DOI: 10.1002/ejoc.200700469

(5-Imino-4,5-dihydro-3*H*-pyrrol-2-yl)amines as Sterically Restrained 1,3,5-Triazapenta-1,3-dienes: Useful Building Blocks for the Synthesis of Oligonitriles[‡]

Edgar A. Marihart,[a] Jan-Bernd Greving,[a] Roland Fröhlich,[a] and Ernst-Ulrich Würthwein*[a]

Keywords: Oligonitriles / Dihydropyrroles / Hydrogen bonds / Imines / Amidines / Cyanides

(5-Imino-4,5-dihydro-3*H*-pyrrol-2-yl)amines **2** may be considered as sterically restrained 1,3,5-triazapenta-1,3-dienes. They were easily prepared from 2,2,3,3-tetramethylsuccinonitrile (**1**) and lithium amides with subsequent aqueous workup to give the monocyclic compounds **2a**–**d** and the bi- and tricyclic compounds **2e**–**g**. X-ray diffraction studies of **2c** and **2d**, which contain a primary NH_2 group, reveal the existence of homodimers held together with paired hydrogen bonds in the solid state. Trapping of the lithiated intermediate **2a-Li** by benzoyl chloride provided access to the 1-oxa-3,5,7-triazahepta-1,3,5-triene **3b**. It is characterized in the solid state by a planar heterocyclic subunit and a strongly twisted *N*-acylamidine part. With 1-oxa-3,5-diazinium salts **4**, compounds **2a**,**b**,**d** or **2a-Li** reacted to give 1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaenes **5a**–**d**. Here again, the planar heterocyclic parts combine with longer, twisted (not helical) oligonitrile moieties. The X-ray diffraction study of **5d** indicates intermolecular N–H···O=C hydrogen bonding in the solid state, producing one-dimensional strands. In a similar way as **1** the trinitrile 2,3,5-trimethyl-2,3,5-tricyanohexane (**6**), a byproduct of the thermal decomposition of azoisobutyronitrile (AIBN), reacted with lithium benzylamide to give a bicyclic intermediate which was successfully converted into the corresponding 1-oxa-3,5,7,9,11,13-hexaazatrideca-1,3,5,7,9,11-hexaene **7** when treated with 1-oxa-3,5-diazinium salt **4b**. Similar to **5d**, this extended oligonitrile forms one-dimensional hydrogen-bonded polymers in the solid state. Its UV spectrum (λ_{max} = 286 nm) is interpreted in terms of a planar conjugated π–π^* azapolyene substructure forced into planarity by the heterocycles.

Introduction

1,3,5-Triazapenta-1,3-dienes are nitrogen-rich analogues of penta-1,3-dienes containing two amidine subunits combined to form an unsaturated N–C–N–C–N chain.[1] Open-chain 1,3,5-triazapenta-1,3-dienes show high molecular flexibility due to low rotational barriers about the C–N bonds, and they prefer non-planar ground-state conformations.[2] As potent 1,5-chelating ligands in coordination chemistry they adopt U-shaped structures in metal complexes.[3] They also serve as potent building blocks for the synthesis and elongation reactions of oligonitriles, three-dimensional, often helical chain compounds with a C=N–$(C=N)_n$–C=N backbone.[2]

However, there are interesting scientific targets for which the molecular flexibility of 1,3,5-triazapenta-1,3-dienes is not desirable, for example, in the synthesis of longer, linear oligonitriles with increased chemical stability and in the study of the electronic, photoelectronic and optical properties of planar 1,3,5-triazapenta-1,3-dienes and their homologues. For such projects we developed a synthetic route that uses (5-imino-4,5-dihydro-3*H*-pyrrol-2-yl)amines as 1,3,5-triazapenta-1,3-dienes. By embedding them into the five-membered ring structure, the 1,3,5-triazapenta-1,3-diene moiety is fixed by ring strain in the W shape and to extensive planarity. These compounds serve as new building blocks for the preparation of various oligonitrile derivatives with tailor-made structural properties. They have also turned out to be useful ligands for metal complexation.[4]

Open-chain 1,3,5-triazapenta-1,3-dienes are usually prepared by a variety of methods based on the assembly of various C=N-containing subunits and also in the presence of metal ions in template-directed synthesis.[5] For the preparation of sterically fixed derivatives based on five-membered heterocycles we took advantage of a reaction sequence known in polymer science, for example, the nucleophile-induced C–N bond formation in polyacrylonitriles as applied in carbon fibre production.[6,7] Wöhrle has studied this reaction in detail with regard to the synthesis of polynitriles, starting with dinitriles, for example, succinonitrile and fumaronitrile.[8–10]

[‡] Unsaturated Hetero Chains, XV. Part XIV: Ref.[2]

[a] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität,
Corrensstraße 40, 48149 Münster, Germany
Fax: +49-251-83-39772
E-mail: wurthwe@uni-muenster.de

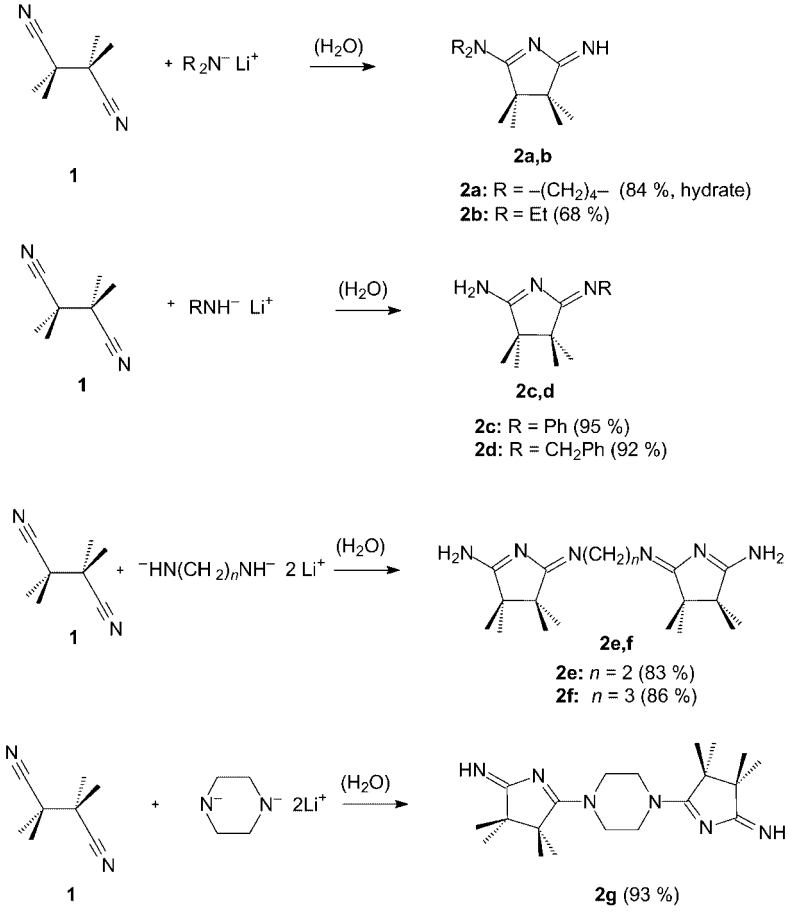
In this report we describe the synthesis of such sterically restrained 1,3,5-triazapenta-1,3-dienes and their use in chain elongation reactions to give oligonitriles. We also report on the structural properties of these new compounds as studied by X-ray diffraction.

Results and Discussion

In order to synthesize (5-imino-4,5-dihydro-3*H*-pyrrol-2-yl)amine derivatives we adapted a procedure used by Wöhrle,[8,9] who started from succinonitrile, for the conversion of the corresponding 2,2,3,3-tetramethylsuccinonitrile (**1**) which is easily available by controlled decomposition of azoisobutyronitrile (AIBN).[11] Dinitrile **1** was added at –78 °C to a freshly prepared solution of the corresponding lithium amide (from the amine and butyllithium at –78 °C). After warming up and stirring at room temperature for 3 h, aqueous workup gave the corresponding (5-imino-3,3,4,4-tetramethyl-4,5-dihydro-3*H*-pyrrol-2-yl)amines **2** in 68–95% yield. Simple primary and secondary amines as well as primary and secondary diamines were successfully used in this nucleophilic ring-closure reaction (Scheme 1).

All the compounds **2** were completely characterized by spectroscopic methods and X-ray structure determinations for **2c**, **2d** and **2g**. Compounds **2c** and **2d** exhibit a parallel pair of hydrogen bonds connecting the two amidine subunits forming an eight-membered ring system. For **2c**, the N–N distance amounts to 2.919 Å (Figure 1), for **2d** to 2.992 Å. Furthermore, **2d** shows additional NH···N interactions (2.988 Å) to neighbouring molecules resulting in a polymeric two-dimensional sheet structure formed from two parallel strands (Figure 2) resembling a β-sheet of peptides. In contrast, **2g** does not form hydrogen bonds; it crystallizes as a monomer with an *anti* orientation of the two five-membered rings (centre of inversion in the middle of the central ring) as shown in the formula.

In order to study the ability of the compounds **2** to undergo chain elongation reactions with respect to the synthesis of oligonitriles, we treated **2a** with methyl iodide in the presence of triethylamine to give the iminium salt **3a** (Scheme 2). As a byproduct, the 1,3,5-triazapentadienylium salt **2a·HI** was isolated in low yield after aqueous workup. The isolation of both salts **3a** and **2a·HI** reflects the high basicity of the parent dihydropyrroles which is due to the aza-vinylogous amidine structure (2-azatrimethinium salt). The molecular structure of **2a·HI** in the crystalline state was elucidated by X-ray diffraction. Its most interesting feature is the pair of hydrogen bonds which lead to a planar head-to-tail homodimer in the solid state (Figure 3), similar to those found in the neutral compounds **2c**,**d** (Figures 1 and



Scheme 1.

2). The N–N distance of this N–H interaction amounts to 3.097 Å and is relatively long, possibly due to the repulsion of the positive charges of the two amidinium units. The other N–H bond is directed towards the iodide counterions (3.607 Å) (Figure 3).

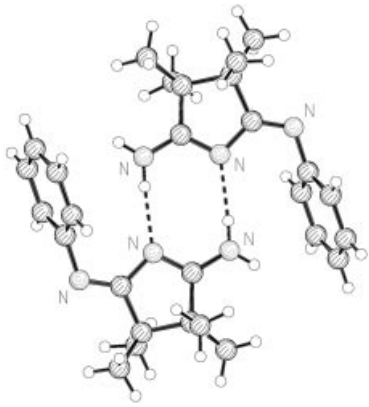


Figure 1. Molecular structure of **2c** in the crystalline state as obtained by X-ray diffraction (SCHAKAL plot).

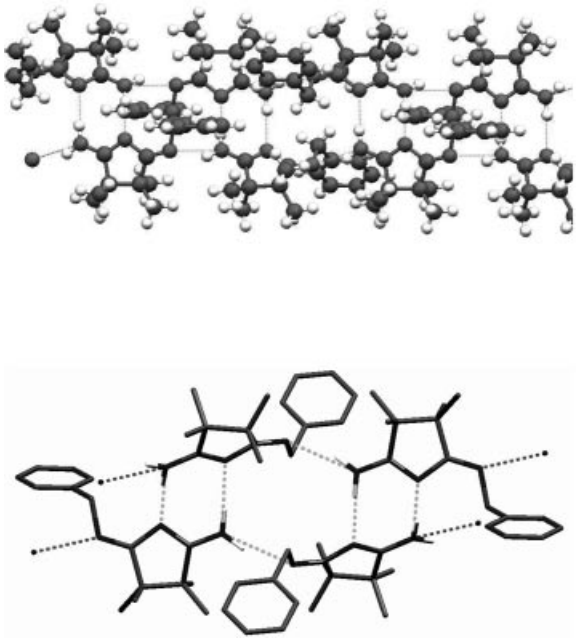


Figure 2. Aggregate formed from four molecules of **2d** by hydrogen bonding in the crystalline state as obtained by X-ray diffraction (MERCURY plot).

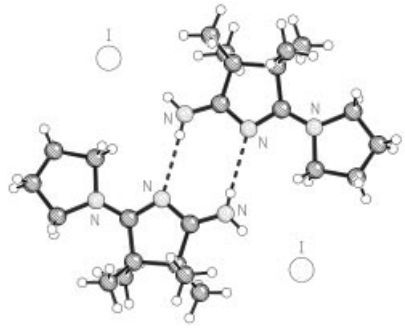
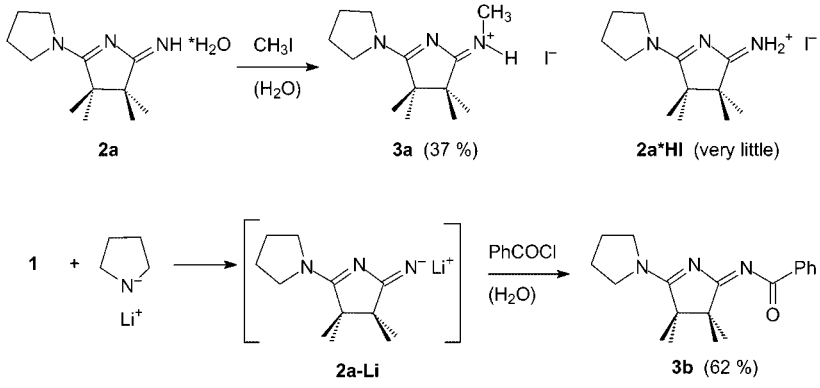


Figure 3. Molecular structure of **2a·HI** in the crystalline state as obtained by X-ray diffraction (SCHAKAL plot).

To investigate the reactions with other electrophiles, the intermediate lithium compound **2a-Li** was treated with electrophiles in situ, that is, before the aqueous workup of the reaction of **1** with the lithium amides. Use of benzoyl chloride as the trapping electrophile gave the 1-oxa-3,5,7-triazahepta-1,3,5-triene derivative **3b**. According to the X-ray determination, **3b** combines the structural features typical of an *N*-acylimine[12] or a 1-oxa-3,5-diaza-1,3,5-hexatriene,[13] a gauche conformation (62.4°) of the C=O group with respect to the adjacent C=N bond as a consequence of intense nitrogen lone pair/C=O π*-orbital interactions (Scheme 2, Figure 4), with the planar π system of the dihydropyrrole subunit.

With regard to chain-elongation reactions, which are interesting for the synthesis of longer-chain oligonitriles, oxadiazinium salts **4**[4,14,15] were also used as powerful electrophiles[16] with **2a**,**b**,**d** as well as with the intermediate lithium compound **2a-Li**. In all cases, nucleophilic ring opening of the oxadiazinium salts was observed, giving rise to new oligonitriles 1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaenes **5a**–**d** with five adjacent double bonds (Scheme 3).



Scheme 2.

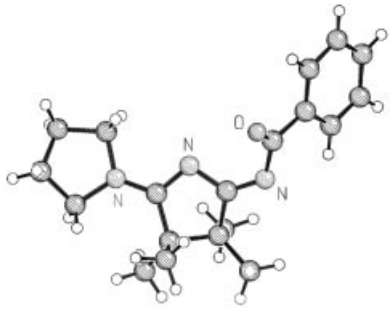


Figure 4. Molecular structure of **3b** as obtained by X-ray diffraction (SCHAKAL plot).

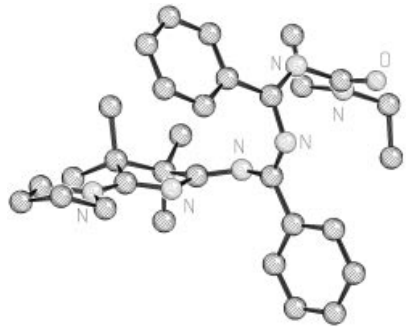
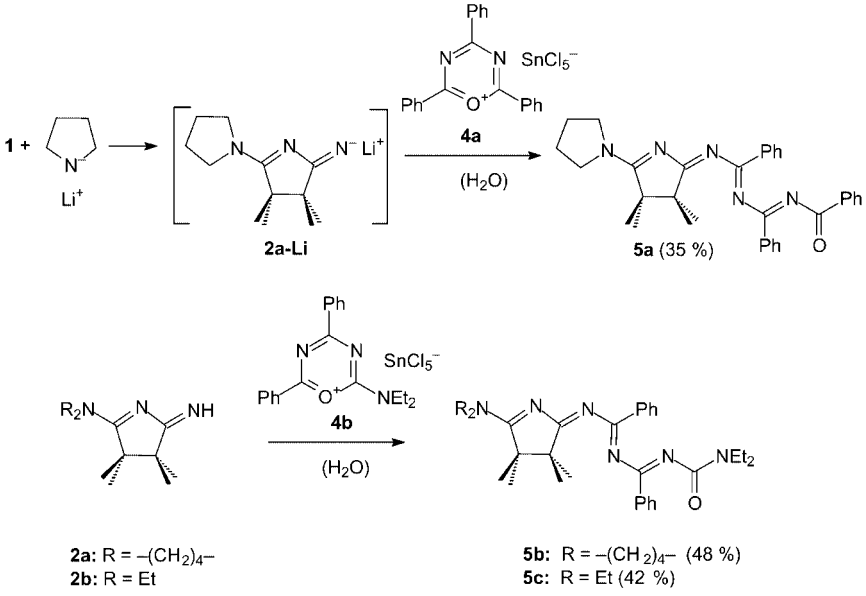


Figure 5. Molecular structure of **5b** in the crystalline state as obtained by X-ray diffraction (SCHAKAL plot).

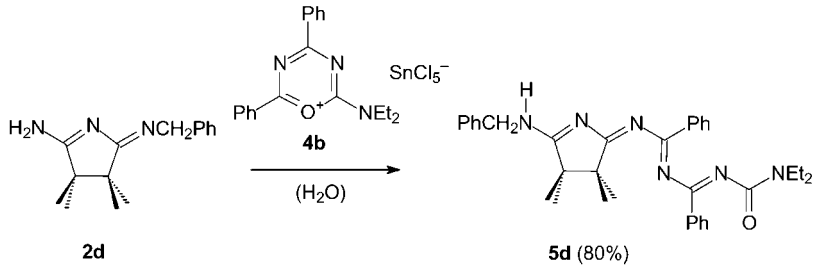
X-ray structure determinations of **5b** and **5d** demonstrate the unique structural properties of these compounds in the solid state. Compound **5b**, without acidic hydrogen atoms, is characterized by its planar heterocyclic subunit and the strongly twisted chain of the 1-oxa-3,5-diazahexatriene subunit (Figure 5). The two independent molecules in the unit cell may be described by the following sequence of C=N(O) and C–N bonds, starting from the oxygen atom: (+g)-*Z*-(+g)-*Z*-(+g)-*Z*-s-*trans*-*E*, reflecting the helical exocyclic part and the planar fixed heterocyclic subunit. The dihedral angles of the O–C–N–C–N–C–N–C–N–C–N chain of one of the independent molecules, starting from the oxygen atom, are 81.24, 1.79, 95.44, –0.19, 95.50, –0.13, –169.41 and 179.36°.

However, compound **5d**, synthesized from a primary amine (Scheme 4), shows an intermolecular hydrogen bond formed between the amine proton of one molecule and the carbonyl oxygen atom of the next, giving rise to a strand superstructure in the solid state (Figure 6). A rather similar sequence of torsional angles is observed within the molecule, as for **5b**.

The concept of constructing a (5-imino-4,5-dihydro-3*H*-pyrrol-2-yl)amine by nucleophilic attack on 2,2,3,3-tetramethylsuccinonitrile (**1**) could be extended to the related trinitrile 2,3,5-trimethyl-2,3,5-tricyanohexane (**6**), a compound that was first observed by Bickel and Waters as a byproduct of the thermal decomposition of azoisobutyronitrile (AIBN) to give **1**.[17] However, if **6** was treated with various lithium amides (from *n*-butyllithium and the corresponding amine), it was difficult to isolate the expected 6-imino-3a,4,5,6-tetrahydro-3*H*-pyrrolo[2,3-*b*]pyridin-2-ylamine, which was clearly identified in the mass spectra. Thus, the reaction mixture was directly treated with oxadiazinium salt **4b** in order to trap the intermediate lithium compound and to obtain access to an oligonitrile. Indeed, aqueous workup gave the 1-oxa-3,5,7,9,11,13-hexaazatrideca-1,3,5,7,9,11-hexaene **7** in 32% yield (Scheme 5). Compound **7** is one of the longest monodisperse *N*-acyloligonitriles known,[18] combining a planar 1,3,5,7-tetraazaheptatrienyl and a strongly twisted (not helical) 1-oxa-3,5,7-triazaheptatrienyl subunit. The X-ray structure of one of two independent molecules in the unit cell is displayed in Figure 7. The



Scheme 3.



Scheme 4.

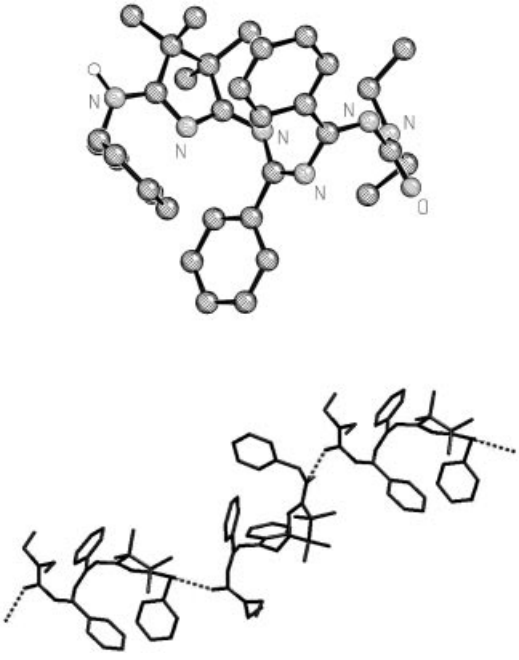
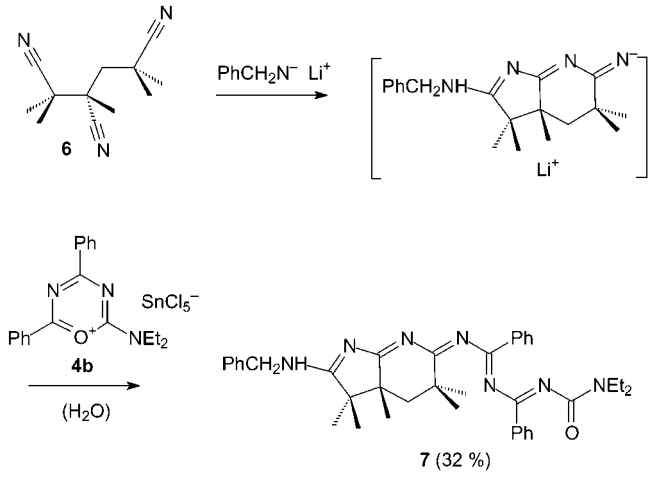


Figure 6. Molecular structure of **5d** in the crystalline state as obtained by X-ray diffraction. Top: single molecule (SCHAKAL plot); bottom: ensemble of three molecules, formed by hydrogen bonding (MERCURY plot).

corresponding torsional angles of the chain, starting at the oxygen atom, are 82.72, 2.90, 104.33, –7.84, 103.53, –4.35, –152.15, –174.26, 175.86 and 175.97°. Owing to the presence of an NH proton, again the formation of an intermolecular hydrogen bond is observed, giving rise to a strand superstructure similar to the one observed for **5d**.

It should be mentioned that longer, open-chain oligonitriles sometimes tend to decomposition reactions, possibly by ring/chain tautomerism in which, within the oligonitrile, one thread of a 3_1-helix attacks the next one forming a dihydrotriazine subunit which in turn leads to aromatic triazines by elimination reactions. The oligonitriles described here seem to show higher thermal stability. Possibly the planar W configuration prevents such rearrangement reactions by not allowing the helix motif in the planar part of the molecule.

Because of their three-dimensional, often helical structure, oligonitriles in general do not show strong absorptions at longer wavelengths, quite in contrast to the well-known polyenes (polyacetylenes) which adopt planar structures.



Scheme 5.

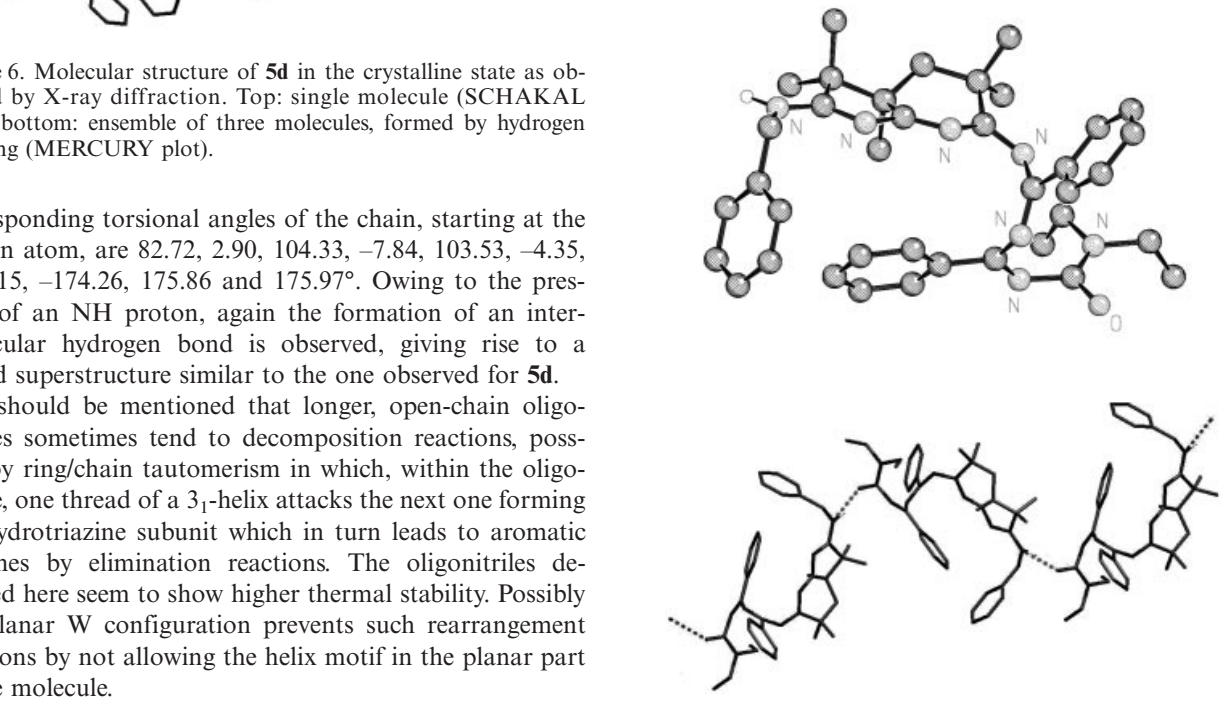


Figure 7. Molecular structure of **7** in the crystalline state as obtained by X-ray diffraction. Top: single molecule (SCHAKAL plot); bottom: ensemble of three molecules, formed by hydrogen bonding (MERCURY plot).

Often, the longest-wavelength maximum for oligonitriles is observed near 240–260 nm[19] which is mainly due to the benzaldimine substructures of the aryl-substituted derivatives (e.g., **3b**, **5d**). However, the effect on the longest wavelength maximum of chain elongation using an extended planar subunit in going from **5** to **7** is seen in the UV spectrum of **7** in which a strong absorption at 286 nm is observed. This indicates that **7** may be considered as one of the longest so far experimentally accessible monodisperse derivatives of the often theoretically studied planar "polyimines" or polynitriles, which, as long as they are not sterically restrained, do not exist as such due to the inherent predominance of the n–π* interaction over the π–π* interaction leading to three-dimensional ground-state structures.[20–23]

Conclusions

We have described the synthesis of (5-imino-4,5-dihydro-3*H*-pyrrol-2-yl)amines **2** and their use in oligonitrile elongation as sterically restrained 1,3,5-triazapentadienes. The reaction of 2,2,3,3-tetramethylsuccinonitrile (**1**) with lithium amides and subsequent aqueous workup provides the monocyclic derivatives **2a**–**d** and the bi- and tricyclic compounds **2e**–**g**. Trapping of the lithiated intermediate **2a-Li** by methyl iodide or benzoyl chloride gives access to the 1-oxa-3,5,7-triazahepta-1,3,5-trienes **3a**,**b**. Use of 1-oxa-3,5-diazinium salts **4** as electrophiles in the reactions of compounds **2a**,**b**,**d** or **2a-Li** yielded 1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaenes **5a**–**d**. Similarly, the trinitrile 2,3,5-trimethyl-2,3,5-tricyanohexane (**6**) reacted with lithium benzylamide to give the 1-oxa-3,5,7,9,11,13-hexaazatrideca-1,3,5,7,9,11-hexaene **7** after treatment with the 1-oxa-3,5-diazinium salt **4b**.

The properties of selected examples of compounds **2**, **3**, **5** and **7** in the solid state were studied by X-ray diffraction with respect to molecular structure and aggregation phenomena caused by N–H···O hydrogen bonding. Thus, **2c** and **2d**, which contain a primary NH_2 group, form homodimers held together by pairs of hydrogen bonds. Compounds **3**, **5** and **7** are characterized by a planar heterocyclic subunit and a strongly twisted *N*-acylamidine or *N*-acyloligonitrile part. In all cases the planar heterocyclic parts are combined with shorter or longer, twisted (not helical) oligonitrile moieties. The X-ray diffraction study of **5d** and **7** indicates intermolecular N–H···O=C hydrogen bonding, producing one-dimensional strands. One of the longest monodisperse oligonitrile molecules is compound **7**. Its UV spectrum (λ_{max} = 286 nm) is interpreted in terms of a planar conjugated π–π* azapolyene substructure forced by the heterocycles into planarity.

Experimental Section

Materials and Methods: IR: Nicolet 5DXC spectrometer. ^{1}H NMR: Bruker WM 300 (300.13 MHz), Bruker AMX 400 (400.13 MHz), Varian INOVA 500 (499.8 MHz) and Varian Unity 600 (599.86 MHz) spectrometers; internal reference: tetramethylsilane. ^{13}C NMR: Bruker WM 300 (75.47 MHz), Bruker AMX 400 (100.61 MHz), Varian INOVA 500 (125.7 MHz) and Varian Unity 600 (150.84 MHz) spectrometers; internal reference: solvent. CHN elemental analysis: Elementar Vario El III. Melting points were measured with a Paterno-Büchi melting point B-540 apparatus and are uncorrected. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum/syringe technique) in glassware that had been thoroughly dried by repeated heating under argon and subsequent evacuation.

General Procedure for the Synthesis of the 1,3,5-Triazapentadiene Compounds 2a–f:[24] A primary or secondary amine (10 mmol) was dissolved in anhydrous tetrahydrofuran (THF) (40 mL) in a dry Schlenk tube under argon. This solution was cooled to –78 °C. Then an equimolar amount of *n*-butyllithium (1.6 M solution in *n*-hexane) was added with stirring. The solution was warmed to room temperature and stirred for 1 h. The mixture was again cooled to –78 °C and, under vigorous stirring, an equimolar amount of 2,2,3,3-tetramethylsuccinonitrile (**1**) dissolved in anhydrous THF (40 mL) was slowly added. After the addition, the mixture was stirred at –78 °C for 30 min and then at room temperature for 3 h. Then methanol (40 mL) and water (40 mL) were added. The organic layer was separated and the aqueous layer was extracted with three portions of chloroform. The combined organic layers were dried with magnesium sulfate. Finally, the solvent was removed in vacuo to yield the crude product.

3,3,4,4-Tetramethyl-5-(pyrrolidin-1-yl)-3,4-dihydro-2*H*-pyrrol-2-imine Hydrate (2a): From pyrrolidine (0.21 g, 0.25 mL, 3.0 mmol), *n*-butyllithium (1.9 mL, 3.0 mmol) and **1** (0.41 g, 3.0 mmol). The colourless solid crystallizes with one molecule of water. Yield: 0.87 g (4.2 mmol, 84%), m.p. 65 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 6 H, CH_3), 1.16 (s, 6 H, CH_3), 1.90 (m, 2 H, NCH_2CH_2), 2.02 (m, 2 H, NCH_2CH_2), 3.58 (t, ^3J = 6.9 Hz, 2 H, NCH_2), 3.64 (t, ^3J = 7.1 Hz, 2 H, NCH_2), 3.90–5.00 (br., 2 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 22.5 (CH_3), 23.6, 26.5 (NCH_2CH_2), 49.9, 50.0 (C_q), 46.9, 50.0 (NCH_2), 179.0, 186.5 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3456 (s, NH), 3425 (s, NH), 3377 (sh, OH), 3233 (m), 3065 (m), 2974 (m, $CH_{aliph.}$), 1686 (m), 1655 (s, C=N), 1626 (vs, C=N), 1611 (sh), 1578 (sh), 1560 (s), 1541 (vs), 1535 (vs), 1528 (sh), 1522 (sh), 1510 (sh), 1500 (m), 1489 (s), 1468 (s, CH), 1458 (s, CH), 1448 (s), 1429 (s), 1398 (s), 1389 (s), 1377 (s), 1369 (s), 1340 (m), 1327 (vs), 1231 (m), 1185 (w), 1165 (m), 1150 (m), 1009 (w), 983 (w), 914 (w), 885 (w), 852 (w), 820 (w), 692 (w) cm^{-1}. MS (ESI, CH_3OH): *m*/*z* = 208 $[M + H]^+$, daughters 208: 178 $[M + H - 2\ CH_3]^+$, 70 $[(CH_2)_4N]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 208.1808; found 208.1809. MS (70 eV): *m*/*z* (%) = 207 (45) $[M]^+$, 192 (100) $[M - CH_3]^+$, 165 (61) $[M - (CH_2)_3]^+$, 123 (48), 95 (40), 70, (30) $[(CH_2)_4N]^+$. $C_{12}H_{21}N_3 \cdot H_2O$ (225.33): calcd. C 63.96, H 10.29, N 18.65; found C 63.91, H 10.24, N 18.64.

***N*,*N*-Diethyl-2-imino-3,3,4,4-tetramethyl-3,4-dihydro-2H-pyrrol-5-amine (2b):** From diethylamine (0.73 g, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mmol) and **1** (1.36 g, 10.0 mmol). After recrystallization from acetone, **2b** was used in the reaction with oxadiazinium salt **4b** to give **5c** (see below) without further purification. Yield: 1.43 g (6.8 mmol, 68%), colourless oil, b.p. 119 °C (1.2×10^{-2} mbar). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.76, 0.86, 1.12 (br. s, 18 H, CCH_3, CH_3), 3.16 (br., 4 H, NCH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.2, 13.4 (CH_3), 21.7 (CCH_3), 41.6, 42.9 (NCH_2), 49.1, 49.6 (C_q), 179.5, 185.4 (CN) ppm. IR (neat): $\tilde{\nu}$ = 3423 (s, NH), 2989 (s, $CH_{aliph.}$), 2977 (s $CH_{aliph.}$), 2939 (s, $CH_{aliph.}$), 2885 (m, $CH_{aliph.}$), 1654 (m, C=N), 1543 (vs, C=N), 1460

(s), 1384 (s), 1348 (s), 1311 (s), 1290 (w), 1232 (m), 1184 (m), 1151 (m), 1118 (m), 1080 (w), 1004 (vw), 977 (vw), 958 (vw), 879 (vw), 794 (vw), 754 (w), 671 (vw), 580 (w) cm^{-1}. MS (ESI): m/z = 210 $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 210.1965; found 210.1976.

(2*E*)-3,3,4,4-Tetramethyl-2-(phenylimino)-3,4-dihydro-2*H*-pyrrol-5-amine (2c): From aniline (0.93 g, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mmol) and **1** (1.36 g, 10.0 mmol). Recrystallization from acetone. Yield: 2.18 g (9.5 mmol, 95%), colourless solid, m.p. 243 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (s, 6 H, CH_3), 1.15 (s, 6 H, CH_3), 3.75 (br., 2 H, NH_2), 6.79–6.81 (m, 2 H, *o*-$CH_{arom.}$), 7.01–7.04 (m, 1 H, *p*-$CH_{arom.}$), 7.24–7.26 (m, 2 H, *m*-$CH_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.4, 23.1 (CH_3), 47.5, 48.0 (C_q), 121.2 (*o*-$C_{arom.}$), 122.3 (*p*-$C_{arom.}$), 128.5 (*m*-$C_{arom.}$), 154.0 (*i*-$C_{arom.}$), 178.1, 185.2 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3452 (vs, NH), 3072 (m, $CH_{arom.}$), 3016 (m, $CH_{arom.}$), 2974 (s, $CH_{aliph.}$), 2923 (s, $CH_{aliph.}$), 2873 (m, $CH_{aliph.}$), 1674 (s, C=N), 1645 (C=N), 1593 (vs, C=N), 1539 (s, C=C), 1473 (s, C=N), 1448 (s, C=C), 1369 (m), 1294 (s), 1228 (vs), 1190 (s), 1155 (vs), 1124 (s), 1107 (s), 1066 (s), 1043 (w), 997 (m), 960 (w), 910 (s), 842 (s), 802 (m), 767 (s), 730 (w), 703 (s), 665 (m), 621 (m), 549 (m) cm^{-1}. MS (ESI): m/z = 252 $[M + Na]^+$, 230 $[M + H]^+$, 159 $[C_8H_{12}N_2 + Na]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 230.1652; found 230.1636. $C_{14}H_{19}N_3$ (229.16): calcd. C 73.33, H 8.35, N 18.32; found C 73.17, H 8.31, N 18.25.

X-ray Crystal Structure Analysis of 2c:[25] Formula $C_{14}H_{19}N_3$, M = 229.32, colourless crystal, 0.30 × 0.30 × 0.20 mm, a = 6.099(1), b = 12.316(1), c = 17.576(1) Å, β = 92.14(1)°, V = 1319.3(3) Å^3, $\rho_{calcd.}$ = 1.155 g cm^{-3}, μ = 0.543 mm^{-1}, empirical absorption correction ($0.854 \leq T \leq 0.899$), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 9255 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 2311 independent (R_{int} = 0.032) and 2198 observed reflections [$I \geq 2\sigma(I)$], 166 refined parameters, R = 0.039, wR_2 = 0.107, max. (min.) residual electron density = 0.24 (–0.13) e Å^{-3}, hydrogen atoms at N1 from difference Fourier calculations, others calculated and refined using a riding model.

(2*E*)-2-(Benzylimino)-3,3,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-5-amine (2d): From benzylamine (1.07 g, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mmol) and **1** (1.36 g, 10.0 mmol). Recrystallization from acetone. Yield: 2.23 g (9.2 mmol, 92%), colourless solid, m.p. 184 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 6 H, CH_3), 1.11 (s, 6 H, CH_3), 4.63 (s, 2 H, Aryl-CH_2), 6.34 (br., 2 H, NH_2), 7.23–7.31 (m, 5 H, $CH_{arom.}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.6, 22.7 (CH_3), 48.4, 48.8 (C_q), 49.7 (Aryl-CH_2), 126.8, 127.4, 128.5 ($C_{arom.}$), 139.8 (*i*-$C_{arom.}$), 179.7, 185.6 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3230 (m, NH), 3084 (m, $CH_{arom.}$), 3057 (s, $CH_{arom.}$), 3026 (s, $CH_{arom.}$), 2989 (m, $CH_{aliph.}$), 2968 (s, $CH_{aliph.}$), 2931 (m, $CH_{aliph.}$), 2862 (m, $CH_{aliph.}$), 1687 (m, C=N), 1647 (s, C=N), 1589 (m, C=C), 1544 (vs, C=C), 1475 (s, C=C), 1454 (m, C=C), 1427 (m), 1375 (m), 1367 (m), 1330 (s), 1290 (s), 1209 (m), 1180 (s), 1159 (s), 1124 (m), 1078 (w), 1029 (w), 997 (w), 985 (vw), 912 (vw), 759 (vw), 748 (m), 698 (m), 661 (w), 619 (vw), 580 (vw) cm^{-1}. MS (ESI): m/z = 244.18 $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$: 244.1808; found 244.1826. $C_{15}H_{21}N_3$ (243.17): calcd. C 74.03, H 8.70, N 17.27; found C 73.90, H 8.61, N 17.27.

X-ray Crystal Structure Analysis of 2d:[25] Formula $C_{15}H_{21}N_3$, M = 243.35, colourless crystal, 0.50 × 0.25 × 0.15 mm, a = 20.324(1), b = 10.199(1), c = 14.164(1) Å, β = 103.96(1)°, V = 2849.3(4) Å^3, $\rho_{calcd.}$ = 1.135 g cm^{-3}, μ = 0.528 mm^{-1}, empirical absorption correction ($0.778 \leq T \leq 0.925$), Z = 8, monoclinic, space group $C2/c$ (no. 15), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 17897 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 2540 independent (R_{int} = 0.034) and 2426 observed reflections [$I \geq 2\sigma(I)$], 175 refined parameters, R = 0.047, wR_2 = 0.128, max. (min.) residual electron density = 0.24 (–0.21) e Å^{-3}, hydrogen atoms at N1 from difference Fourier calculations, others calculated and refined using a riding model.

***N*,*N*′-Bis[5-amino-3,3,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-2-ylidene]ethane-1,2-diamine (2e):** From ethane-1,2-diamine (0.62 g, 10.0 mmol), *n*-butyllithium (12.5 mL, 20.0 mmol) and **1** (2.72 g, 20.0 mmol). Recrystallization from methanol. Yield: 2.76 g (8.3 mmol, 83%), colourless solid, m.p. 228 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.08 (s, 12 H, CH_3), 1.09 (s, 12 H, CH_3), 3.46 (br., 4 H, NCH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.4, 23.5 (CH_3), 46.2 (NCH_2), 50.1, 50.8 (C_q), 185.1, 189.5 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3321 (s, NH), 2966 (vs, $CH_{aliph.}$), 2929 (s, $CH_{aliph.}$), 1687 (s, C=N), 1647 (vs, C=N), 1546 (vs), 1477 (s), 1438 (s), 1375 (m), 1342 (m), 1296 (s), 1276 (s), 1184 (vs), 1161 (s), 1124 (s), 1014 (m), 960 (w), 929 (m), 856 (m), 815 (m), 752 (m), 734 (m), 661 (m), 561 (w), 532 (w) cm^{-1}. MS (ESI): m/z = 333 $[M + H]^+$, 167 $[M + 2 H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 333.2761; found 333.2756. $C_{18}H_{32}N_6$ (332.27): calcd. C 64.82, H 9.62, N 25.25; found C 65.02, H 9.70, N 25.28.

***N*,*N*′-Bis[5-amino-3,3,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-2-ylidene]propane-1,3-diamine (2f):** From propane-1,3-diamine (0.76 g, 20.0 mmol), *n*-butyllithium (12.5 mL, 20.0 mmol) and **1** (2.72 g, 20.0 mmol). Recrystallization from acetone. Yield: 2.98 g (8.6 mmol, 86%), colourless solid, m.p. 210 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.07 (s, 12 H, CH_3), 1.13 (s, 12 H, CH_3), 1.76–1.79 (m, 2 H, CH_2), 3.41 (t, ^3J = 5.7 Hz, 4 H, NCH_2), 6.37 (br., 4 H, NH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 22.6, 22.7 (CH_3), 29.4 (CH_2), 40.2 (NCH_2), 48.3, 49.1 (C_q), 181.8, 186.4 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3321 (s, NH), 3057 (br., NH), 2968 (vs, $CH_{aliph.}$), 2933 (sh, $CH_{aliph.}$), 2869 (m, $CH_{aliph.}$), 1656 (s, C=N), 1625 (vs, C=N), 1550 (vs), 1477 (m), 1448 (m), 1379 (s), 1350 (s), 1282 (s), 1222 (s), 1182 (m), 1164 (s), 1122 (s), 1012 (sh), 958 (w), 937 (w), 875 (s), 810 (w), 759 (w), 713 (w), 661 (m), 547 (m) cm^{-1}. MS (ESI): m/z = 347 $[M + H]^+$, 174 $[M + 2 H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 347.2918; found 347.2927. $C_{19}H_{34}N_6$ (346.28): calcd. C 65.86, H 9.89, N 24.25; found C 65.40, H 9.82, N 23.96.

***N*,*N*′-Bis(2-imino-3,3,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-5-yl)-piperazine (2g):** From piperazine (0.86 g, 20.0 mmol), *n*-butyllithium (12.5 mL, 20.0 mmol) and **1** (2.72 g, 20.0 mmol). Recrystallization from acetone. Yield: 3.35 g (9.3 mmol, 93%), colourless solid, m.p. 211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 12 H, CH_3), 1.15 (s, 12 H, CH_3), 3.72 (s, 8 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 20.4, 21.6, 21.7 (CH_3), 45.2 (CH_2), 49.1, 50.0 (C_q), 181.1, 184.5 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3213 (s, NH), 2981 (m, $CH_{aliph.}$), 2920 (m, $CH_{aliph.}$), 2842 (m, $CH_{aliph.}$), 1589 (vs, C=N), 1573 (s, C=N), 1444 (s), 1429 (s), 1367 (m), 1296 (m), 1203 (vs), 1147 (s), 1002 (s), 918 (m), 779 (s), 702 (vs) cm^{-1}. MS (ESI): m/z = 359 $[M + H]^+$, 180 $[M + 2 H]^{2+}$. HRMS (ESI): calcd. for $[M + H]^+$ 359.2923; found 359.2929. $C_{20}H_{34}N_6$ (358.28): calcd. C 67.00, H 9.56, N 23.44; found C 67.08, H 9.47, N 22.84.

X-ray Crystal Structure Analysis of 2g:[25] Formula $C_{20}H_{34}N_6$, M = 358.53, colourless crystal, 0.50 × 0.25 × 0.20 mm, a = 7.517(1), b = 11.015(1), c = 23.516(2) Å, V = 1947.1(4) Å^3, $\rho_{calcd.}$ = 1.223 g cm^{-3}, μ = 0.587 mm^{-1}, empirical absorption correction ($0.758 \leq T \leq 0.892$), Z = 4, orthorhombic, space group $Pbca$ (no. 61), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 11061 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 1735 independent (R_{int} = 0.038) and 1614 observed reflections [$I \geq 2\sigma(I)$], 122 refined parameters, R = 0.054, wR_2 = 0.163, max. (min.) residual electron density = 0.30 (–0.24) e Å^{-3}, hydrogen atom at N1 from difference Fourier calculations, others calculated and refined using a riding model.

***N*-[3,3,4,4-Tetramethyl-5-(pyrrolidin-1-yl)-3,4-dihydro-2*H*-pyrrol-2-ylidene]methanaminium Iodide (3a):** From **2a** (1.04 g, 5.0 mmol) dissolved in dry dichloromethane at 0 °C using triethylamine (0.70 mL, 0.51 g, 5.0 mmol) as base and methyl iodide (0.31 mL, 0.71 g, 5.0 mmol). The mixture was stirred at room temperature overnight. After addition of satd. sodium hydrogen carbonate solution (40 mL), the organic layer was extracted with chloroform (3 × 20 mL). The combined organic layers were dried with magnesium sulfate. The solvent was partially removed in vacuo. Pentane was added carefully to the residue to form an upper layer. After a few hours, colourless crystals of **3a** were isolated by filtration. Yield: 0.64 g (1.8 mmol, 37%), colourless solid, m.p. 203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 6 H, CH_3), 1.41 (s, 6 H, CH_3), 2.05 (m, 2 H, NCH_2CH_2), 2.20 (m, 2 H, NCH_2CH_2), 3.14 (d, ^3J = 5.0 Hz, 3 H, NCH_3), 3.87 (m, 4 H, NCH_2), 9.57 (br., 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 22.8 (CH_3), 23.3, 26.3 (NCH_2CH_2), 29.7 (NCH_3), 51.3, 52.4 (C_q), 48.5, 52.6 (NCH_2), 184.2, 187.3 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3441 (w, NH), 3246 (m), 3194 (m), 3132 (m), 3072 (m), 2990 (m, $CH_{aliph.}$), 2972 (m, $CH_{aliph.}$), 2945 (m), 2924 (m), 2874 (m), 1674 (s, C=N), 1591 (sh, C=N), 1580 (vs, C=N), 1562 (sh), 1508 (sh), 1483 (s, $CH_{methyl.}$), 1454 (vs, $CH_{methyl.}$), 1414 (vs), 1393 (sh), 1381 (sh), 1329 (vs), 1296 (sh), 1259 (w), 1238 (s), 1182 (w), 1169 (m), 1155 (m), 1123 (m), 918 (w), 851 (w), 750 (w), 737 (w), 690 (w) cm^{-1}. HRMS (ESI): calcd. for $[M + H]^+$ 222.1965; found 222.1961. MS (70 eV): *m*/*z* (%) = 221 (38) $[M]^+$, 206 (100) $[M - CH_3]^+$, 179 (29) $[M - (CH_2)_3]^+$, 164 (10) $[M - CH_3, - (CH_2)_3]^+$, 151 (14) $[M - (CH_2)_4N]^+$, 136 (16) $[M - (CH_2)_4N - CH_3]^+$, 127 (24), 109 (33), 96 (23), 81 (34). $C_{13}H_{24}IN_3$ (349.25): calcd. C 44.71, H 6.93, N 12.03; found C 44.91, H 6.87, N 11.88. In another attempt **1** (0.68 g, 5 mmol) and pyrrolidine (0.36 g, 0.41 mL, 5 mmol) were treated with *n*-butyllithium (3.13 mL, 5 mmol) and trapped with methyl iodide (0.71 g, 5 mmol). After aqueous workup and removal of the solvent **2a·HI** (0.034 g) was isolated as colourless crystals from the resulting yellow oil together with some **3a**. **2a·HI**: m.p. 279 °C (decomp.). MS (ES): *m*/*z* = 208 $[M + H]^+$. HRMS (ESI): calcd. for $[M + H]^+$ 208.1808; found 208.1822).

X-ray Crystal Structure Analysis of 2a·HI:[25] Formula $C_{12}H_{21}N_3 \cdot HI$, M = 335.23, colourless crystal, 0.50 × 0.40 × 0.25 mm, a = 6.764(1), b = 24.259(3), c = 8.749(1) Å, β = 101.34(1)°, V = 1407.6(3) Å^3, $\rho_{calcd.}$ = 1.582 g cm^{-3}, μ = 17.708 mm^{-1}, empirical absorption correction ($0.041 \le T \le 0.096$), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 6153 reflections collected ($+h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 2878 independent (R_{int} = 0.151) and 2600 observed reflections [$I \ge 2\sigma(I)$], 158 refined parameters, R = 0.064, wR_2 = 0.174, max. (min.) residual electron density = 3.26 (–1.97) e Å^{-3} close to iodine, hydrogen atoms at N8 from difference Fourier calculations, others calculated and refined using a riding model.

***N*-[3,3,4,4-Tetramethyl-5-(pyrrolidin-1-yl)-3,4-dihydro-2*H*-pyrrol-2-ylidene]benzamide (3b):** From pyrrolidine (0.36 g, 0.41 mL, 5.0 mmol), *n*-butyllithium (3.13 mL, 5.0 mmol) and **1** (0.68 g, 5.0 mmol). Instead of adding water and methanol, the crude mixture was treated with benzoyl chloride (0.70 g, 0.58 mL, 5.0 mmol) for 1 h. After aqueous workup and extraction with chloroform, the crude product was purified by column chromatography (ethyl acetate). Yield: 1.20 g (3.7 mmol, 62%), colourless crystals, m.p. 137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 6 H, CH_3), 1.23 (s, 6 H, CH_3), 1.80 (m, 2 H, NCH_2CH_2), 1.97 (m, 2 H, NCH_2CH_2), 3.55 (t, ^3J = 7.0 Hz, 2 H, NCH_2), 3.57 (t, ^3J = 6.9 Hz, 2 H, NCH_2), 7.37 (m, 2 H, *m*-$CH_{arom.}$), 7.45 (m, 1 H, *p*-$CH_{arom.}$), 8.00 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9, 22.7 (CH_3), 23.5, 26.4 (NCH_2CH_2), 47.2 (NCH_2), 49.3 (C_q), 50.7 (NCH_2), 51.1 (C_q), 127.8, 129.3 (*o*-/*m*-$CH_{arom.}$), 131.6 (*p*-$CH_{arom.}$), 135.4 (*i*-$C_{arom.}$), 178.5, 181.0 (CN), 181.4 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3422 (vs), 3069 (w, $CH_{arom.}$), 3059 (w, $CH_{arom.}$), 2986 (m, $CH_{aliph.}$), 2976 (m, $CH_{aliph.}$), 2928 (m, $CH_{aliph.}$), 1653 (sh, C=O), 1634 (s, C=N), 1620 (s, C=N), 1601 (vs, C=N), 1568 (vs, C=$C_{arom.}$), 1526 (s), 1497 (vs, C=$C_{arom.}$), 1487 (vs), 1477 (vs, CH), 1462 (vs, CH), 1408 (s), 1379 (vs), 1364 (s), 1340 (m), 1310 (vs), 1296 (vs), 1259 (m), 1236 (m), 1215 (vs), 1186 (m), 1171 (s), 1153 (m), 1115 (m), 1103 (m), 1096 (m), 1069 (w), 1026 (m), 914 (m), 856 (w), 833 (m), 812 (m), 762 (m), 719 (m), 706 (m), 690 (w), 665 (w) cm^{-1}. MS (ESI): *m*/*z* = 312 $[M + H]^+$, 334 $[M + Na]^+$, 623 $[2 M + H]^+$, 645 $[2 M + Na]^+$. MS (70 eV): *m*/*z* (%) = 311 (42) $[M]^+$, 296 (25) $[M - CH_3]^+$, 269 (14) $[M - C_3H_6]^+$, 234 (100) $[M - Ph]^+$, 206 (10) $[M - PhCO]^+$, 175 (3), 164 (4) $[M - (CH_2)_4N - Ph]^+$, 127 (27), 105 (94) $[PhCO]^+$, 77 (46) $[Ph]^+$, 57 (18) $[C_3H_7]^+$. UV/Vis (acetonitrile): λ_{max} ($\tilde{\nu}$, ε) = 260 (38461, 39029), 237 (42194 cm^{-1}, sh, 29223 M^{-1} cm^{-1}) nm. $C_{19}H_{25}N_3O$ (311.42): calcd. C 73.28, H 8.09, N 13.49; found C 73.45, H 8.19, N 13.44.

X-ray Crystal Structure Analysis of 3b:[25] Formula $C_{19}H_{25}N_3O$, M = 311.42, colourless crystal, 0.35 × 0.35 × 0.20 mm, a = 9.288(1), b = 9.803(1), c = 10.528(1) Å, α = 96.45(1), β = 110.99(1), γ = 100.48(1)°, V = 863.4(2) Å^3, $\rho_{calcd.}$ = 1.198 g cm^{-3}, μ = 0.590 mm^{-1}, empirical absorption correction ($0.820 \le T \le 0.891$), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 5873 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 2139 independent (R_{int} = 0.058) and 1253 observed reflections [$I \ge 2\sigma(I)$], 212 refined parameters, R = 0.049, wR_2 = 0.124, max. (min.) residual electron density = 0.20 (–0.24) e Å^{-3}, hydrogen atoms calculated and refined using a riding model.

***N*-[{[{[3,3,4,4-Tetramethyl-5-(pyrrolidin-1-yl)-3,4-dihydro-2*H*-pyrrol-2-ylidene]amino}(phenyl)methylene]amino}(phenyl)-methylene]benzamide (5a):** From pyrrolidine (0.71 g, 0.82 mL, 10.0 mmol), *n*-butyllithium (6.25 mL, 10.0 mmol) and **1** (1.36 g, 10.0 mmol). Instead of adding methanol and water, the crude mixture was treated with oxadiazinium pentachlorostannate **4a**[14] (6.06 g, 10.0 mmol). After aqueous workup and extraction with chloroform, the crude product was purified by column chromatography (ethyl acetate). Yield: 1.8 g (3.5 mmol, 35%), colourless crystals, m.p. 301 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (br., 4 H, NCH_2CH_2), 1.59 (s, 6 H, CH_3), 1.78 (s, 6 H, CH_3), 3.28 (br., 4 H, NCH_2), 7.25–7.65 (m, 9 H, $CH_{arom.}$), 8.00–8.10 (m, 2 H, $CH_{arom.}$), 8.60–8.75 (m, 4 H, $CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0 (NCH_2CH_2), 24.7 (CH_3), 25.5 (NCH_2CH_2), 49.7, 50.4 (NCH_2), 51.8 (C_q), 127.6, 128.5, 128.6, 128.9, 129.1, 130.2, 132.5, 136.1, 137.7 ($C_{arom.}$), 165.2, 169.5, 170.6 (CN), 183.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3424 (vs), 3065 (w, $CH_{arom.}$), 2970 (w, $CH_{aliph.}$), 2924 (w, $CH_{aliph.}$), 2874 (w), 2855 (w), 1724 (w), 1666 (sh, C=O), 1651 (sh, C=O), 1622 (s, C=N), 1599 (s, C=$C_{arom.}$), 1556 (s, C=$C_{arom.}$), 1522 (vs), 1448 (s, CH), 1394 (m), 1369 (s), 1339 (m), 1310 (w), 1288 (w), 1254 (w), 1175 (w), 1146 (w), 1080 (w), 1069 (w), 1026 (w), 829 (w), 795 (w), 775 (w), 706 (m), 692 (m), 644 (m) cm^{-1}. MS (ESI): *m*/*z* = 518 $[M + H]^+$, 540 $[M + Na]^+$. MS (70 eV): *m*/*z* (%) = 517 (5) $[M]^+$, 474 (4) $[M - C_3H_7]^+$, 440 (2) $[M - Ph]^+$, 412 (13) $[M - PhCO]^+$, 343 (12), 341 (2), 275 (18), 244 (78), 201 (8), 140 (7), 105 (100) $[PhCO]^+$, 70 (40) $[(CH_2)_4N]^+$. $C_{33}H_{35}N_5O$ (517.67): calcd. C 76.57, H 6.81, N 13.53; found C 76.49, H 6.67, N 13.49.

General Procedure for the Synthesis of Compounds 5b–d: The corresponding compound **2** was dissolved in dry chloroform (30 mL) and treated with an equimolar amount of triethylamine at 0 °C under argon. After 30 min, an equimolar amount of the appropriate 1-oxa-3,5-diazinium salt **4** was added in small portions to the solution whilst stirring. After complete addition, the reaction mix-

ture was warmed to room temperature and stirred for 12 h. Then, at 0 °C, a 2 M sodium hydroxide solution (20 mL) was added. The aqueous layer was extracted three times with chloroform. The combined organic layers were dried with magnesium sulfate. The solvent was removed in vacuo. The remaining residue was purified by column chromatography or medium-pressure chromatography.

2-(Diethylamino)-4,6-diphenyl-1,3,5-oxadiazin-1-ium Pentachlorostannate (4b):[4,15] Tin tetrachloride (11.6 mL, 0.10 mol) was slowly added to a mixture of diethylcarbamoyl chloride (13.60 g, 0.10 mol) and benzonitrile (20.60 g, 0.20 mol) in dry chloroform (50 mL) at 0 °C. After complete addition, the solution was warmed to room temperature during which time a light yellow precipitate slowly formed. After 48 h of stirring at room temperature, the light-yellow precipitate was removed by filtration, washed several times with chloroform and dried in vacuo. Yield: 41.61 g (0.07 mol, 70%), yellow solid, m.p. 190 °C. ^{1}H NMR (300 MHz, DMSO): δ = 1.28 (t, ^3J = 6.9 Hz, 6 H, CH_3), 3.48 (q, ^3J = 6.9 Hz, 4 H, NCH_2), 7.73–7.87 (m, 6 H, $CH_{arom.}$), 8.13–8.17 (m, 4 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 13.8 (CH_3), 39.1–41.3 (br., CH_2), 128.9, 132.9 ($C_{arom.}$), 134.2 (*i*-C), 158.3 (NCN), 168.0 (NCO) ppm. IR (KBr): $\tilde{\nu}$ = 3355 (br., NH), 3068 (m, $CH_{arom.}$), 2978 (m, $CH_{aliph.}$), 2937 (m, $CH_{aliph.}$), 1664 (vs, C=N$^+$-Et$_2$), 1602 (s, C=O), 1592 (vs, C=N), 1564 (vs, C=N), 1507 (vs, C=C), 1486 (w, C=C), 1465 (w, C=C), 1447 (w), 1387 (s), 1332 (s), 1290 (m), 1229 (m), 1180 (m), 1160 (m), 1122 (w), 1099 (w), 1081 (m), 1025 (w), 999 (w), 974 (w), 804 (w), 755 (vs), 710 (vs), 683 (m), 637 (m), 613 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 789 (1), 674 (39), 612 (2), 575 (1), 468 (5), 409 (1), 393 (20), 306 (39) [M]$^+$, 225 (23), 176 (5), 100 (100) [Et_2NCO^+], 58 (9).

***N*′-[(Diethylamino)carbonyl]-*N*-[{[(2*E*)-3,3,4,4-tetramethyl-5-(pyrrolidin-1-yl)-3,4-dihydro-2*H*-pyrrol-2-ylidene]amino}(phenyl)methylene]benzenecarboximidamide (5b):** From **2a** (0.41 g, 2.0 mmol), triethylamine (0.30 mL, 2.0 mmol) and **4b** (1.24 g, 2.0 mmol).[4] Purification by medium-pressure chromatography (cyclohexane/ethyl acetate, 2:1 + 10% triethylamine) and recrystallization from acetone. Yield: 0.49 g (0.9 mmol, 48%), colourless crystals, m.p. 171 °C. R_f = 0.12 (cyclohexane/ethyl acetate, 2:1 + 10% triethylamine).^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (s, 6 H, CCH_3), 0.93 (s, 6 H, CCH_3), 1.04 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.18 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.74 (m, 2 H, CH_2), 1.92 (m, 2 H, CH_2), 3.28–3.44 (m, 8 H, NCH_2), 7.17–7.37 (m, 6 H, $CH_{arom.}$), 7.90–7.92 (m, 2 H, *o*-$CH_{arom.}$), 8.03–8.05 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3, 13.9 (CH_3), 21.3, 22.5, 22.8, 22.9 (CCH_3), 23.5 (CH_2), 26.5 (CH_2), 39.7, 42.0 (NCH_2), 45.9 ($NCH_{2(pyrro.)}$), 49.0 (C_q), 50.3 ($NCH_{2(pyrro.)}$), 50.8 (C_q), 127.2, 127.7, 128.6, 128.9, 130.1 ($C_{arom.}$), 135.4, 135.7 (*i*-$C_{arom.}$), 163.5 (CN), 163.6 (CO), 177.4, 179.8 ($C_{pyrro.}$N) ppm. IR (KBr): $\tilde{\nu}$ = 3082 (vw, $CH_{arom.}$), 3066 (vw, $CH_{arom.}$), 3028 (vw, $CH_{arom.}$), 2970 (s, $CH_{aliph.}$), 2925 (m, $CH_{aliph.}$), 2885 (m, $CH_{aliph.}$), 1670 (s, C=O), 1643 (vs, C=N), 1610 (vs, C=N), 1573 (s, C=N), 1537 (vs, C=C), 1483 (s, C=C), 1467 (s), 1458 (s), 1448 (s), 1419 (s), 1386 (m), 1377 (m), 1342 (m), 1307 (s), 1269 (vs), 1230 (m), 1166 (s), 1124 (m), 1107 (m), 1072 (m), 1016 (w), 914 (m), 875 (vw), 792 (m), 773 (m), 725 (m), 705 (m), 692 (m), 673 (w), 617 (w) cm^{-1}. MS (ESI): *m*/*z* = 513 [M + H]$^+$, 208 [$C_{12}H_{21}N_3$ + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 513.3336; found 513.3341. $C_{31}H_{40}N_6O$ (512.32): calcd. C 72.62, H 7.86, N 16.39; found C 72.27, H 7.88, N 16.30.

X-ray Crystal Structure Analysis of 5b:[25] Formula $C_{31}H_{40}N_6O$, M = 512.69, colourless crystal, 0.50 × 0.40 × 0.05 mm, a = 10.556(1), b = 27.589(1), c = 10.873(1) Å, β = 111.86(1)°, V = 2938.9(4) Å^3, $\rho_{calcd.}$ = 1.159 g cm^{-3}, μ = 0.566 mm^{-1}, empirical absorption correction (0.765 ≤ T ≤ 0.972), Z = 4, monoclinic, space group $P2_1$ (no. 4), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 19369 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 9107 independent (R_{int} = 0.036) and 7638 observed reflections [$I \geq 2\sigma(I)$], 698 refined parameters, R = 0.053, wR_2 = 0.133, Flack parameter 0.6(3), max. (min.) residual electron density = 0.27 (–0.21) e Å^{-3}, two almost identical molecules in the asymmetric unit, hydrogen atoms calculated and refined using a riding model.

***N*′-[(Diethylamino)carbonyl]-*N*-[{[(2*E*)-5-(diethylamino)-3,3,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-2-ylidene]amino}(phenyl)methylene]benzenecarboximidamide (5c):** From **2b** (0.42 g, 2.0 mmol), triethylamine (0.30 mL, 2.0 mmol) and **4b** (1.24 g, 2.0 mmol).[4] Purification by medium-pressure chromatography (cyclohexane/ethyl acetate, 2:1 + 10% triethylamine) and recrystallization from acetone. Yield: 0.43 g (0.8 mmol, 42%), slowly crystallizing yellow oil, m.p. 28–32 °C. R_f = 0.15 (cyclohexane/ethyl acetate, 2:1 + 10% triethylamine). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 12 H, CCH_3), 1.04 (t, ^3J = 6.9 Hz, 6 H, CH_3), 1.17 (t, ^3J = 7.2 Hz, 6 H, CH_3), 3.21–3.43 (m, 8 H, CH_2), 7.21–7.33 (m, 6 H, $CH_{arom.}$), 7.84 (d, ^3J = 8.1 Hz, 2 H, *o*-$CH_{arom.}$), 7.97 (d, ^3J = 8.4 Hz, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2, 13.7, 14.3, 14.7 (CH_3), 22.6, 22.8 (CCH_3), 40.6, 42.4, 43.0, 44.9 (NCH_2), 49.7, 51.5 (C_q), 127.7, 128.0, 128.9, 129.2, 130.4, 130.6 ($C_{arom.}$), 135.8, 136.4 (*i*-$C_{arom.}$), 164.1, 164.3 (CN), 164.8 (CO), 177.6, 181.4 ($C_{pyrro.}$N) ppm. IR (KBr): $\tilde{\nu}$ = 3060 (w, $CH_{arom.}$), 3026 (w, $CH_{arom.}$), 2974 (s, $CH_{aliph.}$), 2931 (m $CH_{aliph.}$), 2871 (w, $CH_{aliph.}$), 1647 (vs, C=O), 1618 (vs, C=N), 1575 (m, C=N), 1535 (vs, C=C), 1448 (s), 1421 (s), 1379 (m), 1359 (m), 1317 (s), 1269 (s), 1228 (m), 1164 (m), 1107 (m), 1078 (w), 1051 (vw), 1002 (vw), 964 (w), 925 (vw), 881 (w), 786 (w), 694 (s) cm^{-1}. MS (ESI): *m*/*z* = 537 [M + Na]$^+$, 515 [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 515.3493; found 515.3486. $C_{31}H_{42}N_6O$ (514.34): calcd. C 72.34, H 8.22, N 16.33; found C 72.15, H 7.78, N 16.28.

***N*′-[(Diethylamino)carbonyl]-*N*-[{[(2*E*)-5-(benzylamino)-3,3,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-2-ylidene]amino}(phenyl)methylene]benzenecarboximidamide (5d):** From **2d** (0.93 g, 10.0 mmol), triethylamine (0.30 mL, 2.0 mmol) and **4b** (1.24 g, 2.0 mmol).[4] Purification by medium-pressure chromatography (cyclohexane/ethyl acetate, 2:1 + 5% triethylamine). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.39 (br. s, 2 H, CCH_3), 0.91 (br. s, 4 H, CCH_3), 1.06 (br. s, 6 H, CCH_3), 1.16–1.21 (m, 6 H, CH_3), 3.26 (br. m, 1 H, NCH_2), 3.38 (br. m, 2 H, NCH_2), 3.52 (br. m, 1 H, NCH_2), 4.51 (q, ^3J = 7.2 Hz, 2 H, Aryl-CH_2) 7.24–7.47 (m, 11 H, $CH_{arom.}$), 7.88 (d, ^3J = 7.2 Hz, 2 H, *m*-$CH_{arom.}$), 8.12 (d, ^3J = 7.2 Hz, 2 H, *m*-$CH_{arom.}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.9, 13.9 (CH_3), 20.9, 21.2, 22.8 (CCH_3), 40.5, 42.2 (NCH_2), 45.7, 46.5 (C_q), 52.4 (Aryl-CH_2) 125.6, 127.1, 127.6, 127.8, 128.2, 128.4 ($C_{arom.}$), 131.0, 131.1 (*o*-Aryl-$C_{arom.}$), 131.6 (*o*-N-$C_{arom.}$), 134.9 (*i*-Aryl-$C_{arom.}$), 141.0 (*i*-N-$C_{arom.}$), 159.7, 162.3 (CN), 164.9 (CO), 176.4, 178.8 ($C_{pyrro.}$N) ppm. IR (KBr): $\tilde{\nu}$ = 3211 (m, NH), 3082 (m, $CH_{arom.}$), 3064 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2974 (s, $CH_{aliph.}$), 2931 (m, $CH_{aliph.}$), 2869 (w, $CH_{aliph.}$), 1668 (s, C=O), 1629 (vs, C=N), 1616 (vs, C=N), 1564 (s, C=C), 1523 (vs, C=C), 1458 (s), 1448 (s), 1427 (s), 1398 (m), 1375 (m), 1357 (m), 1313 (s), 1271 (vs), 1242 (s), 1213 (s), 1174 (m), 1159 (s), 1097 (m), 1080 (m), 1053 (w), 1026 (m), 931 (vw), 883 (w), 800 (w), 773 (w), 748 (m), 719 (m), 702 (s), 690 (m), 671 (w), 636 (w) cm^{-1}. MS (ESI): *m*/*z* = 571 [M + Na]$^+$, 549 [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 549.3336; found 549.3333. UV/Vis (acetonitrile): λ_{max} ($\tilde{\nu}$, ε) = 256 (39062 cm^{-1}, 34800 M^{-1} cm^{-1}) nm. $C_{34}H_{40}N_6O$ (548.32): calcd. C 74.42, H 7.35, N 15.32; found C 74.19, H 7.24, N 15.27.

X-ray Crystal Structure Analysis of 5d:[25] Formula $C_{34}H_{40}N_6O$, M = 548.72, colourless crystal, 0.30 × 0.15 × 0.15 mm, a = 24.202(1), b = 19.489(1), c = 15.925(1) Å, β = 123.59(1)°, V = 6257.1(6) Å^3, $\rho_{calcd.}$ = 1.165 g cm^{-3}, μ = 0.566 mm^{-1}, empirical absorption correction (0.849 ≤ T ≤ 0.920), Z = 8, monoclinic, space group $C2/c$ (no. 15), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 44251 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 5477 independent (R_{int} = 0.048) and 4758 observed reflections [$I \geq 2\sigma(I)$], 379 refined parameters, R = 0.042, wR_2 = 0.107, max. (min.) residual electron density = 0.17 (–0.15) e Å^{-3}, hydrogen atoms at N11 from difference Fourier calculations, others calculated and refined using a riding model.

***N*-[{[(6*E*)-2-(Benzylamino)-3,3,3a,5,5-pentamethyl-3,3a,4,5-tetrahydro-6*H*-pyrrolo[2,3-*b*]pyridin-6-ylidene]amino}(phenyl)methylene]-*N*′-[(diethylamino)carbonyl]benzenecarboximidamide (7):** Benzylamine (0.21 g, 2.0 mmol) was dissolved in dry tetrahydrofuran (40 mL) under argon. The solution was cooled to –78 °C with stirring and *n*-butyllithium (1.4 mL, 2.2 mmol, 1.6 M solution in *n*-hexane) was added dropwise. The mixture was warmed to room temperature and stirred for 30 min. This solution was again cooled to –78 °C and 2,3,5-trimethyl-2,3,5-tricyanohexane (**6**) (0.46 g, 2.0 mmol) dissolved in dry tetrahydrofuran (5 mL) was added dropwise. The mixture was stirred for 1 h and then warmed to 0 °C. After 30 min at 0 °C, **4b** (1.20 g, 2.0 mmol)[4] was added in small portions. Then the mixture was warmed to room temperature with stirring overnight. At 0 °C, an ice-cold 2 M aqueous sodium hydroxide solution (40 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 20 mL). The organic layers were dried with magnesium sulfate. The solvent was removed in vacuo. Purification was achieved by medium-pressure chromatography (cyclohexane/ethyl acetate, 5:1 + 5% triethylamine) and recrystallization from acetone. Yield: 0.59 g (0.9 mmol, 32%), colourless crystals, m.p. 211–213 °C. R_f = 0.09 (cyclohexane/ethyl acetate, 5:1 + 5% triethylamine). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.66 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.02 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.05 (s, 3 H, $CCH_{3(pyrro.)}$), 1.27 (s, 3 H, $CCH_{3(pyr.)}$), 1.33, 1.34 (s, 6 H, $CCH_{3(pyr.)}$, $CCH_{3(pyrro.)}$), 1.75 (d, ^2J = 14.4 Hz, 1 H, CH_2), 1.86 (s, 3 H, $CCH_{3(br)}$), 2.46–2.53 (m, 1 H, NCH_2), 2.78–2.82 (m, 2 H, NCH_2), 2.97 (d, ^2J = 14.4 Hz, 1 H, CH_2), 3.68–3.72 (m, 1 H, NCH_2), 3.79 (d, ^2J = 16.2 Hz, 1 H, Aryl-CH_2), 3.98 (d, ^2J = 16.2 Hz, 1 H, Aryl-CH_2), 7.12–7.19 (m, 3 H, $CH_{(benz.)}$), 7.25–7.28 (m, 2 H, *m*-$CH_{(benz.)}$), 7.39–7.42 (m, 4 H, *o*-$CH_{arom.}$), 7.47–7.49 (m, 2 H, *p*-$CH_{arom.}$), 8.62 (d, ^3J = 6.6 Hz, 4 H, *m*-$CH_{arom.}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 12.9, 14.47 (CH_3), 16.2, 17.3 ($CCH_{3(pyr.)}$), 25.1 ($CCH_{3(pyrro.)}$), 26.2 ($CCH_{3(bridge)}$), 34.9 ($CCH_{3(pyrro.)}$), 40.8 (NCH_2), 42.9 (C_q), 43.4 (NCH_2), 47.9, 48.3 (CH_2), 50.7 (C_q), 52.4 (Aryl-CH_2), 126.2, 127.1 ($C_{benz.}$), 128.1 (*m*-$C_{benz.}$), 128.4, 128.8 ($C_{arom.}$), 132.0 (*m*-$C_{arom.}$), 136.4 (*i*-$C_{benz.}$), 140.2 (*i*-$C_{arom.}$), 161.9, 162.6 (CN), 170.4 (CO), 171.4, 184.2 (CN) ppm. IR (KBr): $\tilde{\nu}$ = 3205 (m, NH), 3168 (m, NH), 3064 (s, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2966 (s, $CH_{aliph.}$), 2931 (m, $CH_{aliph.}$), 2868 (w, $CH_{aliph.}$), 1633 (s, C=O), 1610 (vs, C=N), 1573 (s, C=N), 1543 (s, C=C), 1504 (s, C=C), 1463 (s), 1417 (s), 1375 (m), 1321 (s), 1284 (vs), 1264 (sh), 1267 (s), 1203 (m), 1155 (s), 1110 (m), 1080 (m), 1066 (w), 1051 (m), 1002 (m), 956 (vw), 923 (w), 900 (w), 871 (m), 821 (m), 812 (m), 798 (m), 779 (m), 761 (m), 750 (m), 727 (s), 692 (vs), 665 (w), 653 (m), 632 (m), 609 (m), 576 (m) cm^{-1}. MS (ESI): m/z = 616 [M + Na]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 616.3758; found 616.3756. UV/Vis (acetonitrile): λ_{max} ($\tilde{\nu}$, ε) = 286 (34965, 27800), 250 (40000 cm^{-1}, 30100 M^{-1} cm^{-1}) nm. $C_{38}H_{45}N_7O$ (615.36): calcd. C 74.12, H 7.37, N 15.92; found C 73.71, H 7.17, N 15.94.

X-ray Crystal Structure Analysis of 7:[25] Formula $C_{38}H_{45}N_7O$, M = 615.81, colourless crystal, 0.20 × 0.20 × 0.03 mm, a = 12.417(1), b = 20.782(1), c = 26.786(1) Å, β = 92.46(1)°, V = 6905.8(7) Å^3, $\rho_{calcd.}$ = 1.185 g cm^{-3}, μ = 0.575 mm^{-1}, empirical absorption correction (0.894 ≤ T ≤ 0.983), Z = 8, monoclinic, space group $P2_1/n$ (no. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 113357 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 12225 independent (R_{int} = 0.148) and 7239 observed reflections [$I \geq 2\sigma(I)$], 852 refined parameters, R = 0.077, wR_2 = 0.186, max. (min.) residual electron density = 0.25 (–0.23) e Å^{-3}, two almost identical molecules in the asymmetric unit, hydrogen atom at N13 from difference Fourier calculations, others calculated and refined using a riding model.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 424 and the European Graduate College "Template Directed Chemical Synthesis") and the Fonds der Chemischen Industrie (Frankfurt) for financial support.

[1] J. A. Elvidge, N. R. Barot in *The Chemistry of Functional Groups, Suppl. A. The Chemistry of Double-Bonded Functional Groups, Part 2* (Ed.:S. Patai), Wiley, London, **1977**, ch. 13.
[2] N. Heße, R. Fröhlich, B. Wibbeling, E.-U. Würthwein, *Eur. J. Org. Chem.* **2006**, 3923–3937.
[3] N. Heße, R. Fröhlich, I. Humelnicu, E.-U. Würthwein, *Eur. J. Inorg. Chem.* **2005**, 2189–2197.
[4] J.-B. Greving, Dissertation, University of Münster, **2007**.
[5] M. N. Kopylovich, M. Haukka, A. M. Kirillov, V. Yu. Kukushkin, A. J. L. Pombeiro, *Chem. Eur. J.* **2007**, *13*, 786–791.
[6] J.-B. Donnet, S. Rebouillat, T. K. Wang, J. C. M. Peng, *Carbon Fibers*, 3rd ed., Marcel Dekker, New York, **1989**.
[7] See also: J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1954**, 442–448.
[8] D. Wöhrle, *Adv. Polym. Sci.* **1972**, *10*, 34–107.
[9] D. Wöhrle, *Makromol. Chem.* **1972**, *160*, 83–97.
[10] See also: R. Scheffold, J. Löliger, H. Blaser, P. Geisser, *Helv. Chim. Acta* **1975**, *58*, 49–64.
[11] W. Barbe, H. D. Beckhaus, H.-J. Lindner, C. Rüchardt, *Chem. Ber.* **1983**, *116*, 1017–1041.
[12] R. Allmann, R. Kupfer, M. Nagel, E.-U. Würthwein, *Chem. Ber.* **1984**, *117*, 1597–1605.
[13] M. Buhmann, M. H. Möller, E.-U. Würthwein, *Chem. Ber.* **1993**, *126*, 957–967.
[14] R. R. Schmidt, *Chem. Ber.* **1965**, *98*, 334–345.
[15] C. Möllers, J. Prigge, B. Wibbeling, R. Fröhlich, A. Brockmeyer, H. J. Schäfer, E. Schmälzlin, C. Bräuchle, K. Meerholz, E.-U. Würthwein, *Eur. J. Org. Chem.* **2003**, 1198–1208.
[16] R. Fuks, M. Strebelle, A. Wenders, *Synthesis* **1977**, 788–789.
[17] A. F. Bickel, W. A. Waters, *Recl. Trav. Chim. Pays-Bas* **1950**, *69*, 1490–1494.
[18] A. Beckmann, R. Fröhlich, E.-U. Würthwein, *Tetrahedron Lett.* **1997**, *31*, 5481–5484.
[19] M. Buhmann, M. H. Möller, U. Rodewald, E.-U. Würthwein, *Angew. Chem.* **1994**, *106*, 2386–2389; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2337–2339.
[20] M.-H. Whangbo, R. Hoffmann, R. B. Woodward, *Proc. R. Soc. London, Ser. A* **1979**, *366*, 23–26.
[21] J. Chandrasekhar, P. K. Das, *J. Phys. Chem.* **1992**, *96*, 679–685.
[22] A. Karpfen, *Chem. Phys. Lett.* **1979**, *64*, 299–302.
[23] D. Jaquemin, B. Champagne, J.-M. André, *J. Mol. Struct.* **1998**, *425*, 69–79, and references cited therein.
[24] E. A. Marihart, Dissertation, University of Münster, **2006**.
[25] Data sets were collected with an Enraf-Nonius CAD or a Nonius-Kappa CCD diffractometer. Programs used: data collection: Express (Nonius B. V., **1994**) and COLLECT (Nonius B. V., **1998**); data reduction: MolEN (K. Fair, Enraf-Nonius

B. V., **1990**) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol* **1997**, *276*, 307–326); absorption correction: MolEN (K. Fair, Enraf–Nonius B. V., **1990**) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr., Sect. A* **2003**, *59*, 228–234),; structure solution: SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473); structure refinement: SHELXL-97 (G. M. Sheldrick, University of Göttingen, **1997**); graphics: SCHAKAL (E. Keller, **1997**), MERCURY: visualization and analysis of crystal structures (C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.* **2006**, *39*, 453–457). CCDC-639811 (**2a·HI**), -639812 (**2c**), -639813 (**2d**), -639814 (**2g**), -639815 (**3b**), -639816 (**5b**), -639818 (**5d**) and -639817 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: May 24, 2007
Published Online: August 10, 2007

