1-carbonitrile (**9a**):* M. p. 130–132 °C. – IR (KBr pellet): ν = 2210w (CN), 1600, 1580, 1500, 805, 760 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 4.87 and 4.76 (AB-system, $|^2J_{AB}|$ = 15.4 Hz, 3-C*H*$_2$), δ = 5.81 (s, 1H, 1-H); 7.10 (m, 1H), 7.26 (m, 2H), 7.35–7.55 (m, 6H), 7.81 (m, 1H), 7.90 (m, 1H) (all aryl-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 49.37 (C-3), 54.96 (C-1), 116.70 (*C*N); 119.04 (C-2′, C-6′); 123.00, 123.08, 123,32, 125.71, 126.26, 126.74, 128.94, (all aryl-*C*H); 129.60 (C-3′, C-5′); 126.45, 127.45, 130.91, 133.39, 148.27 (all quart. aryl-C). – MS (EI, 70 eV): *m/z* (%) = 270 (88) [M^+], 269 (100), 244 (73), 243 (77) [M^+-HCN], 166 (65), 77 (37) [Phenyl$^+$]. – $C_{19}H_{14}N_2$ (270.3): calcd. C 84.42, H 5.22, N 10.36; found C 84.10, H 5.45, N 9.96.

*2-(4-Methylphenyl)-2,3-dihydro-1H-benz[d,e]-isoquinoline-1-carbonitrile (**9b**):* M.p. 145–146 °C. – IR (KBr pellet): ν = 2210w (CN), 1600, 1575, 1510 (aryl), 1210, 950, 825, 815, 785 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.29 (s, 3H CH_3); δ = 4.75 and 4.63 (AB system,$|^2J_{AB}|$= 15.4 Hz, 3-C*H*$_2$), 5.71 (s, 1H, 1-H); 7.13 (m, 4H), 7.26 (m, 1H), 7.29–7.46 (m, 3H), 7.79 (m, 1H), 7.82 (m, 1H) (all aryl-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 20.93 (CH_3), 49.47 (C-3), 55.36 (C-1), 116.19

(*C*N), 119.16 (2′-C,6′-C), 130.08 (3′-C, 5′-C); 122.92, 123.23, 125.61, 126.16, 126.60, 128.80 (aryl-*C*H); 126.37, 127.53, 131.02, 132.66, 133.29, 145.90 (all quart. aryl-C). – MS (EI, 70 eV): *m/z* (%) = 284 (65) [M^+], 283 (79) [M^+-H], 258 (67), 257 (100) [M^+-HCN], 166 (44), 91 (14) [$C_7H_7^+$]. – $C_{20}H_{16}N_2$ (284.4): calcd. C 84.48, H 5.67, N 9.85; found C 84.48, H 5.72, N 9.82.

*2-(4-Methoxyphenyl)-2,3-dihydro-1H-benz[d,e]-isoquinoline-1-carbonitrile (***9c***):* M. p. 122 °C. – IR (KBr pellet): 2220w (CN), 1510, 1240, 1080, 810 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.79 (s, 3H, OCH_3), δ = 4.81 and 4.55 (AB system, $|^2J_{AB}|$ = 15.4 Hz, 3-CH_2), 5.62 (s, 1H, 1-H); 6.93 (m, 2H), 7.85 (m, 2H), 7.34–7.51 (m, 4H), 7.85 (m, 1H), 7.87 (m, 1H) all aryl-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 49.47 (CH_2), 55.50 (OMe), 55.66 (C-1), 114.81 (C-2′, C-6′), 116.18 (*C*N), 121.57 (C-3′, C-5′); 122.95, 123.23, 125.66, 126.23, 126.68, 128.88 (aryl-*C*H); 126.41, 127.79, 131.30, 133.41, 142.04, 156.16 (all quart. aryl-C). – MS (EI, 70 eV): *m/z* (%) = 300 (67) [M^+], 299 (56), 274 (70), 273 (100) [M^+-HCN], 166 (21). – $C_{20}H_{16}N_2O$ (300.3): calcd. C 79.98, H 5.37, N 9.33; found: C 79.88, H 5.44, N 9.36.

*2-(4-Chlorophenyl)-2,3-dihydro-1H-benz[d,e]-isoquinoline-1-carbonitrile (***9d***):* Colourless crystals, 137 mg (45%). – M. p. 126–128 °C. – IR (KBr pellet): 2230w (CN), 1590, 1510, 1500 (aryl), 1230, 810, 770 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 4.71 and 4.60, (AB system, $|^2J|$= 15.4 Hz, 3-H_2), 5.70 (s, 1H, 1-H); 7.07 (m, 2H), 7.25–7.30 (m, 3H), 7.35–7.46 (m, 3H), 7.74 (m, 1H), 7.81 (m, 1H), (all aryl-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 49.20 (CH_2), 54.58 (C-1), 115.97 (*C*N), 120.07 (C-2′, C-6′), 129.48 (C-3′, C-5′); 123.01, 123.35, 125.67, 126.23, 126.79, 128.97 (all aryl-*C*H); 126.17, 126.88, 128.04, 130.31, 133.23, 146.71 (all quart. aryl-C). – MS (EI, 70 eV): *m/z* (%) = 304 (99) [M^+], 303 (100) [M^+-1], 277 (90) [M^+-HCN], 276 (90), 268 (22) [M^+-HCl], 267 (22), 241 (27), 166 (52), 139 (28). – $C_{19}H_{13}ClN_2$ (304.8): calcd. C 74.87, H 4.30, N 9.19; found 74.85, H 4.40, N 9.12.

Reaction of **6** with **4** in acetonitrile, general procedure: To a solution of 1.0 mmol of **6** in 50 ml acetonitrile 420 mg (2.0 mmol) of **4** were added. Within two minutes, the initially yellow solution first turned red and then green and was stirred for 3 h at 20 °C, after which time a colourless precipitate of **15** was collected and crystallized from acetonitrile. By plc of the original filtrate starting material **6** and 1-carbonitriles **9** were recovered as follows: From the run using **6a**: no **6a**; 51 mg (19%) of **9a**, m. p. 130–132 °C together with 55 mg (13%) of **15**; from **6b**: 7 mg (3%) of donor **6b** and 52 mg (19%) of **9b**, m. p. 145–146 °C, along with 80 mg (19%) of **15**; from **6c**: 129 mg (43%) of **9c**, m. p. 122 °C, along with 61 mg (15%) of **15**; from **6d**: 6 mg (2%) unchanged **6d**, and 90 mg (30%) **9d**, m. p. 126–128 °C, along with 50 mg (12%) of **15**.

*(1,3-Dihydroxy-2H-inden-2-ylidene)propanedinitrile (***15***):* Subl. p. 285 °C (lit. [15] m. p. > 300 °C). – IR (KBr pellet): ν = 3269 (broad, OH), 2229s (CN), 1572, 1452, 1430, 1297, 1248, 988, 961, 773 cm^{-1}. – ^1H NMR (300.13 MHz, $(CD_3)_2SO$): δ = 7.86 (m, 2H) and 8.36 (m, 2H) (habitus of an AA′BB′-system, 4 aryl-H), 11.50 (very broad, 2H, OH). – ^{13}C NMR (75.47 MHz, $(CD_3)_2SO$): δ = 92.03 (*C*$(CN)_2$), 115.67 (*C*N), 124.00 (aryl-*C*H), 128.13 (3a′-C, 7a′-C), 130.22 (aryl-*C*H), 153.46 (1′-C, 3′-C). – MS (EI, 70 eV): *m/z* (%) = 210 (100) [M^+], 183 (8) [M^+-HCN], 155 (30), 127 (64), 105 (18). – $C_{12}H_6N_2O_2$ (210.2): calcd. C 68.54, H 2.88, N 13.32; found C 68.54, H 2.92, N 13.25.

Reaction of **6** with **4** in ethanol, general procedure: A solution of 1.0 mmol of **6** and 420 mg (2.0 mmol) of **4** in 100 ml of dry ethanol was stirred at room temperature for three days, during which time the colour changed from yellow to red and a fine colourless precipitate formed, which was collected and recrystallized from acetonitrile to give colourless needles of **17**. The mother liquor was separated by plc using cyclohexane/ethyl acetate (5:1). The significant zones (R_f values given below) were recovered while still moist and worked up quickly. The following quantities of materials have been obtained:

From **6a**: 211 mg (60%) of **17**; R_f = 0.48: 32 mg (13%) of **6a**; R_f = 0.33: 101 mg (43%) of **9a**, m. p. 130–132 °C. – From **6b**: 190 mg (54%) of **17**, R_f = 0.52: 39 mg (15%) **6b**; R_f = 0.38: 157 mg **9b**, m. p. 145–146 °C. From **6c**: No **17**; R_f = 0.33: 28 mg (10%) **6c**; R_f = 0.23: 59 mg (22%) **9c**, m. p. 122 °C. – From **6d**: 161 mg (46%) **17**; R_f = 0.64: 132 mg (47%) of **6d**; R_f = 0.47: 40 mg (25%) **9d**, m. p. 126–128 °C.

*1,1″,3,3″-Tetraoxo-[indane-2-spiro-1′-cyclopropane-2′-spiro-2″-indane]-3′,3′-dicarbonitrile (***17***):* M. p. 239–242 °C (from acetonitrile). – IR (KBr pellet): ν = 2255w (CN), 1728 (C=O), 1593, 1245, 1098, 819, 767, 753 cm^{-1} – ^1H NMR (300.13 MHz, DMSO-D_6): δ = 7.90 (narrow m, 8H, aryl-H). – ^{13}C NMR (75.47 MHz, DMSO-D_6): δ = 22.42 (3′-C), 48.12 (spiro-C), 109.79 (CN), 122.81 and 135.54 (aryl-*C*H), 141.87 (quart. aryl-C), 185.83 (C=O). – MS (EI, 70 eV): *m/z* (%) = 354 (18) [M^+ +2], 352 (63) [M^+], 324 (25) [M^+ - CO], 296 (33) [M^+ – 2CO], 282 (11), 268 (22) [M^+ – 3CO], 239 (13), 104 (100) [$C_6H_4CO^+$], 76

(87) [$C_6H_4^+$]. – $C_{21}H_8N_2O_4 \cdot CH_3CN$ (393.3): calcd. C 70.23, H 2.83, N 10.68; found C 69.80, H 2.78, N 10.22.

Reactions of compounds **11** *with ethenetetracarbonitrile (***2***):* Solutions (1.0 mmol each) of **11a-d** in 100 ml of benzene were treated with 260 mg (2.0 mmol) of **2** and stirred at 20 °C for 48 h, during which time the original colour changed from yellow to green. After concentration the solid residue was treated with few ml of ethyl acetate. In all cases, except the run with **11a**, a colourless solid residue consisting of the carbonitriles **13b,c** or **d** was filtered off. This was later combined with the same materials obtained by plc and crystallized from the solvent listed.

From **11a** were obtained: no solid; R_f = 0.52: 8.0 mg (3%) of **11a**; R_f = 0.36: 124 mg (43%) of **13a**.

From **11b** were obtained: 82 mg solid **13b**; R_f = 0.58: 16 mg (6%) of **11b**; R_f = 0.28: 60 mg of **13b**, combined yield 142 mg (46%).

From **11c** were obtained: 62 mg solid **13c**; R_f 0.43: 6 mg (2%) of **11c**; R_f = 0.32: 40 mg of **13c**, combined yield 102 mg (31%).

From **11d** were obtained: 124 mg of solid **13d**; R_f = 0.67: 32 mg (11%) of **11d**; R_f = 0.49: 15 mg of **13d**, combined yield 139 mg (42%).

*6-Phenyl-6,7-dihydro-5H-dibenz[c,e]azepine-5-carbonitrile (***13a***):* M. p. 175–176 °C (from ethanol). – IR (KBr pellet): ν = 2929 and 2860 (CH_2), 2226w (CN), 1594, 1499, 1374, 1219, 763s, 749s, 692 cm^{-1}. – ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.95 and 4.40, (AB system, $|^2J|$ = 12.5 Hz, 7-CH_2), δ = 5.47 (s, 1H, 5-H); 6.95 (m, 1H, 4′-H); 7.04 (m, 2H), 7.30–7.49 (m, 6H), 7.49–7.65 (m, 3H), (all aryl-H). – ^{13}C (75.47 MHz, $CDCl_3$): 51.39 (*C*H_2), 55.79 (C-5), 117.89 (*C*N), 120.64 (C-4′); 116.30, 128.08, 128.58, 128.89, 129.21, 129.41, 129.51 (2C), 129.61, 130.16, 130.24 (all aryl-CH), 130.00, 133.53, 139.45, 139.99 (all quart. aryl-C), 148.20 (1′-C). – MS (EI, 70 eV): *m/z* (%) = 296 (100) [M^+], 295 (74) [M^+-1], 270 (30) [M^+-CN], 204 (16), 203 (14), 191 (23), 190 (18), 165 (32), 106 (33), 104 (29), 93 (18), 77 (42). – $C_{21}H_{16}N_2$ (296.4): calcd. C 85.11, H 5.44, N 9.45; found C 84.98, H 5.49, N 9.40.

*6-(4-Methylphenyl)-6,7-dihydro-5H-dibenz[c,e]-azepine-5-carbonitrile (***13b***):* M. p. 222–225 °C (acetonitrile). – IR (KBr pellet): ν = 2918, 2863 (CH_2), 2224w (CN), 1612, 1513s, 1383, 1205, 797, 762 cm^{-1}. – ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.31 (s, 3H, CH_3), δ = 4.31 and 3.93 (AB system, $|^2J|$= 12.5 Hz, 7-CH_2), 5.40 (s, 1H, 5-H); 6.96 (m, 2H, 2′-, 6′-H), 7.14 (m, 2H, 3′-, 5′-H); 7.33–7.46 (m, 4H) and 7.51–7.63 (m, 4H) (all biphenylylene-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 20.51 (CH_3), 52.05 (CH_2), 56.25 (C-5), 118.08 (*C*N); 117.21, 128.11, 128.59, 128.90, 129.22, 129.38, 129.56, 130.02, 130.06 (2C), 130.20, 130.27 (all aryl-*C*-H); 130.62, 133.71, 139.54, 140.08, 146.30 (all quart. aryl-C). – MS (EI, 70 eV): *m/z* (%) = 310 (100) [M^+], 309 (65) [M^+-1], 284 (33) [M^+-CN], 204 (13), 203 (12), 191 (16), 165 (21), 120 (25), 118 (15), 91 (25) [$C_7H_7^+$]. – $C_{22}H_{18}N_2$ (310.4): calcd. C 85.12, H 5.86, N 9.03; found C 85.01, H 5.94, N 8.96.

*6-(4-Methoxyphenyl)-6,7-dihydro-5H-dibenz[c,e]-azepine-5-carbonitrile (***13c***):* M. p. 195–196 °C (acetonitrile). – IR (KBr pellet): ν = 2957 (CH_3), 2933 and 2837 (CH_2), 2218w (CN), 1510s, 1246s, 1043, 819, 766 cm^{-1}. – ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OCH_3), δ = 4.16 and 3.91 (AB system, $|^2J|$= 12.5 Hz, 7-CH_2), 5.25 (s, 1H, 5-H), 6.87 (m, 2H, 2′-, 6′-H), 7.05 (m, 2H, 3′-, 5′-H), 7.34–7.48 (m, 4H) and 7.48–7.64 (m, 4H), (biphenylylene-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$). δ = 53.40 (*C*H_2), 55.56 (O*C*H_3), 56.91 (C-5), 118.09 (CN); 114.69, 120.56, 128.03, 128.53, 128.79, 129.10, 129.24 (2C), 129.88, 130.15 (all aryl-*C*H); 133.64, 139.47, 140.03, 142.82, 155.17 (all quart. aryl-C). – MS (EI, 70 eV): *m/z* (%) = 326 (100) [M^+], 325 (55) [M^+-1], 311 (14), 300 (29) [M^+-CN], 286 (56), 204 (34), 203 (20), 191 (15), 178 (16), 177 (16), 166 (17), 165 (24), 136 (25), 108 (27). – $C_{22}H_{18}N_2O$ (326.4): calcd. C 80.95, H 5.56, N 8.58; found C 80.80, H 5.62, N 8.59.

*6-(4-Chlorophenyl)-6,7-dihydro-5H-dibenz[c,e]-azepine-5-carbonitrile (***13d***):* M. p. 217–219 °C (acetonitrile). – IR (KBr pellet): ν = 2925 (CH_2), 2212w (CN), 1591, 1492s, 1222, 811, 761, 750, 741 cm^{-1}. – ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 4.34 and 3.95 (AB system, $|^2J|$= 12.5 Hz, CH_2), 5.39 (s, 1H, 5-H), 6.96 (m, 2H, 2′-, 6′-H), 7.30 (m, 2H, 3′-, 5′-H), 7.32–7.50 (m, 4H) und 7.60 (m, 4H, all biphenylylene-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 51.71 (CH_2), 55.77 (C-5), 117.71 (CN), 125.79 (4′-C), 117.51, 128.13, 128.63, 128.95, 129.27, 129.39 (2C), 129.53 (2C), 130.37 (all aryl-*C*H), 129.89, 133.13, 139.93, (quart. aryl-C), 146.23 (C-1′). – MS (EI, 70 eV): *m/z* (%) = 330 (100) [M^+], 329 (53) [M^+-1], 304 (29) [M^+-CN] 204 (25), 203 (14), 191 (38), 166 (25), 165 (29), 140 (26), 138 (23), 127 (14), 111 (15) [$C_6H_4Cl^+$]. – $C_{21}H_{15}N_2Cl$ (330.8): Calcd. C 76.23, H 4.58, N 8.46; found C 76.18, H 4.64, N 8.39.

Reaction of *N-alkyl-N-benzylanilines* **18a,b** with **4** in ethanol: A solution of 420 mg (2.0 mmol) of **4** in 80 ml of ethanol was treated with a) 200 mg (1.0 mmol) of *N-benzyl-N-methylaniline*, b) 210 mg (1.0 mmol) of *N-benzyl-N-ethylaniline* and stirred at 20 °C for 94 h (a) and 120 h (b), respec-

tivily, during which time the colour of the solution changed from yellow to light red and a light yellow precipitate started to separate. Concentration of the solution gave more of this material. Recrystallization gave 269 mg **19a** (66%) and 380 mg (91%) **19b**, respectively, as light yellow crystals.

*[4-(N-Benzyl-N-methylamino)phenyl]-(1,3-dioxoindan-2-yl)propanedinitrile (***19a***):* M. p. 149–152 °C (from ethanol, with dec. and colouration to purple). – IR (KBr pellet): ν = 2242w (CN), 1753, 1713 (C = O), 1613, 1526, 1244, 744 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.97 (s, 3H, CH_3), 3.79 (s, 1H, indanyl-2-H), 4.47 (s, 2H, Ph-CH_2); 6.57 (m, 2H), 7.07 (m, 2H), 7.24 (m, 3H), 7.28 (m, 2H), 7.84 (m, 2H), 7.93 (m, 2H), all aryl-H, the latter two m and those at 6.57 and 7.28 appear as symmetric AA′BB'systems. – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 38.54 (CH_3), 39.30 ($C(CN)_2$), 55.98 (CH_2), 56.46 (indanyl-2-H); 112.06, 123.84, 126.42, 128.11, 128.70, 136.57 (all 2C, aryl-*C*H); 127.15 (phenyl-C-4); 113.25 (CN); 114.34, 137.74, 141.96, 150.44 (all quart. aryl-C); 192.01 (2× C = O). MS (EI, 70 eV): *m/z* (%) = 405 (0.5) [M^+], 378 (59) [M^+ – HCN], 91 (100) [$C_7H_7^+$]. – $C_{26}H_{19}N_3O_2$ (405.4): calcd. C 77.02, H 4.73, N 10.36; found C 76.93, H 4.74, N 10.37.

*[4-(N-Benzyl-N-ethylamino)phenyl]-(1,3-dioxoindan-2-yl)propanedinitrile (***19b***):* M. p. 150–153 °C (from methanol, with dec. and colouration to purple). – IR (KBr pellet): ν = 2252w (CN), 1712 (C = O), 1609, 1518, 1357, 1290, 742 cm^{-1}. – ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.13 (t, ^3J = 7.1 Hz, 3H, CH_3), 3.44 (q, ^3J = 7.1 Hz, 2H, CH_2), 3.78 (s, 1H, indanyl-2-H); 6.55 (m, 2H), 7.07 (m, 2H), 7.25 (m, 5H), 7.63 (m, 2H), 7.91 (m, 2H), all aryl-H. The 7.91 and 7.63 multiplets have the habitus of an AA′BB' system as have parts of the 7.25 and 6.55 ppm multiplets. – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.00 (CH_3), 39.37 ($C(CN)_2$), 45.33 (CH_3-CH_2), 53.65 (Ph-CH_2), 56.57 (indanyl-C-2), 113.29 (CN); 112.03, 123.89, 126.35, 128.22, 128.73, 136.57 (all for 2C each, aryl-*C*H); 127.11 (phenyl-4-*C*H); 114.00, 137.99, 142.04, 149.47 (all quart. aryl-C); 192.06 (2× C = O). – MS (EI, 70 eV): *m/z* (%) = 392 (1) [M^+ – HCN], 367 (3) [M^+- 2 CN?], 211 (19), 196 (19), 91 (100) [$C_7H_7^+$]. – $C_{27}H_{21}N_3O_2$ (419.5): calcd. C 77.31, H 5.06, N 10.01; found C 77.29, H 5.05, N 10.08.

Table 2. Crystal data and structure refinement for **13b** and **17** · MeCN.

	13b	**17** · MeCN
Chemical formula	$C_{22}H_{18}N_2$	$C_{23}H_{11}N_3O_4$
Formula weight	310.38	393.35
Temperature	150 K	150 K
Wavelength (Mo-K_α)	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
Unit cell dimensions	a = 12.410 (2) Å b = 10.415 (2) Å c = 12.470 (2) Å β = 95.83 (2)°	a = 9.309 (9) Å b = 9.668 (6) Å c = 10.915 (9) Å α = 95.29 (7)° β = 112.10 (7)° γ = 90.60 (7)°
Volume	1603.4 $Å^3$	905.2 $Å^3$
Z, calculated density	4, 1.286 Mg/m^3	2, 1.443 Mg/m^3
Absorption coefficient	0.076 mm^{-1}	0.102 mm^{-1}
F (000)	656	404
Crystal size	0.47 × 0.35 × 0.33 mm	0.77 × 0.29 x.0.23 mm
Theta range	2.21 to 27.00°	2.02 to 26.99°
Limiting indices	$0>h<15$, $-13>k<13$, $-15>l<15$	$0>h<11$, $-12>k<12$, $-13>l<12$
Reflections collected / unique	7124 / 3505 [R(int) = 0.0213]	3952 / 3952 [R(int) = 0.0000]
Completeness to theta = 27.00 deg	100.0%	100.0%
Absorption correction	psi-scan	psi-scan
Max. and min. transmission	0.997 and 0.966	0.989 and 0.938
Refinement method	full-matrix least-squares (F^2)	full-matrix least-squares (F^2)
Data / restraints / parameters	3505 / 0 / 219	3952 / 0 / 273
Goodness-of-fit on F^2	1.041	1.060
Final R Indices [$I>2\sigma(I)$]	R_1 = 0.0393, wR_2 = 0.0976	R_1 = 0.0446, wR_2 = 0.1117
R Indices (all data)	R_1 = 0.0466, wR_2 = 0.1035	R_1 = 0.0565, wR_2 = 0.1214
Extinction coefficient	0.0106 (14)	0.018 (3)
Largest diff. peak and hole	0.299 and −0.301 e$Å^{-3}$	0.323 and −0.266 e$Å^{-3}$

Crystal structure determination: Data collection was performed using a Siemens P4 four-circle diffractometer with rotating anode generator, graphite monochromator and scintillation counter, λ = 0.71073 Å (Mo-K_α). Both structures were solved with direct methods using SHELXS-97. Structure refinements were performed against F^2 using SHELXL-97. For both compounds empirical absorption corrections were applied. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with isotropic displacement parameters (see Table 2).

X-ray data of both structures have been deposited at the Cambridge Crystallographic Data Centre (**13b**: CCDC 177254; **17**: CCDC 177253). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CD21EZ, U. K. [Fax (internat.) +44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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