Polyamino-Substituted 1-Oxa-3,5-diazahexatrienes and 1-Oxa-3,5,7-triazaoctatetraenes (*N*-Acyl-oligocyanamides): Synthesis, Structures, Cyclovoltammetry and NLO Properties – Experiment and Theory[‡]

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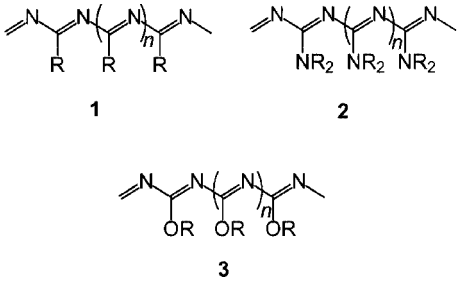
A homologous series of *N*-acylcyanamides of the formula $R_2N–[C(NMe_2)=N]_n–C(NMe_2)=O$ with n = 1–3 has been prepared among similar amino-substituted *N*-acyl-oligonitriles by treatment of guanidine **4** with carbamoyl chloride **5** yielding compound **6** (n = 1) and by ring opening of 1,3,5-oxadiazinium salts **7** with morpholine (**8**) to give compounds **9** (n = 2) or with guanidine **4** to give compounds **10** (n = 3). The all-dimethylamino-substituted compound **10d** reacts with $ZnCl_2$ to yield a six-membered chelate complex **10d·ZnCl$_2$**. The molecular structures of **9e,f, 10a–d** and **10d·ZnCl$_2$** have been elucidated by X-ray crystallography and partly by DFT calculations. They deviate strongly from planarity with some examples showing helical structures. From the calculations, **10d** is predicted to be a rather strong neutral base. One or two oxidation peaks, depending on the chain length, were observed by cyclic voltammetry. For the most extended derivative **10d** a first oxidation potential of 1.12 V was measured. The molecular first hyperpolarizabilities β^0 were determined by hyper-Rayleigh scattering (HRS) measurements. The β^0 values increase with chain length and reach 5×10^{-30} esu for the longest derivative **10d**.

Introduction

The synthesis of unsaturated compounds containing multiple amino groups is of interest because of, inter alia, their acid–base[1–5] and redox properties.[6] During our investigations in the field of oligonitriles[7,8] **1** we also became interested in amino-substituted oligonitriles, which may be formally regarded as polymers of dialkylcyanamides as monomers. In these so-called polycyanamides **2**, dialkylcyanamides are linked to produce a polyunsaturated chain of C=N units with peripheral amino groups (Scheme 1).

In the field of oligonitrile chemistry, oligocyanamides **2** as well as oligocyanates[8] **3** are of special interest since in both classes of compounds the inherent electron demand of the oligonitrile chain is partially compensated by the electron-donor properties of the functional groups attached to the periphery of the chains.



Scheme 1

In this paper we present initial reports on the synthesis of short examples of oligocyanamides with a terminal acyl or carbamoyl function, the so-called *N*-acyl-oligocyanamides, together with spectroscopic and structural data regarding their molecular structure in solution and in the solid state. In our subsequent studies, the terminal acyl group proved to be an important feature for possible chain elongation reactions. On the other hand, we expect no dras-

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tic deviations of the chemical and electronic properties of these *N*-acyl or carbamoyl derivatives from "real" oligocyanamides carrying a terminal guanidine group.

To characterize the consequences of the unusual electronic structures of these *N*-acyl-oligocyanamides, we present cyclovoltammetric studies and non-linear optical (NLO) investigations. We discuss the experimental and structural results using quantum chemical calculations at the DFT level.

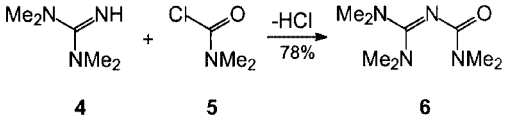
The parent compound, cyanamide, is rather unstable.[9] It is known to undergo exothermic dimerization to dicyandiamide (*N*-cyanoguanidine); at higher temperatures cyclization reactions lead to triazine derivatives ("Melam", "Melem", "Melon"). In contrast, dimethylcyanamide is more stable, giving the trimer hexamethylmelamine upon stirring in the presence of sodium.[10] Monodisperse open-chain oligomers and polymers of cyanamides do not seem to have been synthesized yet. Therefore, we decided to investigate synthetic approaches to such compounds based on reliable organic procedures.

Results and Discussion

Experimental Results

For a detailed study of the properties of *N*-acyl-oligocyanamides we synthesized a homologous series of derivatives with increasing chain length, namely oligomers with one, two and three dimethylcyanamide monomer units bearing a terminal dimethylcarbamoyl group.

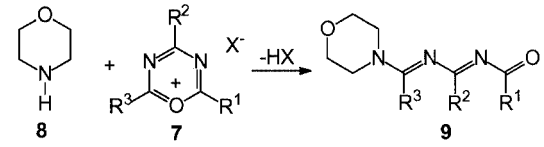
The first member of this series is simply *N*-dimethylcarbamoyl-*N*′,*N*′,*N*′′,*N*′′-tetramethylguanidine or 2,4,4-tris-(dimethylamino)-1-oxa-3-azabutadiene (**6**). This compound is easily accessible in 78% yield from two equivalents of *N*,*N*,*N*′,*N*′-tetramethylguanidine (**4**) and one equivalent of dimethylcarbamoyl chloride (**5**), while the guanidine acts also as a base that removes the HCl produced in this reaction (Scheme 2). Jochims et al. earlier prepared this colorless oil from carbonylbis(isocyanide dichloride) and dimethylamine.[11]



4 **5** **6**

Scheme 2

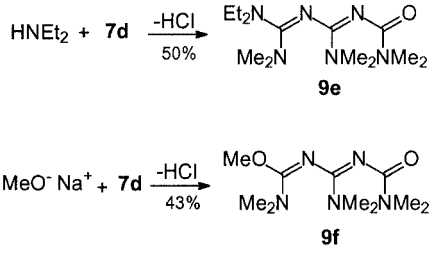
For the synthesis of the next longer homologue we used an approach which proved to be quite useful in oligonitrile chemistry in general, the nucleophilic ring-opening reaction of the corresponding 1,3,5-oxadiazinium salts **7**.[12] This method is based on the findings of Fuks and Strebele,[13] who prepared compound **9a** for the first time from **7a**. From the 1,3,5-oxadiazinium salts **7b−d** we were able to prepare a series of new crystalline 1-oxa-3,5-diazahexatrienes **9b−d** in 30−71% yield by treatment with morpholine (**8**). For the preparation of **9b,c** one equivalent of *n*-butyllithium was used to increase the nucleophilicity of the secondary amine. In the case of **7b,c** the reaction leads mainly to the product of nucleophilic attack at the heterocyclic carbon atom [C(2)/C(6)] which does *not* carry the dimethylamino group and is therefore more electrophilic. The *N*-acyldialkylcyanamide dimer **9e** results from addition of diethylamine to **7d.** We also prepared crystalline **9f** by using sodium methoxide as a nucleophile (see Scheme 3). In the literature, preparations of 1-oxa-3,5-diazahexatrienes bearing three amino groups have been reported both from a 1,3,5-thiadiazinium salt by ring opening using anilines[14] and by ring opening of 4,5-diamino-1-aroyl-4,5-dihydroimidazoles[15]. Phenyl isocyanate gives a 1-oxa-3,5-diazahexatriene with four amino groups upon treatment with 1,2,2,2,3,3-hexamethylisobiguanide.[16]



8 **7** **9**

7a-c: $X^- = SnCl_5^-$
7d: $X^- = Cl^-$

7,9	R^1	R^2	R^3	Yield **9** (%)
a	Ph	Ph	Ph	75[13]
b	NMe_2	Ph	Ph	71
c	NMe_2	NMe_2	Ph	30
d	NMe_2	NMe_2	NMe_2	64



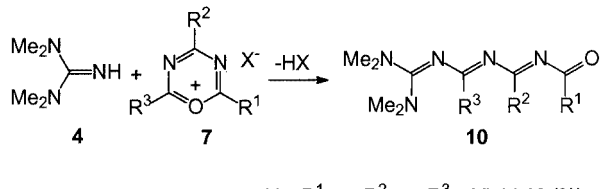
9e

9f

Scheme 3

The same method could also be successfully applied to the synthesis of the next longer homologues **10** by use of *N*,*N*,*N*′,*N*′-tetramethylguanidine (**4**) as nucleophile for the ring-opening reaction of 1,3,5-oxadiazinium salts **7a−d** (yield: 31−72%). For the preparation of **10a−c** one equivalent of *n*-butyllithium was used to generate the more nucleophilic guanidine anion. The fully dimethylamino-substituted 1-oxa-3,5,7-triazaoctatetraene **10d** is the linear *N*-carbamoyl dimethylcyanamide trimer and at present represents the longest *N*-acyl-oligocyanamide derivative with a well-defined monodisperse structure. It was also prepared in 50% yield by using *N*-trimethylsilyl-*N*′,*N*′,*N*′′,*N*′′-tetramethylguanidine as a nucleophile for ring opening in the presence of fluoride ions.

In order to check the ability of such *N*-carbamoylcyanamides to act as ligands for metal complexation, compound **10d** was reacted with zinc chloride in dichloromethane (Scheme 5). After crystallization from toluene colorless crystals were obtained, and an X-ray structure determina-

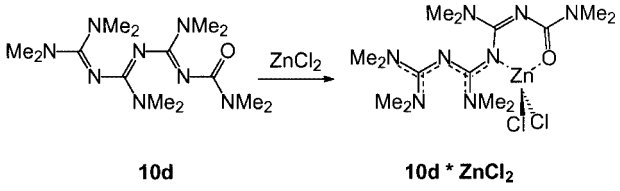


7,10	R^1	R^2	R^3	Yield **10** (%)
a	Ph	Ph	Ph	72
b	NMe_2	Ph	Ph	54
c	NMe_2	NMe_2	Ph	31
d	NMe_2	NMe_2	NMe_2	70

7a-c: $X^- = SnCl_5^-$
7d: $X^- = Cl^-$

Scheme 4

tion was performed. According to Figure 4 (see below), the metal center coordinates to the oxygen atom of the carbamoyl moiety and to nitrogen atom N(5), forming a six-membered non-planar chelate structure with a tetrahedral Zn center. The remaining chain with its additional donor centers is not used for coordination, indicating the superior donor ability of the oxygen atom with respect to zinc which obviously governs the mode of the complexation reaction. (For a detailed comparison of the geometrical parameters of **10d** and **10d·ZnCl$_2$** see below.)



Scheme 5

Structures and Calculations

X-ray structure determinations could be performed on the "dimeric" compounds **9e,f** and on the "trimers" **10a−d**. All six molecules are characterized by non-planar, strongly twisted three-dimensional structures, of which **9e, f**, and **10d** fulfil the characteristics of a helix (unidirectional gauche conformations of the C−N bonds, (*Z*)-C=N configurations).

Owing to the oily nature of compound **6** we were not able to determine its molecular structure in the solid state. Quantum chemical calculations on the B3LYP/6−31G* level (program GAUSSIAN 98)[17] (Figure 1) predict a non-planar structure with a gauche conformation of the central C−N bond [torsional angle O(1)−C(2)−N(3)−C(4) = 73.2°]. The preference of 3-oxa-1-azabutadienes for gauche conformations has previously been demonstrated by experimental and theoretical data and was discussed in terms of the competing π-interactions of the carbonyl C=O bond with the lone pair on the central nitrogen atom on the one hand and the π-system of the C=N bond on the other. The smaller dipole moment of the gauche conformation is more favorable than the larger dipole moment of the *trans* conformation.[18] Of course, severe steric interactions of the dimethylamino groups also favor the gauche conformation. The bonds of the 1-oxa-3-azabutadiene chain [C(2)=O(1) 1.234 Å, C(2)−N(3) 1.389 Å, N(3)=C(4) 1.289 Å] alternate in length, but, as expected, not to the same extent as in the parent compound *N*-methylene formamide, because of the conjugative interactions of the C=N double bond with the adjacent dimethylamino groups.

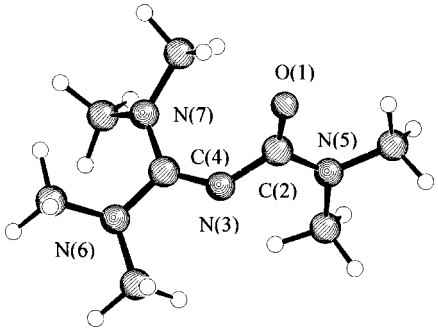


Figure 1. Molecular structure of **6** obtained by DFT B3LYP/6−31G* calculation; selected bond lengths [Å], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.2341, C(2)−N(3) 1.3887, N(3)−C(4) 1.2893, C(2)−N(5) 1.3837, C(4)−N(6) 1.4054, C(4)−N(7) 1.3878. O(1)−C(2)−N(3) 123.29, C(2)−N(3)−C(4) 131.34, O(1)−C(2)−N(5) 121.26. O(1)−N(2)−N(3)−C(4) 73.16, C(2)−N(3)−C(4)−N(6) 179.99, C(2)−N(3)−C(4)−N(7) 2.05, N(5)−C(2)−N(3)−C(4) −113.10.

For the next longer system two molecular structures **9e** and **9f** in the solid state could be determined by X-ray diffraction. For both compounds we found nonplanar, helical structures. In **9e** (Figure 2), the O(1)=C(2)−N(3)=C(4)−, C(2)−N(3)=C(4)−N(5)− and N(3)=C(4)−N(5)=C(6) subunits all show unidirectional *gauche* conformations (28.2°, 17.1°, 35.6°) with bond-length alternation (1.234, 1.370, 1.319, 1.370, 1.308 Å). The observed X-ray data are in good agreement with gas-phase DFT structural data (Table 1). Similar geometrical parameters are observed for the methoxy compound **9f** with dihedral angles along the chain of 30.4°, 15.9° and 31.31° and bond lengths of 1.233, 1.373, 1.315, 1.363, and 1.295 Å. The observed structures differ from those of an earlier reported non-helical arrangement of 2,4,6,6-tetraphenyl-1-oxa-3,5-diazahexatriene.[19] Steric effects of the dimethylamino groups and crystal packing forces may be responsible for these differences.

The four 1-oxa-3,5,7-triazaoctatetraenes **10a−d** could also be characterized by X-ray diffraction. **10d** (Figure 3) shows a 3_1 helix for the main chain, whereas the other three derivatives **10a−c** have more irregular three-dimensional structures.[12] In **10b** all C=N double bonds exhibit (*Z*)-configurations with different C−N single-bond torsion angles, whereas in **10a** and **10c** one (*E*)-configured C=N bond is observed.

For **10d** (Figure 3), the calculated and experimental bond parameters agree with regard to the bond lengths. The torsional angles deviate more. This may be attributed to low barriers of rotation about C−N bonds, as found in the gas-phase calculations. Hence, the torsional angles of longer oli-

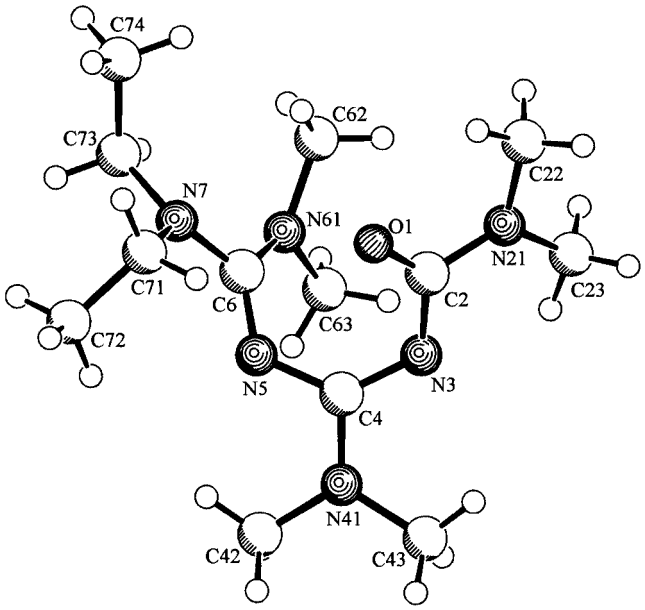


Figure 2. Molecular structure of **9e** obtained by X-ray crystallography; selected bond lengths [Å], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.2343(18), C(2)−N(3) 1.3697(18), N(3)−C(4) 1.3191(18), C(4)−N(5) 1.3695(18), N(5)−C(6) 1.3080(18), C(2)−N(21) 1.373(2), C(4)−N(41) 1.3556(17), C(6)−N(7) 1.3598(16), C(6)−N(61) 1.3765(18). O(1)−C(2)−N(3) 126.71(14), C(2)−N(3)−C(4) 120.97(12), N(3)−C(4)−N(5) 128.31(12), C(4)−N(5)−C(6) 121.39(12), O(1)−C(2)−N(21) 119.46(14), N(3)−C(4)−N(41) 117.34(12), N(5)−C(6)−N(7) 119.01(12), N(5)−C(6)−N(61) 123.75(12). O(1)−C(2)−N(3)−C(4) 28.24(0.24), C(2)−N(3)−C(4)−N(5) 17.06(0.23), N(3)−C(4)−N(5)−C(6) 35.61(0.21), O(1)−C(2)−N(21)−C(22) 1.70(0.26), N(3)−C(4)−N(41)−C(43) 4.78(0.21), N(5)−C(6)−N(7)−C(73) −143.59(0.13), N(5)−C(6)−N(61)−C(63) 20.14(0.20).

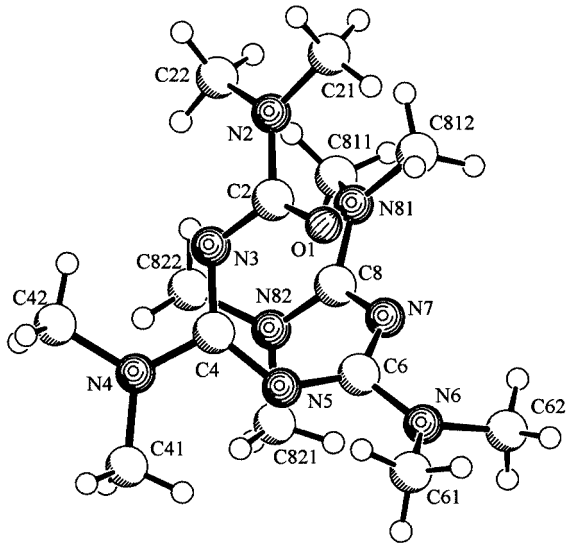


Figure 3. Molecular structure of **10d** obtained by X-ray crystallography; selected bond lengths [Å], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.234(3), C(2)−N(3) 1.358(3), N(3)−C(4) 1.324(3) C(4)−N(5) 1.350(3), N(5)−C(6) 1.316(3), C(6)−N(7) 1.357(3), N(7)−C(8) 1.305(3), C(2)−N(2) 1.380(3), C(4)−N(4) 1.367(3), C(6)−N(6) 1.354(3), C(8)−N(81) 1.356(3), C(8)−N(82) 1.367(3). O(1)−C(2)−N(3) 127.4(2), C(2)−N(3)−C(4) 121.3(2), N(3)−C(4)−N(5) 130.5(2), C(4)−N(5)−C(6) 126.0(2), N(5)−C(6)−N(7) 130.1(2), C(6)−N(7)−C(8) 124.6(2), O(1)−C(2)−N(2) 119.2(2), N(3)−C(4)−N(4) 115.6(2), N(5)−C(6)−N(6) 115.9(2), N(7)−C(8)−N(81) 117.2(2), N(7)−C(8)−N(82) 125.5(2). O(1)−C(2)−N(3)−C(4) −19.59(0.35), C(2)−N(3)−C(4)−N(5) −26.56(0.35), N(3)−C(4)−N(5)−C(6) −35.69(0.37), C(4)−N(5)−C(6)−N(7) −17.77(0.38), N(5)−C(6)−N(7)−C(8) −25.25(0.38), O(1)−C(2)−N(2)−C(21) 0.55(0.36), N(3)−C(4)−N(4)−C(41) −179.02(0.21), N(5)−C(6)−N(6)−C(61) −14.06(0.31), N(7)−C(8)−N(81)−C(811) 149.49(0.22), N(7)−C(8)−N(82)−C(821) −25.32(0.36).

Table 1. Measured and calculated geometrical parameters for **9e** (the calculation was performed for the all-NMe_2 compound; B3LYP/6−31G*//B3LYP/6−31G*)

Bond lengths [Å]					
	O1=C2	C2−N3	N3=C4	C4−N5	N5=C6
X-ray	1.234	1.370	1.319	1.370	1.308
DFT	1.244	1.376	1.325	1.364	1.312

Torsional angles [°]			
	O1=C2−N3=C4	C2−N3=C4−N5	N3=C4−N5=C6
X-ray	28.24	17.06	35.61
DFT	14.63	16.83	30.64

gomers may be substantially influenced by crystal-packing forces. As Table 1 and 2 indicate, the longer chain of **10d** shows smaller bond-length alternation for the CN bonds (1.305−1.358 Å) than the shorter chain of **9e** (1.308−1.370 Å). The same is true for the torsional angles: in **10d** all the torsional angles are found to be similar (17−36°) irrespective of the C−N single-bond or C=N double-bond notation in formula **10d**. Thus, against expectation, intense conjugative interactions along the chain are possible in these helical molecules and planarity is not a prerequisite for conjugation.

The X-ray structure of the metal complex **10d**·$ZnCl_2$ (Figure 4) reveals interesting differences in structure compared to that of the free ligand **10d** (Figure 3). Although the bond lengths in the chelate ring are surprisingly similar to those of **10d**, the bond orders in the remaining chain are interchanged. N(5)−C(6) and N(7)−C(8) are now longer (1.369 and 1.331 Å), whereas C(6)−N(7) is shorter (1.339 Å) indicating significant electronic delocalization in the sense of a 2-azaallyl cation submoiety in this part of the molecule.[20] The helix-type structure is not completely realized in the complex, since the torsion angle N(3)−C(4)−N(5)−C(6) is widened from −35.7° in **10d** to −139.4° giving rise to a turn of the chain away from the chelate ring.

In order to get some insight into the gas-phase basicity of oligocyanamides, DFT calculations on the B3LYP/6−31G* level were performed on various protonated forms of **10d** (Figure 5). Among several calculated structures the N(3) protonated oligonitrile **10d** is lowest in energy. This cation shows a deformed helix-type structure [torsional angles O(1)−C(2)−N(3)−C(4) 7.26°, C(2)−N(3)−C(4)−N(5) −131.20°, N(3)−C(4)−N(5)−C(6) 26.64°, C(4)−N(5)−C(6)−N(7) 40.43°, N(5)−C(6)−N(7)−C(8) 30.80°] with the possibility of delocalization of the positive charge over the

Table 2. Measured (X-ray) and calculated (B3LYP/6−31G*//B3LYP/6−31G*) geometrical parameters for **10d**

Bond lengths [Å]							
	O1=C2	C2−N3	N3=C4	C4−N5	N5=C6	C6−N7	N7=C8
X-ray	1.234	1.358	1.324	1.350	1.316	1.357	1.305
DFT	1.244	1.370	1.332	1.338	1.329	1.363	1.313

Torsional angles [°]					
	O1=C2−N3=C4	C2−N3=C4−N5	N3=C4−N5=C6	C4−N5=C6−N7	N5=C6−N7=C8
X-ray	−19.59	−26.56	−35.69	−17.77	−25.25
DFT	6.2	21.6	25.6	40.3	17.0

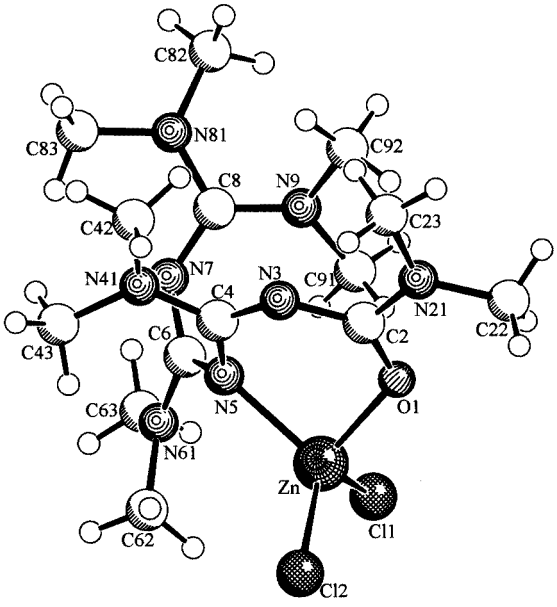


Figure 4. Molecular structure of Zn complex **10d**·$ZnCl_2$ obtained by X-ray crystallography; selected bond lengths [Å], bond angles [°], and torsion angles [°]: O(1)−C(2) 1.269(2), C(2)−N(3) 1.357(3), N(3)−C(4) 1.323(3) C(4)−N(5) 1.375(2), N(5)−C(6) 1.369(2), C(6)−N(7) 1.339(2), N(7)−C(8) 1.331(2), C(2)−N(21) 1.344(3), C(4)−N(41) 1.349(3), C(6)−N(61) 1.340(2), C(8)−N(81) 1.347(2), C(8)−N(9) 1.352(2), Zn−O(1) 1.9730(15), Zn−N(5) 2.0305(16), Zn−Cl(1) 2.2287(5), Zn−Cl(2) 2.2169(7). O(1)−C(2)−N(3) 128.64(18), C(2)−N(3)−C(4) 124.91(17), N(3)−C(4)−N(5) 126.43(18), C(4)−N(5)−C(6) 120.67(16), N(5)−C(6)−N(7) 126.62(16), C(6)−N(7)−C(8) 124.05(16), O(1)−C(2)−N(21) 117.01(18), N(3)−C(4)−N(41) 114.56(17), N(5)−C(6)−N(61) 117.19(16), N(7)−C(8)−N(81) 117.91(17), N(7)−C(8)−N(9) 123.79(16), O(1)−Zn−N(5) 91.23(7), O(1)−Zn−Cl(2) 108.25(6), N(5)−Zn−Cl(2) 116.18 (5), O(1)−Zn−Cl(1) 110.25, N(5)−Zn−Cl(1) 111.50(5). O(1)−N(2)−C(3)−N(4) −16.04(0.35), C(2)−N(3)−C(4)−N(5) 8.46(0.33), N(3)−C(4)−N(5)−C(6) −139.39(0.20), C(4)−N(5)−C(6)−N(7) 29.16(0.27), N(5)−C(6)−N(7)−C(8) 26.30(0.29), O(1)−C(2)−N(21)−C(22) −2.61(0.33), N(3)−C(4)−N(41)−C(42) 10.39(0.30), N(5)−C(6)−N(61)−C(62) 17.90(0.27), N(7)−C(8)−N(81)−C(82) −143.10(0.20), N(7)−C(8)−N(9)−C(91) 23.00(0.29), N(5)−Zn−O(1)−C(2) 32.09(0.17), Cl(2)−Zn−O(1)−C(2) −86.05(0.17), Cl(1)−Zn−O(1)−C(2) 145.58(0.15), Zn−O(1)−C(2)−N(3) −12.25(0.31).

N(3)−C(8) part of the molecule including the respective dimethylamino groups. The calculated gas-phase basicity of **10d** amounts to −264.6 kcal/mol, which is ca. 11 kcal/mol more than that of pentamethylguanidine (−253.7 kcal/mol), corresponding to a basicity about three orders of magnitude higher at room temperature. It is expected that oligocyanamides without a terminal acyl group display even higher gas-phase basicities.

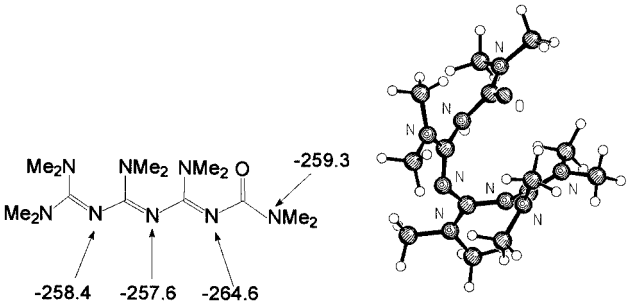


Figure 5. Calculated protonation enthalpies (kcal/mol) at various basic sites of **10d** and structure of the energy lowest protonation product (ΔH_{prot} = −264.6 kcal/mol) (B3LYP/6−31G*).

Cyclovoltammetry

As for the corresponding hydrocarbon analogues,[21] oligoenes, easier oxidation and reduction might be expected with extension of the chain length. With regard to the electron-rich nature of the compounds **6, 9, 10** due to the dimethylamino substituents, we concentrated our efforts on the cyclovoltammetric determination of the oxidation potentials of our homologous series of *N*-acyl-oligocyanamides. As expected from the geometrical data (see above), the ease of oxidation (Table 3, Figure 6) increases with increasing chain length from tetramethylurea (1.68 V) to **6** (1.64 V), **9e** (1.34 V) and **10d** (1.12 V). These first oxidations steps are chemically irreversible. In the case of **10d** a faster scan (up to 1.0 V/s between 0 and 1.8 V) also revealed no chemical reversibility. However, by scanning at 1.0 V/s to negative potentials two reduction peaks at −0.65 V and −1.15 V and an accompanying oxidation peak at −0.46 V were detected (not shown). The currents for each of the reduction peaks amounted to 12% and that for the oxidation at −0.46 V to 24% of the initial oxidation current at 1.12 V. For the more extended derivatives **9d** and **10d** a second oxidation step at 2.20 and 1.98 V, respectively, can be seen (Figure 6). Under the experimental conditions employed, these second oxidations are chemically partly reversible. For **10d** this reversibility increases at faster scan rates.

The observations point to an EC (E: electrochemical, C: chemical step) mechanism leading to two or more products. The major or whole part is further oxidized to a di-cation that can be partly reversibly reduced. A minor part of the

Table 3. Oxidation of *N*-acyl-oligodimethylcyanamides Me_2N-[$C(NMe_2)$=N]$_n$−$CONMe_2$. Calculated vertical and adiabatic ionization potentials (UB3LYP/6-316) and experimental (cyclic voltammetry) oxidation potentials

n	Vertical Ionization Potential, calcd. (eV)[a]	Adiabatic Ionization Potential, calcd. (eV)[b]	Oxidation Potential exp. (V)[c]
0 (tetramethylurea)	6.151	8.030	1.676
1 (**6**)	5.834	6.993	1.644
2 (**9d**)	5.345	6.585	1.335, 2.220
3 (**10d**)	5.032	6.175	1.120, 1.977

[a] Negative of HOMO energy. [b] $E_{(tot),\ neutral} - E_{(tot),\ radical\ cation}$ [c] Reference electrode: Ag/AgCl/satd. LiCl in ethanol (+0.26 vs. NHE)

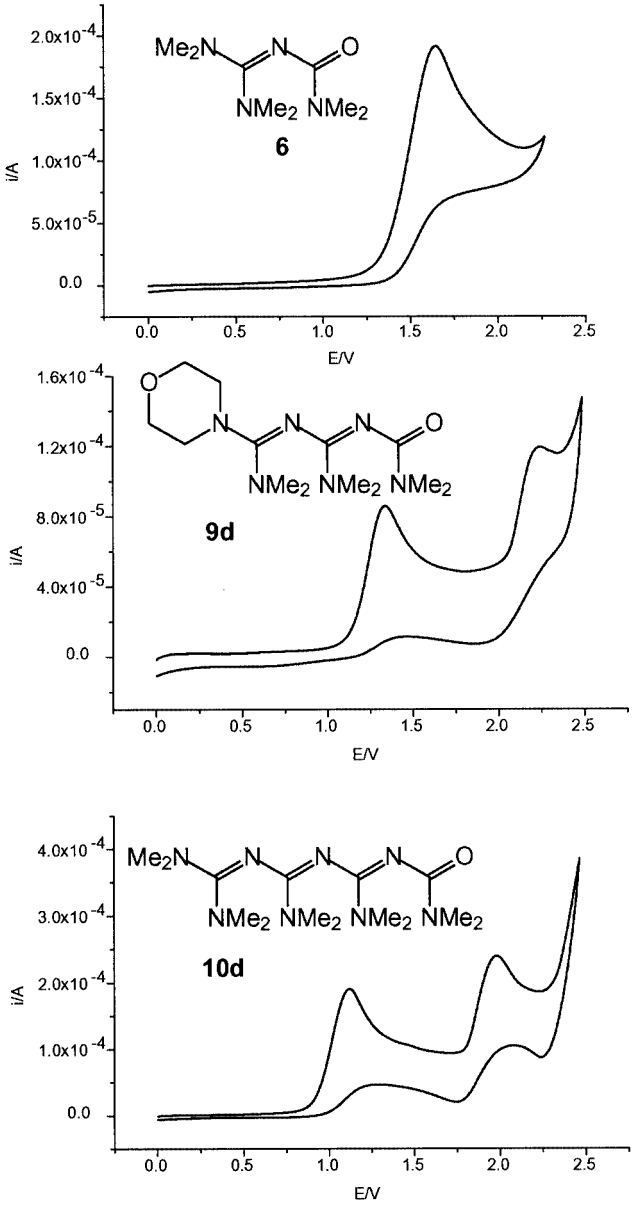


Figure 6. Cyclovoltammograms for **6, 9d** and **10d** (0.1 M $(Bu)_4N^+ClO_4^-$ in CH_3CN; potentials vs. Ag/AgCl/LiCl, scan rate 0.1 V/s).

product is reducible. Elaboration of the structure of these products and of the mechanism for their interconversion will be the subject of further investigations.

The cyclovoltammetric data are well in line with calculated DFT vertical ionization potentials (HOMO energies, correlation coefficient: $r = 0.98$) and electron-detachment energies (adiabatic ionization enthalpies, correlation coefficient: $r = 0.87$) for **6, 9e** and **10d** (Table 3).

Calculations show a very interesting structural behavior of the longer derivatives **9e** and **10d** during oxidation. In both cases the bond lengths and torsion angles are changed significantly during oxidation, resulting in non-alternating, non-helical structures with almost planar substructures, which are strongly twisted with respect to each other (Table 4). Calculations for the radical cations of **9e** and **10d** show increased O(1)−C(6) and O(1)−C(8) distances compared to their neutral precursors (difference: ca. 1.2 Å), mainly due to altered torsional angles. These observations suggest stronger, but more localized, π-interactions in the radical cations. According to the calculations, molecules like *N*-acyl-oligocyanamides change their extension during oxidation. If it will be possible to make this electron transfer for compounds like **10** a chemically reversible redox process, the picture of a molecular redox machine emerges, that converts electrical energy into linear motion.

NLO Measurements

In *N*-acyl-oligocyanamide derivatives the bond dipoles of the polar C=N and C−N bonds add to the calculated molecular gas-phase dipole moments of 3−5 Debye. For the longer examples the dipole vector of the molecules is aligned along the axis of the helix. This accumulation of adjacent polar C=N bonds in oligonitrile derivatives in general, and the chemical relationship of the *N*-acyl-oligocyanamides to urea derivatives and merocyanine dyestuff molecules, prompted us to look also at the NLO properties of these compounds (Table 5). The first hyperpolarizability β for frequency doubling was determined by HRS measurements.[22,23]

In comparison to the literature value [$\beta = 0.41 \pm 0.02\times10^{-30}$ esu (liquid, without solvent)][24] of tetramethylurea, compound **9f** shows a significantly increased β^0-value (2×10^{-30} esu). Further elongation of the chain doubles the β^0-value to 5×10^{-30} esu, as seen in compound **10d**. With regard to the molecular mass of **10d** (M_w = 326 g/mol), this value is not unusually high, but deserves attention considering the often lower β^0 values of C=N compared with C=C compounds.[25] A further increase of β^0 is measured for **10b**, (18×10^{-30} esu), possibly due to the presence of the

Table 4. Calculated (UB3LYP/6−31G*//UB3LYP/6−31G*) geometrical parameters for the radical cations of **9e** and **10d**

Bond lengths [Å]							
	O1=C2	C2−N3	N3=C4	C4−N5	N5=C6	C6−N7	N7=C8
9e	1.234	1.402	1.380	1.324	1.346	−	−
10d	1.232	1.408	1.390	1.308	1.368	1.343	1.329

Torsional angles [°]					
	O1=C2−N3=C4	C2−N3=C4−N5	N3=C4−N5=C6	C4−N5=C6−N7	N5=C6−N7=C8
9e	−22.53	58.17	5.90	−	−
10d	−18.91	68.39	0.93	59.86	24.94

Table 5. UV/Vis data and First molecular hyperpolarizabilities β at 1064 nm resp. static β^0 values in $CHCl_3$

No.	λ_{max}[nm]	β^{1064} [esu]	β^0 [esu]
Tetramethylurea	≈200[22]	$0.41 \pm 0.02\times10^{-30}$ [24]	
9f	247	3×10^{-30}	2×10^{-30}
10b	246	27×10^{-30}	18×10^{-30}
10d	251	7×10^{-30}	5×10^{-30}

phenyl substituents and the increased molecular mass of the compound (M_w = 404 g/mol). For two aryl-substituted 1-oxa-3,5,7,9-tetraazadecapentaene derivatives (without amino groups attached to the chain) β^0-values of 21×10^{-30} esu and 26×10^{-30} esu have been measured.[26]

As expected, the β^0 values increase with increasing chain lengths, similarly to the increase in the calculated dipole moments of the helical forms.

However, different configurations and conformations may be present in solutions, compared to the solid state (X-ray results) and to the gas phase (calculations). The high molecular flexibility of such oligonitrile derivatives, which arises from low barriers to rotation around the C−N bonds, might be responsible for such structural changes.[7]

Conclusion

In this paper we have reported on the synthesis of a homologous series of *N*-acyl and *N*-carbamoyl-oligonitriles with one, two, and three dimethylcyanamide subunits. For the synthesis of the longer systems, nucleophilic ring opening of the corresponding amino-substituted 1,3,5-oxadiazinium salts by amines and amidines is the method of choice. All the oligonitriles obtained adopt three-dimensional non-planar geometries in the solid state, frequently including helix-type structures. Derivative **10d** forms a stable six-membered chelate complex with $ZnCl_2$. With increasing chain length the ease of electrochemical one- and two-electron oxidation increases reaching an oxidation potential of 1.12 V for **10d**. The molecular first hyperpolarizabilities β^0 increase with chain length to give a maximum value for **10d** of 5×10^{-30} esu.

Experimental Section

Materials and Methods: IR: Perkin−Elmer PE 298. ^{1}H NMR: Bruker WM 300 (300.13 MHz) and Varian Unity plus (599.86 MHz), internal reference tetramethylsilane. ^{13}C NMR: Bruker WM 300 (75.47 MHz), Bruker AM 360 (360.13 MHz) and Varian Unity plus (150.85 MHz), internal reference tetramethylsilane or solvent. CHN: Perkin−Elmer Dia CHN 240. Melting points 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, which was thoroughly dried by repeated heating under argon and subsequent evacuation. For cyclic voltammetry the Metrohm/Eco Autolab System PG STAT 20 and Metrohm VA-Stand 663 V with the software GPES Version 4.8 were used, together with a platinum disc anode (3 mm diameter) and a glassy carbon rod cathode. The reference electrode was Ag/AgCl/satd. LiCl in ethanol (+ 0.26 vs. NHE). The measurements were obtained in Aldrich UV-grade acetonitrile with 0.1 mol/L tetrabutylammonium perchlorate as supporting electrolyte.

NLO Measurements: The first hyperpolarizability β for frequency doubling was determined by HRS measurements.[22,23] The β^{B*} convention of Willets at al.[27] was adopted for the unit of β. The measurements were carried out at the 1064 nm fundamental wavelength in $CHCl_3$. Since the compounds show no fluorescence around 532 nm, fluorescence enhancement at the second harmonic frequency can be excluded.[28] 4-Nitronaniline, β^{1064} nm = 17×10^{-30} esu in $CHCl_3$,[29] was used as an external standard. For rod-like molecules all elements of the β tensor vanish, except β_{333}. In this paper β_{333} is simply denoted as β. The dispersion-free β^0 values were extrapolated using the two-state model.[30] A detailed description of the experimental setup and the data evaluation has been described previously.[28,31]

2,4,4-Tris(dimethylamino)-1-oxa-3-azabutadiene (6): *N*,*N*,*N*′,*N*′-Tetramethylguanidine **(4)** (5.0 mL, 4.6 g, 40 mmol) was added dropwise to a solution of dimethylcarbamoyl chloride **(5)** (1.8 mL, 2.1 g, 20 mmol) in dry toluene (50 mL). The reaction mixture was heated to reflux for 1 h and the precipitate was removed by filtration. The filtrate was freed from the solvent under reduced pressure. The resulting colorless oil was purified by kugelrohr distillation (130 °C, 5×10^{-3} mbar). 2.9 g (78%)(ref.[11] 86−87 °C/0.1 Torr), colorless oil. IR (Film): $\tilde{\nu}$ = 2934 cm^{-1} (s, CH_3), 2887 (s, CH_3) 1624 (vs, C=O/C=N), 1565 (vs, C=O,C=N), 1530 (s), 1495 (s), 1431 (s), 1378 (vs), 1278 (m), 1238 (w), 1185 (s), 1155 (s), 1038 (vs), 933 (w), 857 (w), 758 (m), 623 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.80 (s, 12 H, CH_3), 2.99 (s, 6 H, CH_3) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 35.9 ppm, 39.1 (CH_3), 162.9, 164.4 ($C_{quat.}$), C=O, C=N). MS (70 eV): *m*/*z* (%) = 186 (2) [M^+], 142 (100) [$M^+ - NMe_2$], 99 (11), 83 (11), 72 (72) [Me_2NCO^+], 70 (9) [(Me_2NCN^+]. MS (ESI)): *m*/*z* (%) = 258 (20) [M + Me_2NCO^+], 187 (100) [M + H^+]. UV (acetonitrile): λ_{max} (lg ε) = 248.0 nm (7.19). Precise mass determination: calcd. 187.1559 ($C_8H_{18}N_4O$ + H^+); found 187.1566.

2-Dimethylamino-4,6-diphenyl-1,3,5-oxadiazinium Pentachlorostannate (7b): To a solution of benzonitrile (10.3 g, 0.1 mol) and dimethylcarbamoyl chloride **(6)** (5.4 g, 0.05 mol) in dry chloroform (35 mL), tin tetrachloride (5.8 mL, 12.5 g, 0.05 mol) was added slowly at 0 °C. After complete addition the reaction mixture was allowed to warm to room temperature. A colorless precipitate was formed, which disappeared again after 2 h of stirring. After 2 d at room temperature the light-yellow precipitate was removed by filtration and washed several times with dry chloroform. 19.1 g (60%), yellow solid; m.p. 136−138 °C. IR (KBr): $\tilde{\nu}$ = 1680 (vs) cm^{-1}, 1600 (vs), 1590 (vs), 1560 (vs), 1500 (vs), 1480 (vs), 1440 (s), 1405 (vs), 1335 (vs), 1310 (w), 1250 (m), 1170 (m), 1120 (w), 1000 (w), 930 (vw), 820 (vw), 750 (s), 700 (m), 680 (m), 630 (m) cm^{-1}. ^{1}H NMR (300 MHz, CD_3NO_2): δ = 3.93 ppm (s, 3 H, CH_3), 4.01 (s, 3 H, CH_3), 7.63−7.94 (m, 6 H, $H_{arom.}$), 8.53−8.56 (m, 2 H, *o*-H), 8.70−8.73 (m, 2 H, *o*-H). ^{13}C NMR (75.47 MHz, CD_3NO_2): δ = 37.3 ppm (CH_3), 38.1 (CH_3), 125.9, 129.0, 129.3, 129.6, 130.4, 131.5, 131.9, 132.9 ($C_{arom.}$), 137.4, 137.7 (*i*-C), 159.1, 167.3, 172.7 (NCN, NCO). TOF-MS: *m*/*z* = cation 278 [M^+], 72 [Me_2NCO^+], anion 297 [$SnCl_5^-$].

1-Oxa-2,4-diazahexatrienes 9b,c from Morpholine and Oxadiazinium Salts. General Procedure: To a solution of morpholine **(8)** in tetrahydrofuran at −78 °C an equimolar amount of *n*-butyllithium (1.6 M in *n*-hexane) was added. This solution was stirred for 20 min at room temperature and was then added to a suspension of an equimolar amount of oxadiazinium salt **7** in dry tetrahydrofuran at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 12 h. The reaction mixture was washed at 0 °C with sodium hydroxide solution (50 mL, 1 M) and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with magnesium sulfate and the solvent was removed in vacuo.

2-Dimethylamino-6-(1-morpholino)-4,6-diphenyl-1-oxa-3,5-diazahexatriene (9b): From morpholine **(8)** (0.52 g, 6 mmol) in tetrahydrofuran (20 mL) and *n*-butyllithium (3.75 mL, 1.6 M in *n*-hexane) and oxadiazinium pentachlorostannate **7b** (3.55 g, 6 mmol). The crude solid product was washed with diethyl ether for 30 min using an ultrasound bath, filtered off and freed from the solvent in vacuo. 1.55 g (71%), colorless solid; m.p. 183 °C. IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, $CH_{arom.}$), CH 2980 (w, $CH_{aliph.}$), 2900 (w, $CH_{aliph.}$), 2840 (m, $CH_{aliph.}$), 1620 (vs), 1580 (vs), 1550 (vs), 1440 (b), 1375 (s), 1310 (s), 1290 (s), 1250 (s), 1150 (s), 1100 (s), 1075 (m), 1060 (s), 1010 (s), 940 (m), 900 (w), 865 (w),780 (s),720 (m), 700 (s), 660 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 ppm (s, 3 H, CH_3), 2.89 (s, 3 H, CH_3), 3.52 (b, 4 H, NCH_2CH_2O), 3.75 (b, 4 H, NCH_2CH_2O), 7.22−7.33 (m, 8 H, $H_{arom.}$), 7.76−7.80 (m, 2 H, $H_{arom.}$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 35.0 ppm (CH_3), 36.1 (CH_3), 46.9 (NCH_2), 66.5 (OCH_2), 127.6, 128.1, 129.7, 130.2 ($CH_{arom.}$), 132.8, 137.2 (i-C), 160.0, 162.7, 164.1 (2CN, CO). MS (70 eV): *m*/*z* (%) = 364 (22) [M^+], 320 (100) [$M^+ - N(CH_3)_2$], 292 (20) [$M^+ - (CH_3)_2NCO$], 278 (30) [$M^+ - O(C_2H_4)_2N$], 235 (22), 217 (36), 206 (23) [$(PhCN)_2^+$], 190 (26), 159 (24), 132 (43), 104 (40) [$PhCN^+ + 1$], 72 (42) [$(CH_3)_2NCO^+$], 70 (47), 57 (39). UV (acetonitrile): λ_{max} (lg ε) = 240.0 nm (4.04), 217 nm (4.03). $C_{21}H_{24}N_4O_2$ (364.19 g/mol): calcd. C 69.21 H 6.64 N 15.37; found C 69.01 H 6.42 N 15.30.

2,4-(Bis)dimethylamino-6-(1-morpholino)-6-phenyl-1-oxa-3,5-diazahexatriene (9c): From morpholine **(8)** (0.28 g, 3.23 mmol) in tetrahydrofuran (10 mL) and *n*-butyllithium (2 mL, 1.6 M in *n*-hexane) and oxadiazinium pentachlorostannate **7c**[32] (1.75 g, 3.23 mmol). The crude product was recrystallized from chloroform/triethylamine. 0.32 g (30%), yellow crystals; m.p. 149−151 °C. IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1} (vw, C−H_{arom}), 2850 (w, CH_{aliph}), 1605 (vs), 1595 (vs), 1580 (vs), 1550 (vs), 1480 (s), 1450 (s), 1425 (s), 1390 (s), 1350 (vs), 1290 (s), 1270 (s), 1250 (s), 1220 (m), 1175 (s), 1135 (s), 1110 (vs), 1060 (m), 1025 (s), 970 (m), 930 (m), 900 (w), 860 (w), 840 (w), 820 (w), 790 (m), 760 (m), 715 (w), 700 (m), 680 (w), 630 (w), 610 (m) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.26 ppm (b, 3 H, CH_3), 2.74 (b, 3 H, CH_3), 2.96 (s, 6 H, CH_3), 3.49 (b, 4 H, NCH_2CH_2O), 3.70 (s, 4 H, NCH_2CH_2O), 7.23−7.39 (m, 5 H, $H_{arom.}$). ^{13}C NMR (150.85 MHz, $CDCl_3$): δ = 34.9 ppm (CH_3), 36.3 (CH_3), 37.0 (CH_3), 45.7 ($NCH_2CH_2CH_2O$), 66.4 ($NCH_2CH_2CH_2O$), 127.6, 127.8, 129.4 ($C_{arom.}$), 132.8 (*i*-C), 160.0, 160.3, 162.8 (C=N,C=O). MS (70 eV): *m*/*z* (%) = 331 (16) [M^+], 287 (90) [$M^+ - N(CH_3)_2$], 245 (20) [$M^+ - N(C_2H_4)_2O$], 230 (18), 217 (17), 200 (17), 184 (15), 147 (12), 83 (36), 72 (100) [$(CH_3)_2NCO^+$]. UV (dichloromethane): λ_{max} (lg ε) = 238.5 nm (4.24). $-C_{17}H_{25}N_5O_2$ (331.20 g/mol) calcd. C 61.61 H 7.60 N 21.13; found C 61.71 H 7.65 N 20.71.

2,4,6-Tris(dimethylamino)-6-(1-morpholino)-1-oxa-3,5-diaza-1,3,5-hexatriene (9d): A solution of 2,4,6-tris(dimethylamino)-1,3,5-oxadiazinium chloride **(7d)**[33] (3.1 g, 12.5 mmol) in dry dichloromethane (35 mL) was treated with morpholine **(8)** (1.1 mL, 12.5 mmol) and stirred for 2.5 h at room temperature. Subsequently, the solvent was removed in vacuo and the residue was treated with a mixture of ethyl acetate and triethylamine (1:1, 20 mL). The resulting suspension was filtered using a short column [Al_2O_3 (neutral, ca. 15 g), eluent: ethyl acetate/triethylamine, (1:1, 200 mL)]. The filtrate was freed from the solvent in vacuo and the residue was dissolved in chloroform (10 mL). The solution was treated with *i*-hexane (35 mL) and mixed. A colorless solid precipitate was filtered off and dried in vacuo. 2.4 g, (64%); m.p. 100 °C. IR (KBR): $\tilde{\nu}$ = 2916 cm^{-1}, 2850 (m, $CH_{aliph.}$), 1597, 1543, 1518 (vs C=O/C=N), 1467 (s), 1427 (s), 1390 (s), 1359 (s), 1277 (m), 1170 (m), 1028 (m), 845 (w), 767 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CHCl_3$): δ = 2.48 [s, 6H $N(CH_3)_2$], 2.66 [s, 6 H, $N(CH_3)_2$], 2.72 [s, 6 H, $N(CH_3)_2$], 2.91 (t, ^3J = 5 Hz, 4 H, NCH_2CH_2O), 3.34 (t, ^3J = 5 Hz, 4 H, NCH_2CH_2O). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 37.2, 37.3, 39.1 [$N(CH_3)_2$], 48.0 (NCH_2CH_2O), 66.8 (NCH_2CH_2O), 160.3, 162.7, 163.2 (C=N, C=O). MS (70 eV): *m*/*z* (%) = 298 (1) [M^+], 254 (100) [$M^+ - NMe_2$], 212 (15) [$M^+ - NC_4H_8O$], 169 (3), 84 (55), 72 (60)[Me_2NCO^+].

6-Diethylamino-2,4,6-tris(dimethylamino)-1-oxa-3,5-diaza-1,3,5-hexatriene (9e): A solution of 2,4,6-tris(dimethylamino)-1,3,5-oxadiazinium chloride **(7d)**[33] (3.7 g, 15 mmol) in dry dichloromethane (30 mL) was treated with diethylamine (3.1 mL, 30 mmol) and stirred for 2 h at room temperature. Subsequently, the solvent was removed in vacuo and the residue was treated with a mixture of ethyl acetate and triethylamine (1:1, 15 mL). The resulting suspension was filtered using a short column [Al_2O_3 (neutral, ca. 15 g), eluent: ethyl acetate/triethylamine, 1:1, 200 mL)]. The filtrate was freed from the solvent in vacuo and the residue was dissolved in dichloromethane (10 mL). The solution was carefully treated with *i*-hexane (30 mL) to form an upper layer. From this crystallization colorless crystals were obtained in the course of a couple of days. They were filtered off and dried in vacuo. 2.2 g, (50%); m.p. 112 °C. IR (CH_2Cl_2, NaCl): $\tilde{\nu}$ = 2862 cm^{-1} (m, $CH_{aliph.}$),1607−1550 (br. C=O/C=N), 1335 (s), 1185 (s), 970 (m), 840 (m), 723 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CHCl_3$): δ = 1.14 (t, ^3J = 7 Hz, 6 H, CH_2CH_3), 2.67 [s, 6 H, $N(CH_3)_2$], 2.94 [s, 6 H, $N(CH_3)_2$], 3.01 [s, 6 H, $N(CH_3)_2$], 3.23 (q, ^3J = 7 Hz, 4 H, CH_2CH$_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.8 [$N(CH_2CH_3)_2$], 37.1, 39.0, 42.1 [$N(CH_2CH_3)_2$]/[$N(CH_3)_2$], 160.5, 162.2, 163.2 (C=N, C=O) ppm. MS (ESI): *m*/*z* (%) = 285 (10) [M + H$^+$], 240 (100) [$M^+ - NMe_2$], 212 (8) [$M^+ - NEt_2$]. $C_{13}H_{28}N_6O$ (326.44) calcd. C 54.90 H 9.92 N 29.55; found C 54.76 H 9.94 N 29.73.

X-ray Crystal Structure Analysis of 9e:[34] Empirical formula $C_{13}H_{28}N_6O$, M = 284.41, colorless crystal 0.40 × 0.25 × 0.15 mm, a = 9.068(1), b = 9.496(2), c = 11.176(3) Å, α = 94.05(2), β = 108.45(2), γ = 114.88(1)°, V = 804.6(3) Å^3, $\rho_{calcd.}$ = 1.174 g cm^{-3}, μ = 6.29 cm^{-1}, empirical absorption correction via ψ scan data ($0.787 \leq T \leq 0.912$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 3453 reflections collected (±h, ±k, −l), [(sinθ)/λ] = 0.62 Å^{-1}, 3279 independent (R_{int} = 0.021) and 2999 observed reflections [$I \geq 2\ \sigma(I)$], 190 refined parameters, R = 0.054, wR^2 = 0.164, max. residual electron density 0.31 (−0.25) e·Å^{-3}, hydrogens calculated and refined as riding atoms.

2,4,6-Tris(dimethylamino)-6-methoxy-1-oxa-3,5-diaza-1,3,5-hexatriene (9f): A suspension of sodium methoxide (2.4 g, 44 mmol) in tetrahydrofuran (70 mL) was treated at −70 °C with 2,4,6-tris(dimethylamino)-1,3,5-oxadiazinium chloride (**7d**)[33] (5.0 g, 20 mmol). The suspension was allowed to warm to room temperature over the course of 18 h. After washing with saturated sodium bicarbonate solution (40 mL), the aqueous layer was extracted with three portions (each 30 mL) of dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo. The remaining oil was treated with *n*-hexane (10 mL). After 24 h at −5 °C a colorless solid was formed. 2.1 g (43%); m.p. 74 °C. IR (Film, NaCl): ṽ = 2929 cm^{-1}, 2873 (m, $CH_{aliph.}$),1623, 1597 (v C=O/C=N), 1539 (s), 1492 (s), 1456 (s), 1419 (m), 1394 (s), 1359 (s) 1298 (m), 1277 (m), 1232 (m), 1209 (m), 1182 (s), 1060 (s), 1033 (s), 987 (w), 950 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72 ppm [s, 6 H, $N(CH_3)_2$], 2.88 [s, 6 H, $N(CH_3)_2$], 2.92 [s, 6 H, $N(CH_3)_2$], 3.73 (s, 3 H, OCH_3). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 36.4 ppm [$N(CH_3)_2$], 36.9 [$N(CH_3)_2$], 37.4 [$N(CH_3)_2$], 55.3 (OCH_3), 158.0, 158.3, 163.5 (C=N, C=O). MS (70 eV): m/z (%) = 243 (4) [M$^+$], 229 (4), 212 (1) [M$^+$ − OMe], 199 (100) [M$^+$ − NMe_2],185 (15), 171 (1) [M$^+$ − Me_2NCO], 154 (4), 142 (8) [M$^+$ − $Me_2NMeOCN$], 140 (31) [$(Me_2NCN)_2^+$], 128 (4), 98 (2), 72 (98) [Me_2NCO^+]. UV (chloroform): λ_{max} (lg ε) = 247.4 nm (4.58).

X-ray Crystal Structure Analysis of 9f:[34] Empirical formula $C_{10}H_{21}N_5O_2$, M = 243.32, colorless crystal 0.50 × 0.50 × 0.30 mm, a = 12.428(1), b = 7.488(1), c = 28.687(2) Å, V = 2669.6(5) Å^3, $\rho_{calcd.}$ = 1.211 g cm^{-3}, μ = 7.15 cm^{-1}, empirical absorption correction via ψ scan data ($0.716 \leq T \leq 0.814$), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 2712 reflections collected (−h, −k, −l), [(sinθ)/λ] = 0.62 Å^{-1}, 2712 independent (R_{int} = 0.000) and 2478 observed reflections [$I \geq 2\ \sigma(I)$], 162 refined parameters, R = 0.045, wR^2 = 0.140, max. residual electron density 0.27 (−0.20) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

1-Oxa-3,5,7-triazaoctatetraenes 10a−c from 1,3,5-Oxadiazinium Salts and *N,N,N′,N′*-Tetra-methylguanidine. General Procedure: To a solution of *N,N,N′,N′*-tetramethylguanidine (**4**) in dry tetrahydrofuran at −78 °C an equimolar amount of *n*-butyllithium (1.6 M in *n*-hexane) was added. After 20−30 min stirring at room temperature the solution was added to a cooled (−78 °C) suspension of an equimolar amount of 1,3,5-oxadiazinium salt **7** in dry tetrahydrofuran and warmed to room temperature with stirring. After washing with sodium hydroxide solution (50 mL, 1 M) the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with magnesium sulfate and the solvent was removed in vacuo. The crude product was suspended in a 1:1 mixture of ethyl acetate and triethylamine. This suspension was filtered by use of a short column [Al_2O_3 (neutral, ca. 15 g), eluent: ethyl acetate/triethylamine (1:1, 200 mL)].

8,8-Bis(dimethylamino)-2,4,6-triphenyl-1-oxa-3,5,7-aza-1,3,5,7-octatetraene (10a): From *N,N,N′,N′*-tetramethylguanidine **(4)** (0.81 g, 7 mmol), *n*-butyllithium (4.4 mL, 1.6 M in *n*-hexane) and triphenyl-1,3,5-oxadiazinium pentachlorostannate[35] **7a** (4.28 g, 7 mmol). The filtrate was freed from the solvent in vacuo and the residue was treated with *i*-hexane (300 mL). Colorless crystals were formed within 3−4 days, 2.15 g (72%), colorless solid; m.p. 149 °C. IR (KBr): ṽ = 3050 cm^{-1} (w, $CH_{arom.}$), 2970 (w, $CH_{aliph.}$), 1650 (vs, C=O), 1605 (s), 1510 (vs), 1465 (s), 1440 (s), 1420 (s), 1390 (s), 1310 (m), 1275 (s), 1240 (s), 1170 (m), 1155 (m), 1090 (m), 1040 (m), 1020 (m), 995 (m), 920 (w), 880 (m), 800 (s), 780 (m), 755 (s), 710 (s), 700 (s), 690 (s), 680 (m), 660 (m), 640 (w), 615 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.69 ppm (s, 12 H, CH_3), 7.25−7.41 (m, 9 H, $H_{arom.}$), 7.72−7.75 (m, 2 H, *o*-H), 7.91−7.94 (m, 2 H, *o*-H), 8.02−8.04 (m, 2 H, *o*-H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 40.5 ppm (CH_3), 129.1, 129.3, 129.4, 129.8, 130.2, 131.6, 132.8 ($C_{arom.}$), 136.6, 137.7, 139.3 (*i*-C), 163.5, 163.8, 164.8 (C=N), 181.7 (C=O). MS (70 eV): m/z (%) = 424 (10) [M$^+$ − 1], 348 (18) [M$^+$ − Ph], 310 (37) [M$^+$ − 1-$((CH_3)_2N)_2CN$], 304 (22) [M$^+$ − Ph−$N(CH_3)_2$], 277 (36), 205 (37), 132 (37), 103 (100) [PhCN$^+$], 77 (54) [Ph$^+$]. UV (acetonitrile): λ_{max} (lg ε) = 241 (4.36), 213.2 (4.36). $C_{26}H_{27}N_5O$ (425.22 g/mol) calcd. C 73.39 H 6.39 N 16.46; found C 73.46 H 6.14 N 16.10.

X-ray Crystal Structure Analysis of 10a:[34] Empirical formula $C_{26}H_{27}N_5O$, M = 425.53, colorless crystal 0.60 × 0.50 × 0.30 mm, a = 14.429(1), b = 15.766(2), c = 10.167(1) Å, β = 90.62(1)°, V = 2312.7(4) Å^3, $\rho_{calcd.}$ = 1.222 g cm^{-3}, μ = 6.10 cm^{-1}, empirical absorption correction via ψ scan data ($0.711 \leq T \leq 0.838$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 4982 reflections collected (±h, +k, -l), [(sinθ)/λ] = 0.62 Å^{-1}, 4705 independent (R_{int} = 0.063) and 4147 observed reflections [$I \geq 2\sigma(I)$], 294 refined parameters, R = 0.051, wR^2 = 0.145, max. residual electron density 0.30 (−0.23) e·Å^{-3}, hydrogens calculated and refined as riding atoms.

2,8,8-Tris(dimethylamino)-4,6-diphenyl-1-oxa-3,5,7-aza-1,3,5,7-octatetraene (10b): From 2-dimethylamino-4,6-diphenyl-1,3,5-oxadiazinium pentachlorostannate (**7b**), (3.13 g, 5.5 mmol), N*N,N′,N′*-tetramethylguanidine **(4)** (0.63 g, 0.69 mL, 5.5 mmol) and *n*-butyllithium (3.44 mL, 1.6 M in *n*-hexane). The filtrate was freed from the solvent in vacuo and the residue was treated with cyclohexane (50 mL). Colorless crystals were formed within 5−7 days, 1.17 g (54%), colorless solid; m.p. 115 °C. IR (KBr): ṽ = 3050 cm^{-1} (vw, $CH_{arom.}$), 2900 (m, $CH_{aliph.}$),1645 (vs, C=O), 1610 (vs, C=N), 1580 (s), 1570 (s), 1530 (s), 1510 (s), 1460 (s), 1440 (s)1420 (s), 1370 (vs), 1305 (m), 1270 (s), 1230 (m), 1170 (s), 1150 (m), 1120 (m), 1060 (m), 1020 (w), 1000 (s), 920 (w), 880 (w), 840 (vw), 800 (w), 770 (w), 750 (w), 730 (vw), 690 (s), 675 (w), 660 (w), 630 (vw), 610 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 ppm (s, 12 H, CH_3), 3.01 (s, 3 H, CH_3), 3.02 (s, 3 H, CH_3), 7.29−7.39 (m, 6 H, $H_{arom.}$), 7.76−7.79 (m, 2 H, *o*-H), 7.91−7.94 (m, 2 H, *o*-H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 35.5 ppm (CH_3), 36.6 (CH_3), 38.9 (CH_3), 127.8, 128.3, 129.7, 130.0 ($C_{arom.}$), 136.6, 138.5 (*i*-C), 162.1, 162.9, 163.0, 165.4 (C=N, C=O). MS (70 eV): m/z (%) = 392 (5) [M$^+$], 348 (100) [M$^+$ − NMe_2], 103 (23) [PhCN$^+$], 72 (37) [Me_2NCO]. UV (Chloroform): λ_{max} (lg ε) = 246.0 nm (4.43), 301.2 (3.93). $C_{23}H_{28}N_6O$ (404.23 g/mol) calcd. C 67.31 H 7.19 N 21.42; found C 67.35 H 7.33 N 21.23.

X-ray Crystal Structure Analysis of 10b:[34] Empirical formula $C_{22}H_{28}N_6O$, M = 392.50, colorless crystal 0.25 × 0.20 × 0.10 mm, a = 7.790(1), b = 9.713(1), c = 28.670(1) Å, V = 2169.3(4) Å^3, $\rho_{calcd.}$ = 1.202 g cm^{-3}, μ = 6.16 cm^{-1}, empirical absorption correction via ψ scan data ($0.861 \leq T \leq 0.941$), Z = 4, orthorhombic,

space group $P2_12_12_1$ (No. 19), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 2547 reflections collected ($-h$, $-k$, $+l$), [(sinθ)/λ] = 0.62 Å^{-1}, 2547 independent (R_{int} = 0.000) and 2261 observed reflections [$I \geq 2\ \sigma(I)$], 269 refined parameters, R = 0.043, wR^2 = 0.126, max. residual electron density 0.24 (−0.20) e·Å^{-3}, Flack parameter −0.9(6), hydrogens calculated and refined as riding atoms.

2,4,8,8-Tetrakis(dimethylamino)-6-phenyl-1-oxa-3,5,7-triaza-1,3,5,7-octatetraene (10c): From oxadiazinium pentachlorostannate **7c**[32] (2.98 g, 5.5 mmol), *N*,*N*,*N*′,*N*′-tetramethylguanidine **(4)** (0.63 g, 0.69 mL, 5.5 mmol) and *n*-butyllithium (3.40 mL, 1.6 M in *n*-hexane). The filtrate was freed from the solvent in vacuo and the residue was treated with *i*-hexane (350 mL). Colorless crystals were formed within 5−7 days,. 0.61 g (31%), colorless crystals; m.p. 147 °C. IR (KBr): ṽ = 3010 cm^{-1} (vw, $CH_{arom.}$), 2910 (m, $CH_{aliph.}$), 1610 (vs), 1600 (vs), 1575 (vs), 1560 (vs), 1520 (vs), 1450 (s), 1410 (vs), 1390 (vs), 1355 (vs), 1280 (s), 1240 (m), 1195 (s), 1170 (s), 1155 (s), 1105 (m), 1060 (w), 1025 (s), 965 (w), 910 (w), 885 (m), 850 (w), 820 (vw), 800 (w), 760 (m), 730 (w), 710 (m), 695 (w), 610 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.46 ppm (s, 12 H, CH_3), 2.74 (s, 3 H, CH_3), 2.77 (s, 9 H, CH_3), 7.08−7.09 (m, 3 H, $CH_{arom.}$), 7.32−7.33 (m, 2 H, *o*-CH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 36.4 ppm, 37.5, 40.1, 40.6 (CH_3), 128.2, 129.8 ($C_{arom.}$), 140.0 (*i*-C), 161.1, 162.1, 162.3, 164. 6 (C=N, C=O). MS (70 eV): *m*/*z* (%) = 359 (21) [M$^+$], 315 (58) [M$^+$ − NMe_2], 289 (10), 262 (52), 245 (60), 218 (80), 174 (58), 140 (64), 115 (87) [$(Me_2N)_2CN^+$], 105 (90), 77 (80) [Ph^+], 72 (100) [Me_2NCO^+]. UV (dichloromethane): λ_{max} (lg ε) = 235.5 nm (4.34), 325.0 nm (4.02). $C_{18}H_{29}N_7O$ (358.47 g/mol) calcd. C 60.14 H 8.13 N 27.28; found C 60.02 H 8.39 N 27.16.

X-ray Crystal Structure Analysis of 10c:[34] Empirical formula $C_{18}H_{29}N_7O$, M = 359.48, colorless crystal 1.00 × 0.65 × 0.45 mm, a = 7.025(1), b = 18.303(1), c = 15.280(1) Å, β = 95.88(1)°, V = 1954.3(3) Å^3, $\rho_{calcd.}$ = 1.222 g cm^{-3}, μ = 6.45 cm^{-1}, empirical absorption correction via ψ scan data (0.565 ≤ T ≤ 0.760), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 4313 reflections collected ($-h$, $-k$, $\pm l$), [(sinθ)/λ] = 0.62 Å^{-1}, 3985 independent (R_{int} = 0.013) and 3708 observed reflections [$I \geq 2\ \sigma(I)$], 232 refined parameters, R = 0.046, wR^2 = 0.127, max. residual electron density 0.28 (−0.20) e·Å^{-3}, hydrogens calculated and refined as riding atoms.

2,4,6,8,8-Pentakis(dimethylamino)-1-oxa-3,5,7-aza-1,3,5,7-octatetraene (10d): The synthesis of **10d** was achieved by two procedures.

Method A: A solution of 2,4,6-tris(dimethylamino)-1,3,5-oxadiazinium chloride (**7d**)[33] (3.72 g, 15 mmol) in dry dichloromethane (30 mL) was treated with *N*,*N*,*N*′,*N*′-tetramethylguanidine (**4**) (3.7 mL, 3.45 g, 30 mmol) and stirred at room temperature for 2 h. The volume of the solution was reduced in vacuo and the residue was suspended in a 1:1 mixture of ethyl acetate and triethylamine. This suspension was filtered using a short column [Al_2O_3 (neutral, ca. 15 g), eluent: ethyl acetate/triethylamine (1:1, 200 mL)]. The filtrate was freed from the solvent in vacuo and the resulting residue was treated with *i*-hexane (50 mL). Colorless crystals were formed within several hours, 3.4 g, (70%); m.p. 98 °C.

Method B: To *N*-trimethylsilyl-*N*′,*N*′,*N*″,*N*″-tetramethylguanidine (0.93 g, 5 mmol) and 2,4,6-tris(dimethylamino)-1,3,5-oxadiazinium chloride **7d**[33] (1.23 g, 5 mmol), dissolved in dry chloroform (20 mL) a very small amount (ca. 1 mg) of tetrabutylammonium fluoride was added. The reaction mixture was heated to reflux for 45 min. After cooling to room temperature the solvent was removed in vacuo. Then the workup followed method A. 0.8 g colorless crystals, (50%); m.p. 98 °C. IR (CH_2Cl_2, NaCl): ṽ = 2910 cm^{-1} (m, $CH_{aliph.}$), 1660 (s, C=N/C=O), 1605 (s, C=N/C=O), 1560 (s, C=N), 1500 (vs), 1380 (vs), 1250 (s), 1160 (s), 1050 (m), 1025 (m), 890 (w), 680 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CHCl_3$): δ = 2.65 ppm [s, 12 H, $N(CH_3)_2$], 2.81 [s, 6 H, $N(CH_3)_2$], 2.91 [s, 6 H, $N(CH_3)_2$], 2.98 [s, 6 H, $N(CH_3)_2$]. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 35.9 ppm, 36.8, 37.2, 38.4 (CH_3), 158.7, 160.8 160.9, 161.5 (C=N, C=O). MS (70 eV): *m*/*z* (%) = 326 (5) [M$^+$], 282 (100) [M$^+$ − NMe_2], 237 (10) [M$^+$ − 2NMe_2], 212 (25) [M$^+$ − $(NMe_2)_2C$=N], 166 (17), 140 (10), 86 (28), 84 (38), 72 (88) [Me_2NCO]. UV (Chloroform): λ_{max} (lg ε) = 251.3 nm (4.55). $C_{14}H_{30}N_8O$ (326.44) calcd. C 51.51 H 9.26 N 34.33; found C 51.30 H 9.36 N 33.73.

X-ray Crystal Structure Analysis of 10d:[34] Empirical formula $C_{14}H_{30}N_8O$, M = 326.46, colorless crystal 0.50 × 0.30 × 0.20 mm, a = 8.664(2), b = 16.951(3), c = 12.499(2) Å, β = 95.44(2)°, V = 1827.4(6) Å^3, $\rho_{calcd.}$ = 1.187 g cm^{-3}, μ = 0.81 cm^{-1}, empirical absorption correction via ψ scan data (0.961 ≤ T ≤ 0.984), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 293 K, ω/2θ scans, 3875 reflections collected ($\pm h$, $-k$, $+l$), [(sinθ)/λ] = 0.62 Å^{-1}, 3708 independent (R_{int} = 0.030) and 2316 observed reflections [$I \geq 2\ \sigma(I)$], 218 refined parameters, R = 0.049, wR^2 = 0.127, max. residual electron density 0.26 (−0.18) e·Å^{-3}, hydrogens calculated and refined as riding atoms.

Zn-Complex of 10d: A solution of **10d** (0.35 g, 1 mmol) in dichloromethane (8 mL) was treated with zinc chloride (0.14 g, 1 mmol). After removal of undissolved $ZnCl_2$ by filtration, toluene (15 mL) was carefully added to the filtrate to form an upper layer. During 5 days some solvent was allowed to evaporate and colorless crystals were formed. These were collected and dried under reduced pressure. m.p. 201 °C. Yield: 0.05 g, 11%.

X-ray Crystal Structure Analysis of 10d·$ZnCl_2$:[34] Empirical formula $C_{14}H_{30}N_8O{\times}ZnCl_2$, M = 462.73, colorless crystal 0.40 × 0.30 × 0.30 mm, a = 11.666(1), b = 14.163(1), c = 13.017(1) Å, β = 93.57(1)°, V = 2146.6(3) Å^3, $\rho_{calcd.}$ = 1.432 g cm^{-3}, μ = 14.13 cm^{-1}, empirical absorption correction via SORTAV (0.602 ≤ T ≤ 0.677), Z = 4, monoclinic, space group *C*c (No. 9), λ = 0.71073 Å, T = 198 K, ω and scans, 8245 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.71 Å^{-1}, 4659 independent (R_{int} = 0.026) and 4548 observed reflections [$I \geq 2\ \sigma(I)$], 245 refined parameters, R = 0.025, wR^2 = 0.066, max. residual electron density 0.30 (−0.30) e·Å^{-3}, Flack parameter 0.000(7), hydrogens calculated and refined as riding atoms.

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