Unsaturated Hetero Chains, II[1]

1-Oxa-3,5,7-triaza-1,3,5,7-octatetraenes – Syntheses and Structures

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Received June 2, 1993

Key Words: 1-Oxa-3,5,7-triaza-1,3,5,7-octatetraenes / Ring-chain tautomerism / Calculations, ab-initio

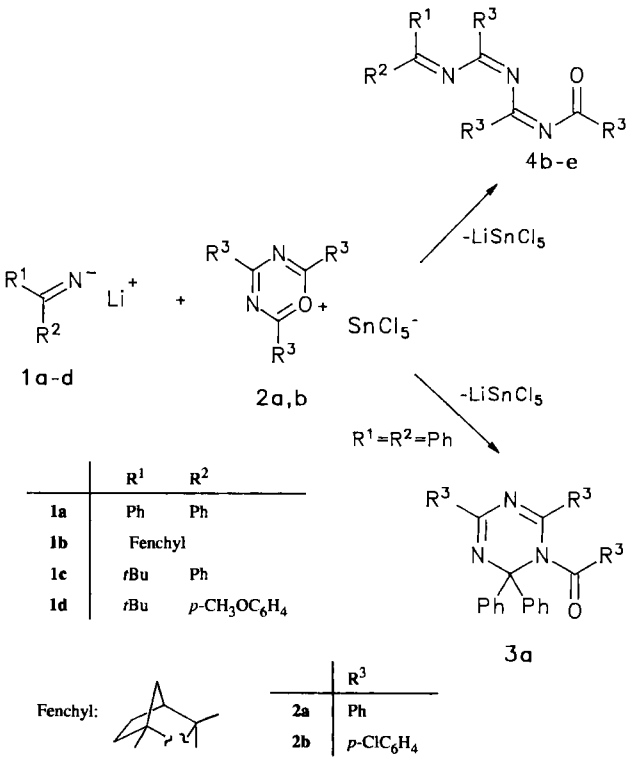
Three independent routes for the synthesis of the hitherto unknown substituted 1-oxa-3,5,7-triazaoctatetraenes **4** have been developed. Method 1 utilizes *N*-lithiated imines **1** and 1,3,5-oxadiazinium salts **2** for the synthesis of **4b–e**. Method 2 takes advantage of the new 6-alkoxy-1-oxa-3,5-diazahexatrienes **5**, which are allowed to react with imino lithium compounds to produce **4f**. Method 3 is based on the combination of the lithiated 1,3-diazabutadiene **7** with the *N*-acylimidate **8** and gives access to **4g–j**. Depending on the substitution pattern, the title compounds show ring-chain tautomerism; in the case of the pentaphenyl system, only the triazine derivative **3a** is observed. An X-ray analysis of **4f** reveals a non-planar structure with (+)-*gauche*-Z-(−)-*gauche*-Z-(+)-*gauche* conformation, resulting from amide-like n/π interactions between C=N−π systems and the lone pair of the adjacent nitrogen atoms. Detailed spectroscopic data for all open-chain and cyclic compounds are given. Quantum mechanical calculations (MP2/6-31G*//6-31G*) of model compounds **13** predict that non-planar isomers with *gauche*-configurated subunits are favored by more than 8 kcal/mol over a planar *all-trans* structure as in polyenes. Most planar isomers correspond to low-lying transition states for the rotation around the C–N bonds, but not to local minima, indicating high molecular flexibility of these oligonitrile chains.

In contrast to butadiene, which prefers the *s-trans* conformation in its ground state, 1,3-diazabutadiene and 1-oxa-3-azabutadiene favor *gauche* conformations as structures of lowest energy[2–4]. As a consequence of this stereochemical preference, complicated three-dimensional structures have to be expected for longer unsaturated chains with nitrogen atoms in odd positions (oligo- and polynitriles). To study such phenomena, we have started a series of experimental and theoretical investigations, with the aim of controlled organic syntheses of defined unsaturated hetero chains and the thorough determination of their stereochemical and dynamic behavior. In the preceding paper of this series[1], we have reported on the syntheses and properties of 1-oxa-3,5-diazahexatrienes. Now we present our results for the next higher systems, the 1-oxa-3,5,7-triazaoctatetraenes. To our knowledge, there are no previous reports on such systems in the literature.

We prefer the 1-oxa system for these studies over the all nitrogen systems (oligonitriles) since the oxygen atom at the terminus of the chain may serve as a tool for the synthetic elongation of the chain[5]; furthermore, the acyl function in these systems facilitates the spectroscopic characterization, without causing additional stereochemical problems (e.g. *E/Z* isomerism of a terminal imine function).

For the preparation of 1-oxa-3,5,7-triazaoctatetraenes **4** we have developed three different synthetic methods based on the formation of a new C–N bond between an imine nucleophile and an appropriate electrophilic reagent.

Method 1: The new compounds **4b–e** are very easily accessible from *N*-lithiated imines **1** and 1,3,5-oxadiazinium



	R^1	R^2
1a	Ph	Ph
1b	Fenchyl	
1c	*t*Bu	Ph
1d	*t*Bu	*p*-$CH_3OC_6H_4$

	R^3
2a	Ph
2b	*p*-ClC_6H_4

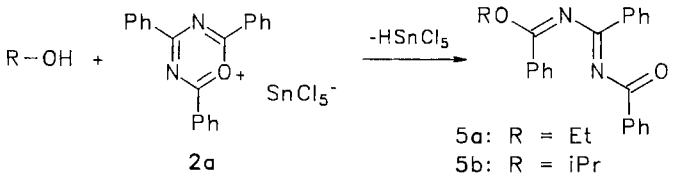
salts[6] **2**. In the case of the diphenyl derivative **1a**, however, the primary step, i.e. the nucleophile-electrophile combination, is followed by a rapid intramolecular cyclization reaction which results in the exclusive formation of the 1-acyl-1,2-dihydro-1,3,5-triazine **3a**; the corresponding open-chain compound (**4a**) is not observed.

Table 1. Yields and melting points of **3a** and **4b–e**

	R^1	R^2	R^3	Yield	m.p.
3a	Ph	Ph	Ph	71%	209°C
4b	Fenchyl		Ph	63%	156°C
4c	Fenchyl		*p*-ClC_6H_4	41%	171°C
4d	*t*Bu	Ph	Ph	32%	101°C
4e	*t*Bu	*p*-$CH_3OC_6H_4$	Ph	30%	140°C

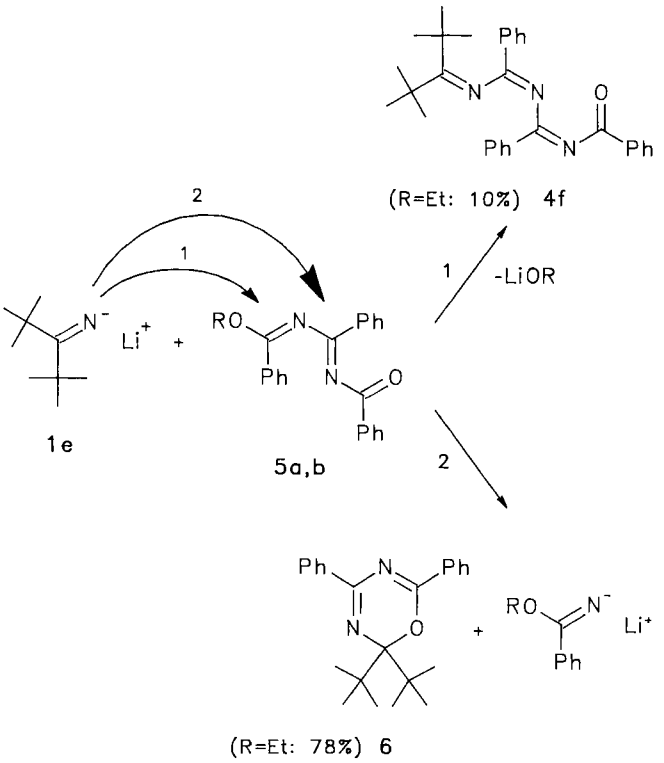
The yields mainly depend on the reactivity of the employed nucleophile **1**. The best results are obtained with the least nucleophilic aromatic lithiated imine **1a**; in contrast, the very reactive lithiated (di-*tert*-butylmethylene)amine (**1e**) gives rise to many side reactions, so that the isolation of a defined product becomes impossible.

Method 2: The reaction of *N*-acylimidates with lithiated imines has been found to be very successful in our synthesis of 1-oxa-3,5-diazahexatrienes and their cyclic tautomers (2*H*-1,3,5-oxadiazines)[1,7]. Analogously, the azavinylogous *N*-acylimidates 6-alkoxy-1-oxa-3,5-diazahexatrienes **5** have seemed to be promising electrophiles for the reactions with imine nucleophiles. These hitherto unknown compounds are easily accessible from the oxadiazinium salts **2** and anhydrous alcohols in a yield of approximately 80%.



In contrast to the oxadiazinium salt **2**, the neutral acyclic compound **5a** may also be successfully treated with more reactive nucleophiles like **1e**. However, it is a serious drawback for the synthesis of compounds **4**, that in this case the nucleophilic attack on carbon atom C-4 (path 2) is strongly favored over an attack at the terminal imidate carbon atom C-6 (path 1). Hence, the open-chain product **4f** is isolated in only 10% yield. The main product of this reaction is 2*H*-1,3,5-oxadiazine **6** (path 2; 78% yield) as a result of nucleophilic displacement of the imidate group by the lithiated imine and subsequent ring closure of the resulting 1-oxa-3,5-diazahexatriene. A variation of the alkoxy substituent in **5** shows that its steric demands influences the ratio of **4f**:**6**; with R = Et (from **5a**) a ratio **4f**:**6** of 13:87 is found, with the more bulky R = *i*Pr (from **5b**) a ratio of 1: >99.

Method 3: Methods 1 and 2 only allow the synthesis of 1-oxa-3,5,7-triazaoctatetraenes with aromatic substituents at C-2, C-4, or C-6, which result from the corresponding 1,3,5-oxadiazinium salts. However, for spectroscopic studies (UV, PES), it is desirable to obtain substances **4** bearing only aliphatic groups. Such compounds can be prepared by reaction of 1-hydrogen-substituted 1,3-diazabutadienes **7** with *N*-acylimidates **8** after deprotonation.



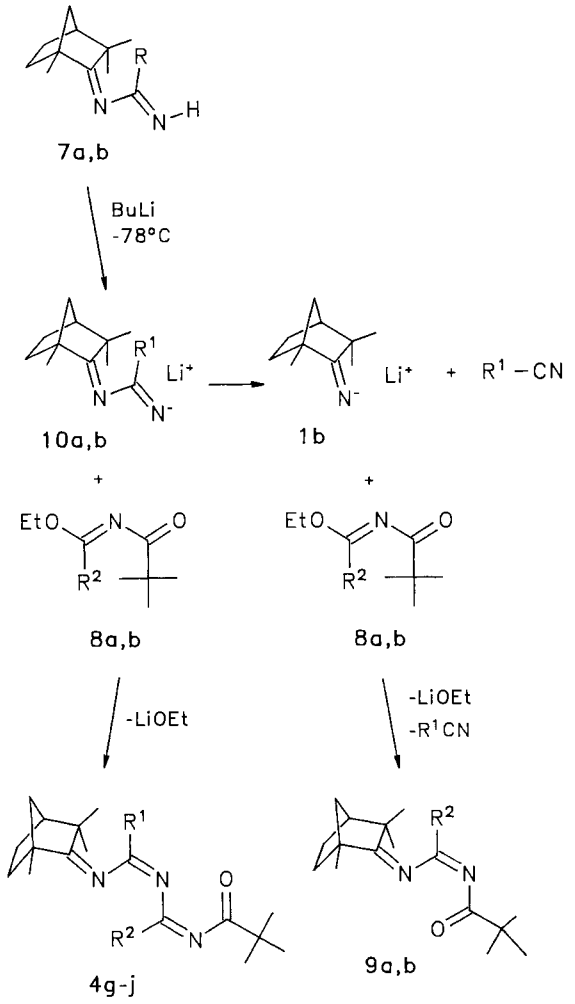
N-Acylimidates **8** are stable, well characterized compounds[8]; in contrast, 1-H-1,3-diazabutadienes are only sparingly known. Only derivatives **7** with bulky substituents at C-4 are isolable[9], less substituted derivatives dimerize spontaneously[10].

The diazabutadienes **7** are deprotonated at −78°C by using *n*-butyllithium, and the resulting solution of the lithium compound **10** is immediately treated with the *N*-acylimidate **8**. After a reaction period of 36–72 h the 1-oxa-3,5,7-triazaoctatetraenes **4g–j** are obtained after workup, together with the 1-oxa-3,5-diazahexatrienes **9a,b**, which are often the main products of the reaction (see Table 2). The formation of the oxadiazahexatrienes **9** may be explained by the decomposition of the lithiated 1,3-diazabutadienes **10**, giving nitrile and lithiated fenchone imine **1b** (nitrile absorption in the IR spectrum); **1b** then competes with **10** in the reaction with imidate **8**, leading to the hexatrienes **9**.

Table 2. Yields and melting points of **4g–j**

	R^1	R^2	Yield	m.p.	Yield of **9**
4g	Ph	Ph	41%	153°C	11%
4h	Ph	*t*Bu	19%	118°C	50%
4i	*t*Bu	Ph	14%	88°C	68%
4j	*t*Bu	*t*Bu	2.9%	47°C	79%

Again, the reactivity of the starting materials **7** and **8** governs the product distribution. Bulky groups in **7** (resp. **10**) and **8** prevent a quick addition to the electrophile, and consequently the decomposition pathway becomes predominant; the 1-oxa-3,5,7-triazaoctatetraene **4j**, which in all positions has bulky aliphatic substituents, is obtained in only 3% yield.



Spectroscopic Properties of 1-Oxa-3,5,7-triazaoctatetraenes

For the unambiguous distinction of the new open-chain compounds **4** and their cyclic isomers **3** the ^{13}C-NMR spectra are very useful. Thus, the compounds **4** show four low-field signals ($\delta > 150$) for the C=O and C=N carbon atoms with the C=O absorption in the range $\delta = 178-195$. The terminal C=N unit gives rise to a signal at $\delta = 180-188$, while the central amidine type carbon atoms absorb near $\delta = 160$.

In contrast, the isomer **3a** shows a signal for a quaternary carbon atom at $\delta = 83$, which we take as a proof for a cyclic structure. In principle, two isomeric cyclic types of compounds are possible, the 1-acyl-1,2-dihydro-1,3,5-triazine **3a** and the 2*H*-1,3,5-oxadiazine **11**. From our previous experience with 2*H*-1,3,5-oxadiazines[1] we know that absorptions for the sp^3 carbon atom are found in the range between $\delta = 92$ and 105, which is significantly lower than in the case of **3a**. An additional hint at the triazine structure **3a** is the absorption for the amide-type carbon atom at $\delta = 173$.

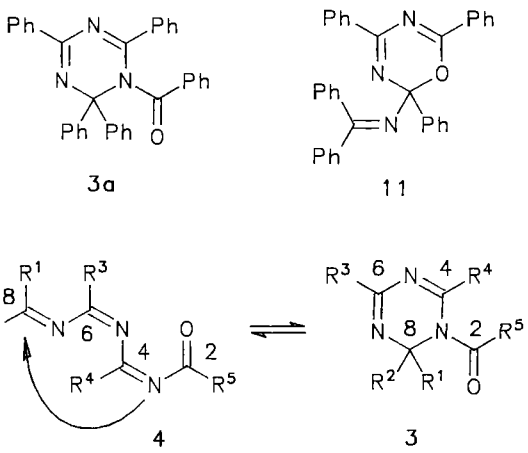


Table 3. ^{13}C-NMR data for selected compounds **3** and **4**. The numbering of the carbon atoms of **3** follows the numbering of the corresponding carbon atoms of **4** (compare formula)

	^{13}C NMR [ppm]			
	C=O	C-4	C-6	C-8
3a	173.4	161.0 / 157.6		83.20
4b	180.0	161.5 / 160.7		186.7
4e/ 3e[a]	180.4[b] 176.6 / 173.6	161.8 / 159.9 162.9/162.8/158.1/ 157.9		178.1[b] 88.61 / 87.33
4f	180.2[b]	161.9	156.0	179.7[b]
4g	194.6	157.6	161.1	186.6
4h	192.2	167.8	158.0	188.3
4j	190.6	167.1 / 165.8		182.7

[a] $T = -50$°C. – [b] The assignment C=O/C-8 is arbitrary.

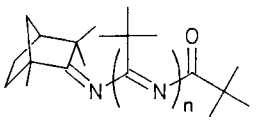
For **3e/4e**, we have been able to detect in solution both isomeric forms. Whereas the room-temperature ^{13}C-NMR spectrum of **4e** is characterized by broadened signals, three sets of sharp lines are observed at -50°C. We assign the most intense set of these lines to the open-chain isomer **4e**; for the other two sets of signals two rotamers of the acyltriazine **3e** are responsible. Obviously, there exists an equilibrium between cyclic and acyclic structures (1-oxa-3,5,7-triazaoctatetraene/1-acyl-1,2-dihydro-1,3,5-triazine tautomerism), similarly as observed for the 1-oxa-3,5-diazahexatriene/2*H*-1,3,5-oxadiazine tautomerism[1]. The preferred side of the equilibrium seems to be determined by the steric properties of the substituents at C-8. Bulky groups at C-8 (**4f, 4b, c, g–j**) destabilize the cyclic form; therefore, only the chain form is observed. However, one aryl substituent at C-8 (as in **4d, 4e**) allows the formation of the ring isomer, which becomes the only form of the pentaphenyl system **3a**.

Low-temperature ^{1}H-NMR studies have been performed to obtain quantitative data for this equilibrium. In $CDCl_3$ at -50°C, for **4e** a ratio of ca. 2:1 in favor of the chain isomer is determined, for **4d** this ratio is 3:2. The ring-chain

equilibrium is very sensitive with regard to solvent polarity. In CD_3CN at $-30\,^{\circ}C$, for **4e** a ratio of 6:1 in favor of the chain form is found, indicating an additional stabilization of the open-chain form in polar media.

The assumption of a dynamic ring-chain equilibrium for **4e** is further proven by the observation of a coalescence phenomenon in the ^{1}H-NMR spectrum at approximately 30 °C. Using the Eyring equation[11], we estimate a free enthalpy of activation of approximately 14.5 kcal/mol for this process. For the oxadiazahexatriene-oxadiazine valence isomerization we have estimated a barrier of $\Delta G^{\neq} = 12.5$ *kcal/mol*[1].

The UV spectra of **4b–i** are dominated by two intense absorptions with maxima near 210 and 250 nm; they are due to aromatic π-π* transitions. n-π* transitions are found as weak absorptions with maxima near 300 nm. More interesting are the π-π* transitions of the 1-oxa-3,5,7-triazaoctatetraene chains; they are observable in the aliphatic substituted derivative **4j**. In diethyl ether a $\lambda_{max} = 214$ nm is observed, in acetonitrile a $\lambda_{max} = 223$ nm. As for simple carbonyl compounds, a bathochromic shift with increasing solvent polarity is found.



12: n=0
9b: n=1
4j: n=2

In comparison with the corresponding data for the π-π* transitions for azavinylogous *N*-methyleneamides (**12**: n = 0: $\lambda_{max} = 214$ nm (hexane), $\lambda_{max} = 220$ nm (acetonitrile)[7]; **9b**: n = 1: $\lambda_{max} = 219$ nm (acetonitrile)[1,7]) it is quite evident that, in contrast to polyenes, elongation of the oligonitrile chain does not lead to a significant bathochromic shift. The reason for this unexpected UV spectroscopic behavior is the nonplanar structure of the C=N–[C=N]$_n$–C=O system with its strongly twisted C=N subunits, which do not allow a widely extended π conjugation.

X-Ray Structure Analysis of 4f

Configuration and conformation of a typical 1-oxa-3,5,7-triazaoctatetraene (**4f**) in the crystalline state are determined by X-ray crystallography (Figure 1); in the following discussion, the crystallographic numbering is used. As expected, an open-chain form is realized in the crystal as well as in solution (vide supra) but not the isomeric heterocycle. The bond lengths in the chain [*r*(C1–O) = 1.215(3), *r*(N1–C1) = 1.387(4), *r* (C2–N1) = 1.279(3), *r*(N2–C2) = 1.388(3), *r*(C3–N2) = 1.288(2), *r*(N3–C3) = 1.364(3), and *r*(C4–N3) = 1.269(3) Å] show pronounced alternating single and double bonds of this doubly azavinylogous *N*-methyleneamide-type molecule. Within the limits of error, the bond lengths coincide exactly with those of 2,4,6,6-tetraphenyl-1-oxa-3,5-diazahexatriene[1]. Steric strain due to the bulky *tert*-butyl groups is observed in the C3–N3=C4 part of the molecule; the bond angle C3–N3–C4 is widened to 140.9(2)° because of repulsions between these *tert*-butyl groups and the phenyl groups at C-2 and C-3. Simultaneously, the bond lengths C3–N3 and N3=C4 are shortened considerably as a result of the increased s-character at N-3. All the other bond angles of the main chain show rather normal sp^2 values [e.g. $\alpha_{N1-C1-O} = 124.5\,(2)^{\circ}$, $\alpha_{N2-C1-N1} = 121.7\,(2)^{\circ}$].

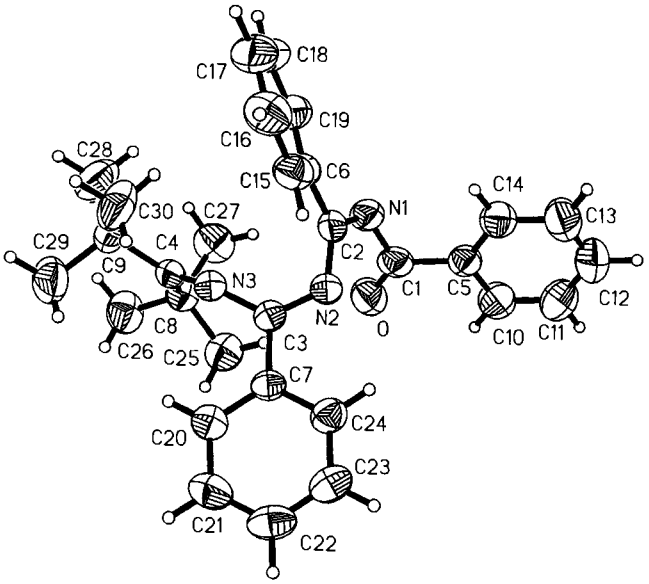


Figure 1. XS plot of the molecular structure of **4f**; crystallographic numbering and thermal ellipsoids (SHELX-PLUS[20]); bond lengths [Å]: O–C(1) 1.215(3), N(1)–C(1) 1.387(4), N(1)–C(2) 1.279(3), N(2)–C(2) 1.383(3), N(2)–C(3) 1.288(2), N(3)–C(3) 1.364(3), N(3)–C(4) 1.269(3); bond angles [°]: O–C(1)–N(1) 124.5(2), C(1)–N(1)–C(2) 121.9(2), N(1)–C(2)–N(2) 121.7(2), C(2)–N(2)–C(3) 122.9(2), N(2)–C(3)–N(3) 125.8(2), C(3)–N(3)–C(4) 140.9(2); torsional angles [°]: C(2)–N(1)–C(1)–O 72.9(3), C(1)–N(1)–C(2)–N(2) 4.7(3), C(3)–N(2)–C(2)–N(1) −129.2(2), C(2)–N(2)–C(3)–N(3) −3.7(3), C(4)–N(3)–C(3)–N(2) 86.9(4), O–C(1)–C(5)–C(14) 179.9(2), N(1)–C(2)–C(6)–C(15) −147.4(2), N(2)–C(3)–C(7)–C(20) −175.7(2), C(3)–N(3)–C(4)–C(8) 0.0(4), C(3)–N(3)–C(4)–C(9) −179.3(2)

The strongly twisted three-dimensional shape of the main chain [(+)-*gauche-Z*-(−)-*gauche-Z*-(+)-*gauche*], which is again similar to that of 2,4,6,6-tetraphenyl-1-oxa-3,5-diazahexatriene[1], is most surprising. The C2=N1–C1=O fragment may be considered to be an amide-type part with its torsional angle $\Theta_{CNCO} = 94.8^{\circ}$, indicating a strong n/π interaction with almost no π/π conjugation. The same phenomenon is observed at the terminal imino function, which is also orthogonal with respect to the C3=N2 bond [$\Theta_{C4=N3-C3=N2} = 86.9(0.4)^{\circ}$]. The central C3=N2–C2=N1 seems to prefer a compromise between the n/π and π/π interaction, since here we find a torsional angle of $-129.2(0.2)^{\circ}$ (2,4,6,6-tetraphenyl-1-oxa-3,5-diazahexatriene: $\Theta_{CNCN} = -110.6^{\circ}$).

The position of the aromatic substituents is mainly determined by electronic factors. The phenyl groups at C-1 and C-3 are coplanar with the adjacent C=O and C3=N2 bonds ($\Theta_{O-C1-C5-C10} = -0.6^{\circ}$, $\Theta_{N2-C3-C7-C24} = -3.0^{\circ}$); probably for steric reasons, the substituent at C-2 is twisted by ca. 30° out of the N3–C2=N1 plane.

The C2=N1 and C3=N2 double bonds have *Z* configuration, analogously to the central C=N bond in the corresponding heterohexatriene[1]. Obviously, the rapid valence isomerization of **4d** and **4e** leading to the cyclic isomers **3**

is facilitated by the *Z* configuration of the imine bonds of the main chain.

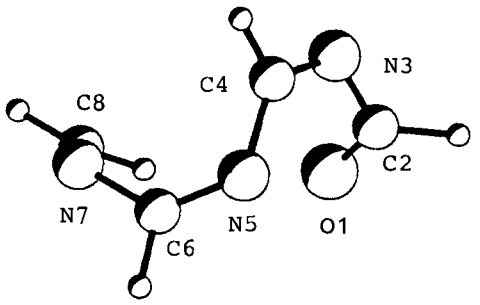
In conclusion, the X-ray analysis of **4f** demonstrates that the main chain of these 1-oxa-3,5,7-triazaoctatetraenes consists of small C=N subunits with n/π interactions to its neighbors, but has no thoroughly conjugated 8π electron systems as in octatetraene. The π/π interactions are mostly weak. A comparison with the quantum mechanical results shows (vide infra), that the twisting of the chain with the aim of giving effective n/π interactions and minimization of the dipole moment are the principal factors which govern configuration and conformation.

Intermolecular and steric factors seem not to be dominant.

Quantum Mechanical ab initio Calculations

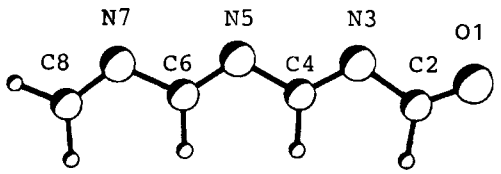
In order to better understand the conformational and dynamic properties and to rationalize the crystallographic and spectroscopic results quantum mechanical model calculations are performed. The 6-31G* basis set[12] of the GAUSSIAN 92 program[13] is used throughout. Effects of electron correlation are estimated by using the second-order Møller-Plesset theory (MP2)[14]. All molecules are completely geometry-optimized within the indicated point group. The character of the stationary points on the hyperface (NIMAG) is determined by frequency analyses. All substituents are replaced by hydrogen atoms; in the following section, results for the parent compound 1-oxa-3,5,7-triazaoctatetraene (**13**), which is experimentally not easily accessible, are discussed (Tables 4, 5). The numbering follows the relative MP2 energies, on which the discussion is based.

The number of possible conformers and configurational isomers **13** is almost unlimited. However, our experience from the shorter 1-oxa-3,5-diazahexatrienes[1] provides helpful guidelines for the search of the global minimum, for energy-low local minima, and for easily accessible transition states. Altogether, 32 planar structures for **13** may be anticipated, of which 16 show strong steric interactions between remote groups. Among the remaining 16 planar isomers only one corresponds to a minimum on the potential energy



13a

Figure 2. Ab initio-optimized structure of **13a** (C_1) (6-31G*//6-31G*); ab initio numbering; bond lengths [Å]: O(1)–C(2) 1.1906, C(2)–N(3) 1.3864, N(3)–C(4) 1.2534, C(4)–N(5) 1.3880, N(5)–C(6) 1.2531, C(6)–N(7) 1.3893, N(7)–C(8) 1.2536; bond angles [°]: O(1)–C(2)–N(3) 125.33, C(2)–N(3)–C(4) 121.98, N(3)–C(4)–N(5) 126.17, C(4)–N(5)–C(6) 122.28, N(5)–C(6)–N(7) 127.64, C(6)–N(7)–C(8) 121.13; torsional angles [°]: O(1)–C(2)–N(3)–C(4) 67.62, C(2)–N(3)–C(4)–N(5) 8.14, N(3)–C(4)–N(5)–C(6) –108.23, C(4)–N(5)–C(6)–C(7) –1.74, N(5)–C(6)–N(7)–C(8) 73.48



13j

Figure 3. Ab initio-optimized structure of **13j** (C_s) (6-31G*//6-31G*); ab initio numbering; bond lengths [Å]: O(1)–C(2) 1.1812, C(2)–N(3) 1.4014, N(3)–C(4) 1.2557, C(4)–N(5) 1.3866, N(5)–C(6) 1.2554, C(6)–N(7) 1.3923, N(7)–C(8) 1.2553; bond angles [°]: O(1)–C(2)–N(3) 123.38, C(2)–N(3)–C(4) 115.30, N(3)–C(4)–N(5) 121.21, C(4)–N(5)–C(6) 116.12, N(5)–C(6)–N(7) 120.68, C(6)–N(7)–C(8) 116.30

Table 4. Ab initio results for different conformations of the $C_4H_5N_3O$ isomers **13**, corresponding to minima on the potential hyperface (NIMAG = 0): Relative energies (6-31G*//6-31G* and MP2/6-31G*//6-31G*) [kcal/mol], dipole moments [Debye], and torsional angles Θ [°]

No.	Sym.	E_{rel} (6-31G*)	E_{rel} (MP2/ 6-31G*)	Dipole Moment	Θ_1[a]	Θ_2[a]	Θ_3[a]	Θ_4[a]	Θ_5[a]
13a	C_1	3.14	0.00	1.634	67.62	8.14	-108.23	-1.74	73.48
13b	C_1	0.00	0.25	4.411	23.78	183.12	-35.98	174.40	44.70
13c	C_1	0.33	0.87	3.394	-27.03	176.45	38.35	181.02	47.94
13d	C_1	3.19	1.41	2.187	-57.17	-6.92	73.99	178.29	53.20
13e	C_1	3.12	1.57	4.043	20.64	186.99	-66.65	-6.55	75.33
13f	C_1	3.64	1.57	4.242	63.56	6.59	-65.32	177.08	45.95
13g	C_1	1.82	1.75	3.412	-29.98	177.61	186.93	182.13	-42.06
13h	C_1	2.67	1.96	3.847	-84.51	-1.77	-191.95	178.21	43.11
13i	C_1	2.08	2.60	5.712	24.94	183.70	-40.34	176.82	183.65
13j	C_s	8.14	8.32	9.353	180.00	180.00	180.00	180.00	180.00

[a] $\Theta_1 = \Theta_{C4-N3-C2-O1}$, $\Theta_2 = \Theta_{N5-C4-N3-C2}$, $\Theta_3 = \Theta_{C6-N5-C4-N3}$, $\Theta_4 = \Theta_{N7-C6-N5-C4}$, $\Theta_5 = \Theta_{C8-N7-C6-N5}$.

Table 5. Ab initio results for different planar conformations of the $C_4H_5N_3O$ isomers **13**, corresponding to transition states on the potential hyperface (NIMAG ≥ 1): Relative energies (6-31G*//6-31G* and MP2/6-31G*//6-31G*) [kcal/mol], dipole moments [Debye], and torsional angles Θ [°]

No.	Sym.	E_{rel} (6-31G*)	E_{rel} (MP2-6-31G*)	Dipole Moment	NIMAG	Θ_1[a]	Θ_2[a]	Θ_3[a]	Θ_4[a]	Θ_5[a]
13k	C_s	3.35	5.82	3.326	2	0.	180.	180.	180.	0.
13l	C_s	4.46	6.04	5.986	2	0.	180.	180.	0.	180.
13m	C_s	3.56	6.05	5.434	2	0.	180.	0.	180.	180.
13n	C_s	2.99	6.38	3.350	3	0.	180.	0.	180.	0.
13o	C_s	4.62	6.40	3.477	1	180.	180.	0.	180.	180.
13p	C_s	5.04	6.43	5.429	1	0.	180.	180.	180.	180.
13q	C_s	6.78	7.71	9.609	1	180.	0.	180.	0.	180.

[a] $\Theta_1 = \Theta_{C4-N3-C2-O1}$, $\Theta_2 = \Theta_{N5-C4-N3-C2}$, $\Theta_3 = \Theta_{C6-N5-C4-N3}$, $\Theta_4 = \Theta_{N7-C6-N5-C4}$, $\Theta_{C8-N7-C6-N5}$.

hyperface (NIMAG = 0); it is the *all-trans* structure **13j**, which is by no means favorable in energy, but characterized by a very high dipole moment (9.353 Debye). The inequality of the C–N–C and N–C–N angles is responsible for the bow-shape of this structure, which is different from the strict linearity of polyenes (Figure 3). From our previous study[1] we know that all conformers with *s-cis* C=N–C=O and C=N–C=N subunits correspond to transition states for (+)-*gauche*-(−)-*gauche* rotation around the single bond. Similarly, we have learned that planar *Z*-configurated C=N–C=N–C=O groups also correspond to maxima on the hyperface, since twisting releases the 1,6 strain. Not surprisingly, in this series of the isomers **13** we recognize, that (*Z*)-C=N–C=N–C=N groups often also show small negative vibrational frequencies indicating transition states, not minima.

Therefore, the *all-trans* isomer **13j** is the only remaining planar minimum structure, in spite of its high relative energy of 8.32 kcal/mol.

Nevertheless, the planar structures are valuable starting points for the search of the best non-planar conformer. Thus, two non-planar conformers **13b** and **13c** with favorable relative energies (**13b**: 0.25 kcal/mol; **13c**: 0.87 kcal/mol) are derived from the *all-trans* form **13j** by full geometry relaxation (complete optimization without symmetry constraint). Both of them show *E*-configurated C=N bonds and *gauche* C–N bonds with different orientations [**13b**: (+)-*gauche-E*-(-)-*gauche-E*-(+)-*gauche* and **13c**: (−)-*gauche-E*-(+)-*gauche-E*-(+)-*gauche*, resp.]. *gauche* Conformations of C–N bonds have earlier been recognized to be significantly lower in energy than *s-trans* (*anti*) C–N bonds[1]. The best structure (**13a**) found in our study is derived from a planar form with two (*Z*)-C=N groups and three *s-trans* C–N bonds (**13q**, E_{rel} = *7.71 kcal/mol*, NIMAG = 1) (Figure 2). Twisting of the C–N bonds from the *s-trans* conformation in **13q** to the corresponding *gauche* conformations lowers the total energy very considerably and leads to this global minimum **13a** [E_{tot} (6-31G*//6-31G*) = −392.53152 a.u.; E_{tot} (MP2/6-31G*//6-31G*) = −393.67573 a.u.; E_{rel} = 0.00 kcal/mol; Zero Point Energy (ZPE) = 64.48 kcal/mol] with (+)-*gauche-Z*-(−)-*gauche-Z*-(+)-*gauche* structure. Much to our satisfaction, this isomer **13a** is the direct analogue to our experimentally found X-ray structure of **4f**. Although a low dipole moment is not the only requirement for a low total energy, we conclude from the by far lowest dipole moment of **13a** (1.634 Debye), that in this series of compounds minimization of the dipole moment by compensation of the bond dipoles is a very important structure-determining property. Numerous other local minima with low relative energies are localized on the potential energy hyperface (for a small selection see Table 4, **13d–i**). At variance with **13a–f** with *gauche* C–N bonds, in the more energy-rich conformers **13g–j** some *s-trans* C–N bonds are realized. Inspection of Table 4 indicates that the planar *all-trans* structure **13j** corresponds most likely to the energy-richest local minimum of the hyperface. Thus, the structural preferences of compounds **4** and **13** are very different from those found for polyenes[15,16].

Calculations using the symmetry constraints for planar structures lead to numerous stationary points (e.g. **13k–q**) with negative imaginary frequencies (transition states of first, second, and third order) (Table 5). Table 5 further indicates a strong relation between the number of *s-cis* and *Z* features (Θ = 0°) and the number of imaginary frequencies (NIMAG). It is interesting to note that all these transition states have lower energies than the *all-trans* local minimum **13j**. Hence, high molecular flexibility of the oligonitrile chain is predicted from these calculations, not only for the twisting about the *s-cis* conformation leading to *gauche* structures, but also including *s-trans* forms, which are as well energetically easily accessible[1].

Two cyclic isomers **14** and **15** were taken as models for the compounds **3** and **11** (see above). Thus, 1-formyl-1,2-dihydrotriazine (**14**) is calculated to be lower in energy by as much as 28.54 kcal/mol (ZPE: 67.21 kcal/mol), compared to the best chain isomer **13a**. On experimental conditions, however, the predominance of such forms in ring-chain equilibria is only observed for systems without bulky substitu-

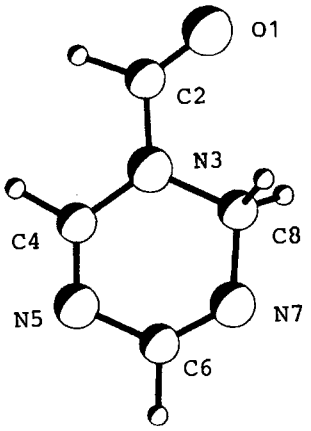


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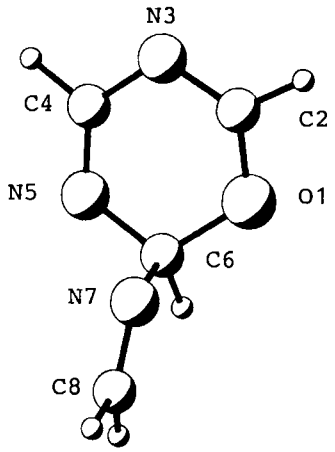
Figure 4. Ab initio-optimized structure of **14** (6-31G*//6-31G*); ab initio numbering; bond lengths [Å]: O(1)–C(2) 1.1873, C(2)–N(3) 1.3702, N(3)–C(4) 1.3670, C(4)–N(5) 1.2598, N(5)–C(6) 1.4055, C(6)–N(7) 1.2518, N(7)–C(8) 1.4330; bond angles [°]: O(1)–C(2)–N(3) 123.43, C(2)–N(3)–C(4) 121.40, N(3)–C(4)–N(5) 125.02, C(4)–N(5)–C(6) 114.96, N(5)–C(6)–N(7) 127.72, C(6)–N(7)–C(8) 120.03; the complete geometry optimization furnished an essentially planar structure ($\approx C_s$)



15

Figure 5. Ab initio-optimized structure of **15** (6-31G*//6-31G*); ab initio numbering; bond lengths [Å]: O(1)–C(2) 1.3171, C(2)–N(3) 1.2596, N(3)–C(4) 1.3961, C(4)–N(5) 1.2565, N(5)–C(6) 1.4288, C(6)–N(7) 1.4389, N(7)–C(8) 1.2474; bond angles [°]: O(1)–C(2)–N(3) 125.89, C(2)–N(3)–C(4) 113.74, N(3)–C(4)–N(5) 126.82, C(4)–N(5)–C(6) 116.23, N(5)–C(6)–N(7) 109.36, C(6)–N(7)–C(8) 117.48; torsional angles [°]: O(1)–C(2)–N(3)–C(4) –2.95, C(2)–N(3)–C(4)–N(5) 10.97, N(3)–C(4)–N(5)–C(6) 3.58, C(4)–N(5)–C(6)–C(7) 95.57, N(5)–C(6)–N(7)–C(8) 105.20

ents at C-8 (see above). As expected, 2-(methyleneamino)-2*H*-1,3,5-oxadiazine (**15**) as a model for **11** is less favorable; nevertheless, its relative energy (–5.23 kcal/mol; ZPE = 66.74 kcal/mol) again is lower than that of the chain compound **13a**. The substitution patterns in our experimentally studied systems obviously preclude the formation of these ring systems.

We thank the *Fonds der Chemischen Industrie* for financial support and the *BASF AG*, Ludwigshafen, for supplying us with chemicals.

Experimental

IR: Perkin-Elmer PE 298: – ^{1}H NMR: Bruker WM-300 (300 MHz), internal reference tetramethylsilane. – ^{13}C NMR: Bruker WM-300 (75.47 MHz) and AM-360 (90.56 MHz), internal reference tetramethylsilane. – MS: Finnigan MAT C 312. – CHN: Perkin Elmer CHN Analysator 240. – Flash chromatography: Kieselgel 60 (Merck), 0.040–0.063 mm. – Melting points are uncorrected. – All experiments are carried out with the exclusion of moisture (Ar). – All solvents are rigorously dried by standard methods.

Reaction of N-Lithiated Imines **1a–d** *with Oxadiazinium Salts* **2a,b**

Synthesis of **1a–d**: By dropwise addition of one equivalent of *n*-butyllithium (1.6 M solution in *n*-hexane) to a solution of the corresponding imine in THF (20 ml) at –78°C a solution of the iminolithium compound **1** is prepared. The mixture is warmed up to room temp. and stirred for 1/2 h. For the imines **1c,d**, a solution of the corresponding nitrile in THF (15 ml) is cooled to –196°C and dropwise treated with one aliquot of *tert*-butyllithium (1.6 M solution in *n*-pentane). The mixture is slowly warmed up to room temp. and then stirred for 0.5 h[17].

General Procedure for the Synthesis of **3a** *and* **4b–e**: A solution of the oxadiazinium salt **2** in THF (40 ml) is cooled to –78°C and slowly treated with an equimolar solution of iminolithium compound **1** (see above). Then, the cooling bath is removed; quickly a clear, yellow solution forms. The reaction mixture is stirred for 2 h at room temp., cooled to 0°C and extracted with 50 ml of ice-cold aqueous 1 N NaOH. After separation of the layers, the aqueous layer is twice extracted with dichlormethane. The combined organic extracts are dried with $MgSO_4$. After removal of the solvent at reduced pressure, the residue is purified by recrystallization or flash chromatography.

1-Benzoyl-1,2-dihydro-2,2,4,6-tetraphenyl-1,3,5-triazine (**3a**): From 1.00 g (5.5 mmol) of (diphenylmethylene)amine, 3.5 ml (5.5 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 3.36 g (5.5 mmol) of **2a**[6] triazine **3a** is obtained after recrystallization from *n*-hexane/chloroform (1:1) as a colorless solid; yield 1.92 g (71%), m.p. 209°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, CH arom.), 1675 (s, C=O), 1635 (m, C=N), 1600 (vs), 1565 (s), 1525 (s), 1480 (m), 1440 (m), 1325 (s), 1245 (vs), 1170 (m), 1155 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09–7.70 (m, 23H, arom. H), 8.51 (d, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 83.2 (N–C–N), 127.8, 128.1, 128.3, 128.4, 128.5, 129.1, 129.2 (arom. CH), 131.0, 131.8, 132.4 (*p*-C), 135.8, 136.7, 137.0, 142.6 (*i*-C), 157.6 (N–C=N), 161.0 (N–C=N), 173.4 (C=O). – MS (70 eV), *m/z* (%): 491 (15) [M$^+$], 414 (3) [M$^+$ – Ph], 386 (17) [M$^+$ – PhCO], 309 (4) [386 – Ph], 283 (21) [386 – PhCN], 180 (55) [(Ph)$_2$CN$^+$], 165 (29), 105 (100) [PhCO$^+$], 77 (81) [Ph$^+$]. – $C_{34}H_{25}N_3O$ (491.6): calcd. C 83.07, H 5.13, N 8.55; found C 82.86, H 4.94, N 8.29.

2,4,6-Triphenyl-6-[(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)-amino]-1-oxa-3,5-diaza-1,3,5-hexatriene (**4b**): From 0.85 g (5.6 mmol) of (1*R*)-fenchone imine[18], 3.5 ml (5.6 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 3.41 g (5.6 mmol) of **2a** compound **4b** is obtained as a colorless solid after flash chromatography (petroleum ether/diethyl ether, 2:1; R_f = 0.44; the crude product is dissolved in little dichloromethane before applying it to the column). Yield of **4b** 1.64 g (63%), m.p. 156°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, CH arom.), 2950 (s), 2860 (m, CH aliph.), 1705 (s, C=O), 1665 (s, C=N), 1610 (sh), 1585 (vs), 1555 (vs,), 1440 (s), 1310 (s), 1270 (s), 1235 (vs), 1170 (m), 1020 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.54 (s, 3H, CH_3), 0.88 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.25–1.88 (m, 7H, fenchyl CH, CH_2), 7.29–7.53 (m, 9H, *m/p*-H), 7.67 (d, 2H,

o-H), 7.95 (m, 2H, *o*-H), 8.07 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 16.17, 22.41 (CH_3), 24.75 (CH_2), 25.58 (CH_3), 33.16, 43.71 (CH_2), 45.66 (CH), 46.60, 53.79 ($C_{qu.}$), 127.8, 128.0, 128.1, 128.2, 128.8, 129.4 (*o*/*m*-C), 131.0, 131.4, 132.0 (*p*-C), 133.4, 134.4, 134.6 (*i*-C), 160.7 (N–C=N), 161.5 (N–C=N), 180.0 (C=O), 186.7 (C=N). – MS (70 eV), *m*/*z* (%): 461 (5) [M^+], 384 (49) [M^+ – Ph], 356 (12) [M^+ – PhCO], 311 (7) [M^+ – $C_{10}H_{16}N$], 277 (5), 105 (100) [$PhCO^+$], 103 (23) [$PhCN^+$], 77 (43) [Ph^+]. – UV (diethyl ether): λ_{max} (lg ε) = 207 nm (4.522), 246 (4.485). – $C_{31}H_{31}N_3O$ (461.6): calcd. C 80.66, H 6.77, N 9.10; found C 80.60, H 6.92, N 9.12.

2,4,6-Tris(4-chlorophenyl)-6-[(1,3,3-trimethylbicyclo[2.2.1]-hept-2-ylidene)amino]-1-oxa-3,5-diaza-1,3,5-hexatriene (**4c**): From 0.83 g (5.5 mmol) of (1*R*)-fenchone imine, 3.4 ml (5.5 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 3.91 g (5.5 mmol) of **2b**[6] compound **4c** is obtained as a colorless solid after flash chromatography (petroleum ether/diethyl ether, 5:1; R_f = 0.39; the crude product is dissolved in little dichlormethane before applying it to the column). Yield of **4c** 1.28 g (41%), m.p. 171°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w, CH arom.), 2960 (m), 2910 (w, CH aliph.), 1710 (s, C=O), 1670 (vs, C=N), 1620 (s, C=N), 1580 (vs), 1550 (s), 1480 (m), 1395 (m), 1280 (m), 1240 (m), 1165 (m), 1085 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.28–1.90 (m, 7H, fenchyl CH, CH_2), 7.26–7.41 (m, 6H, *m*/*p*-H), 7.59 (d, 2H, *o*-H), 7.87 (m, 2H, *o*-H), 7.98 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 16.20, 22.56 (CH_3), 24.75 (CH_2), 25.56 (CH_3), 33.29, 43.71 (CH_2), 45.71 (CH), 46.85, 53.97 ($C_{qu.}$), 128.5, 128.5, 128.7, 129.2, 130.2, 130.8 (*o*/*m*-C), 131.8, 132.8, 132.9 (*i*-C), 137.6, 138.0, 138.5 (C–Cl), 160.2 (N–C=N), 160.8 (N–C=N), 178.4 (C=O), 188.1 (C=N). – MS (70 eV), *m*/*z* (%): 563 (8) [M^+], 424 (7) [M^+ – ClC_6H_4CO], 413 (18) [M^+ – $C_{10}H_{16}N$], 347 (8), 139 (100) [$ClC_6H_4CO^+$], 111 (43) [$ClC_6H_4^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 209 nm (4.591), 257 (4.611). – $C_{31}H_{28}Cl_3N_3O$ (564.9): calcd. C 65.91, H 5.00, N 7.44; found C 66.12, H 5.27, N 7.21.

8-tert-Butyl-2,4,6,8-tetraphenyl-1-oxa-3,5,7-triaza-1,3,5,7-octatetraene (**4d**): From 0.64 g (6.2 mmol) of benzonitrile, 3.8 ml (6.2 mmol) of *tert*-butyllithium (1.6 M solution in *n*-pentane), and 3.80 g (6.2 mmol) of **2a** compound **4d** is obtained as light yellow crystals after flash chromatography (petroleum ether/diethyl ether, 2:1; R_f = 0.44) and recrystallization from diethyl ether. In the low-temperature ^{1}H NMR spectra besides **4d** the tautomeric *1-benzoyl-2-tert-butyl-1,2-dihydro-2,4,6-triphenyl-1,3,5-triazine* (**3d**) is observed [oxatriazaoctatetraene/acyltriazine (two isomers) ca. 1.5:1; the signals, which are unambiguously assigned to the ring tautomer, are marked with "triaz"]; yield of **4d** 0.94 g (32%), m.p. 101°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, CH arom.), 2950 (m), 2860 (w, CH aliph.), 1690 (m, C=O), 1650 (s, C=N), 1615 (vs, C=N), 1595 (m), 1565 (m), 1525 (m), 1445 (m), 1320 (s), 1240 (vs), 1170 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 [s, 9H, $C(CH_3)_3$], 6.58 (d, 2H, arom. H), 7.05 (m, 1H, *p*-H), 7.22–7.48 (m, 9H, arom. H), 7.64 (d, 2H, *o*-H), 7.76 (d, 2H, *o*-H), 8.10 (d, 2H, *o*-H). – ^{1}H NMR (–50°C, 360 MHz, $CDCl_3$): δ = 0.82 [s, 9H, $C(CH_3)_3$], 1.21, 1.41 [s, $C(CH_3)_3$, triaz], 6.47 (d, 2H, arom. H), 6.78 (d, 2H, arom. H), 7.02–7.98 (m, 14H, arom. H), 8.25 (d, 2H, *o*-H), 8.44, 8.55 (d, *o*-H, triaz). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.71 [$C(CH_3)_3$], 40.72 [$C(CH_3)_3$], 125.7, 127.4, 128.0, 128.0, 128.2, 128.7, 129.5 (arom. CH), 131.2, 131.4, 132.0 (*p*-C), 134.6, 135.0, 135.1, 135.8 (*i*-C), 161.0 (N–C=N), 161.2 (N–C=N), 178.1, 180.5 (C=N, C=O). – MS (70 eV), *m*/*z* (%): 471 (4) [M^+], 414 (3.5) [M^+ – *t*Bu], 366 (4) [M^+ – PhCO], 311 (6) [414 – PhCN], 263 (6) [366 – PhCN], 208 (8), 180 (19), 105 (100) [$PhCO^+$], 77 (47) [Ph^+], 57 (17) [tBu^+]. – UV (diethyl ether): λ_{max} (lg ε) = 217 nm (4.352), 254 (4.404). – $C_{32}H_{29}N_3O$ (471.6): calcd. C 81.45, H 6.20, N 8.91; found C 81.26, H 6.25, N 9.05.

8-tert-Butyl-8-(4-methoxyphenyl)-2,4,6-triphenyl-1-oxa-3,5,7-triaza-1,3,5,7-octatetraene (**4e**): From 1.33 g (10.0 mmol) of 4-methoxybenzonitrile, 6.3 ml (10.0 mmol) of *tert*-butyllithium (1.6 M solution in *n*-pentane), and 6.07 g (10.0 mmol) of **2a** compound **4e** is obtained as yellow crystals after flash chromatography (petroleum ether/diethyl ether, 2:1; R_f = 0.23. Low-temperature NMR spectra show besides **4e** the signals of the tautomeric *1-benzoyl-2-tert-butyl-1,2-dihydro-2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine* (**3e**) [oxatriazaoctatetraene/acyltriazine (two isomers) ca. 2:1]; yield of **4e** 1.52 g (30%), m.p. 140°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, CH arom.), 2950 (m, CH aliph.), 1680 (w, sh, C=O), 1640 (vs, C=N), 1620 (vs, C=N), 1595 (m), 1580 (m), 1550 (s), 1500 (m), 1440 (m), 1310 (m), 1260 (s), 1240 (vs), 1170 (m). – ^{1}H NMR (–50°C, 360 MHz, $CDCl_3$): δ = 0.78 [s, 9H, $C(CH_3)_3$], 1.15, 1.18, [s, $C(CH_3)_3$, triaz], 3.60 (s, 3H, OCH_3), 3.70, 3.73 (s, OCH_3, triaz), 6.18 (d, 2H, arom. H), 6.42 (d, 2H, arom. H), 6.77 (m, arom. H, triaz), 7.01–7.85 (m, 13H, arom. H), 8.21 (d, 2H, *o*-H), 8.43, 8.51 (m, *o*-H, triaz). – ^{13}C NMR (–50°C, 90.56 MHz, $CDCl_3$): δ = 25.91, 26.75 [$C(CH_3)_3$, triaz], 27.13 [$C(CH_3)_3$], 40.60 [$C(CH_3)_3$], 41.76, 44.21 [$C(CH_3)_3$, triaz], 54.75 (OCH_3), 54.83, 54.94 (OCH_3, triaz), 87.33, 88.61 (N–C–N, triaz), 111.7 (*m*-C, triaz), 112.1 (*m*-C), 126.8, 127.2, 127.8, 128.0, 128.0, 128.3, 128.6, 129.4 (*o*/*m*-C), 130.8, 131.0, 131.2 (*p*-C, triaz), 131.4 (*p*-C) 131.6 (*p*-C, triaz), 131.7, 132.5 (*p*-C), 132.7 (*p*-C, triaz), 133.8, 134.5 (*i*-C), 134.7 (*i*-C, triaz), 135.1 (*i*-C), 135.4, 136.4, 136.7, 137.1, 137.3 (*i*-C, triaz), 153.1, 157.3 (*C*-OCH_3, triaz), 157.9, 158.1 (N–C=N, triaz), 158.4 (*C*–OCH_3), 159.9, 161.8 (N–C=N), 162.8, 162.9 (N–C=N, triaz), 173.6, 176.6 (C=O, triaz), 178.1, 180.4 (C=N, C=O). – MS (70 eV), *m*/*z* (%): 501 (3) [M^+], 444 (5) [M^+ – *t*Bu], 396 (4) [M^+ – PhCO], 380 (4), 311 (17) [444 – $CH_3OC_6H_4CN$], 293 (6) [396 – PhCN], 180 (28), 135 (26) [$CH_3OC_6H_4CO^+$], 105 (100) [$PhCO^+$], 103 (70) [$PhCN^+$], 77 (43) [Ph^+]. – UV (diethyl ether): λ_{max} (lg ε) = 210 nm (4.495), 254 (4.012). – $C_{33}H_{31}N_3O_2$ (501.6): calcd. C 79.02, H 6.23, N 8.38; found C 78.98, H 6.28, N 8.31.

Synthesis of the 6-Alkoxy-1-oxa-3,5-diazahexatrienes **5a,b**. *General Procedure:* To a suspension of the oxadiazinium salt **2** in dichloromethane (40 ml) a solution of 1.25 equivalents of dry alcohol in dichloromethane (20 ml) is added dropwise. After 15-30 min the reaction mixture becomes clear, and a yellow solution forms. After stirring for 3 h, the mixture is cooled to 0°C; then the solution is vigorously shaken with 50 ml of ice-cold aqueous 1N NaOH. The layers are separated, and the aqueous layer is twice extracted with dichloromethane (20 ml). The combined organic extracts are dried with $MgSO_4$, and the solvent is removed in vacuo. The crude product is purified by flash chromatography.

6-Ethoxy-2,4,6-triphenyl-1-oxa-3,5-diaza-1,3,5-hexatriene (**5a**): From 4.27 g (7.0 mmol) of **2a** and 0.40 g (8.8 mmol) of anhydrous ethanol a viscous yellow oil (**5a**) is obtained after flash chromatography (petroleum ether/diethyl ether, 2:1; R_f = 0.39), which solidifies slowly to form a colorless solid; yield of **5a** 1.94 g (78%), m.p. 62°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w, CH arom.), 2970 (w, CH aliph.), 1660 (s, C=O), 1640 (s, C=N), 1600 (vs), 1570 (s), 1440 (m), 1360 (m), 1305 (s), 1275 (vs), 1240 (s), 1160 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 4.24 (q, ^3J = 7.1 Hz, 2H, OCH_2CH_3), 7.12–7.55 (m, 11H, arom. H), 7.85 (m, 2H, *o*-H), 8.01 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.84 (OCH_2CH_3), 63.72 (OCH_2CH_3), 127.9, 128.1, 128.2, 128.3, 128.4, 129.0 (*o*/*m*-C), 130.6 (*i*-C), 131.2, 131.6, 132.1 (*p*-C), 133.9, 134.3 (*i*-C), 158.4 (C=N), 158.7 (C=N), 179.8 (C=O). – MS (70 eV), *m*/*z* (%): 356 (6) [M^+], 327 (5) [M^+ – C_2H_5], 279 (9) [M^+ – Ph], 251 (30) [M^+ – PhCO], 223 (11), 105 (100) [$PhCO^+$], 103 (24) [$PhCN^+$], 77 (71) [Ph^+]. – UV (diethyl ether): λ_{max} (lg ε) = 208

nm (4.328), 245 (4.378). – $C_{23}H_{20}N_2O_2$ (356.4): calcd. C 77.51, H 5.66, N 7.86; found C 77.37, H 5.58, N 7.90.

6-Isopropoxy-2,4,6-triphenyl-1-oxa-3,5-diaza-1,3,5-hexatriene (**5b**): From 7.2 g (8.4 mmol) of **2a** and 0.65 g (11.1 mmol) of anhydrous 2-propanol **5b** is obtained as a colorless solid after flash chromatography (petroleum ether/diethyl ether, 2:1; $R_f = 0.45$; the crude product is dissolved in little dichloromethane before applying it to the column). Yield of **5b** 2.40 g (77%), m.p. 126°C. – IR (KBr): $\tilde{\nu} = 3060$ cm^{-1} (w, CH arom.), 2970 (m, CH aliph.), 1655 (vs, C=O), 1640 (vs, C=N), 1595 (s), 1570 (s), 1445 (m), 1350 (m), 1310 (s), 1265 (vs), 1095 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ [d, $^3J = 6.2$ Hz, 6H, $CH(CH_3)_2$], 5.06 [sept, $^3J = 6.2$ Hz, 1H, $CH(CH_3)_2$], 7.14 to 7.51 (m, 11H, arom. H), 7.82 (m, 2H, *o*-H), 8.02 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 21.47$ [$CH(CH_3)_2$], 70.95 [$CH(CH_3)_2$], 127.8, 128.1, 128.2, 128.4, 128.4, 129.0 (*o*/*m*-C), 131.0, (*i*-C), 131.1, 131.6, 132.0 (*p*-C), 134.0, 134.5 (*i*-C), 158.3 (C=N), 158.7 (C=N), 179.8 (C=O). – MS (70 eV), *m*/*z* (%): 370 (10) [M^+], 327 (7) [$M^+ - C_3H_7$], 293 (8) [M^+ – Ph], 265 (23) [M^+ – PhCO], 223 (22), 209 (19), 105 (100) [$PhCO^+$], 77 (66) [Ph^+]. – $C_{24}H_{22}N_2O_2$ (370.5): calcd. C 77.81, H 5.99, N 7.56; found C 77.94, H 6.19, N 7.55.

Reaction of **5a** *with Lithium (Di-tert-butylmethylene)amide* (**1e**)

8,8-Di-tert-butyl-2,4,6-triphenyl-1-oxa-3,5,7-triaza-1,3,5,7-octatetraene (**4f**): A solution of 0.34 g (4.1 mmol) of trimethylacetonitrile in diethyl ether (15 ml) is cooled to –196°C and dropwise treated with 2.6 ml (4.1 mmol) of *tert*-butyllithium (1.6 M solution in *n*-pentane). The solution is allowed to warm up to room temp. and stirred for 1/2 h. After cooling to –78°C, a solution of 1.46 g (4.1 mmol) of **5a** in diethyl ether (20 ml) is added. After stirring for 2 h at –78°C, the cooling bath is removed. 24 h later, the yellow solution is twice shaken vigorously with 0.1 N aqueous HCl (20 ml) and once with satd. aqueous $NaHCO_3$. The organic layer is dried with $MgSO_4$, and the solvent is removed in vacuo. The residue is purified by flash chromatography (petroleum ether/diethyl ether, 7:1). The main fraction consists of *2,2-di-tert-butyl-4,6-diphenyl-2H-1,3,5-oxadiazine*[1] (**6**) [1.11 g (78%); colorless solid, $R_f = 0.63$]. Compound **4f** is obtained in a second fraction as a colorless solid ($R_f = 0.07$); 0.18 g (10%), m.p. 143°C. – IR (KBr): $\tilde{\nu} = 3050$ cm^{-1} (w, CH arom.), 2950 (m), 2900 (w, CH aliph.), 1690 (s, C=O), 1660 (s, C=N), 1600 (s), 1580 (s), 1545 (vs), 1440 (m), 1310 (m), 1270 (m), 1240 (s), 1170 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.07$ [s, 9H, $C(CH_3)_3$], 1.08 [s, 9H, $C(CH_3)_3$], 7.30–7.55 (m, 9H, *m*/*p*-H), 7.60 (d, 2H, *o*-H), 7.87 (d, 2H, *o*-H), 8.06 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 29.72$ [$C(CH_3)_3$], 43.85 [$C(CH_3)_3$], 127.5, 128.0, 128.2, 128.3, 128.7, 129.3 (*o*/*m*-C), 130.8, 131.1, 131.9 (*p*-C), 134.5, 134.6 (*i*-C), 156.0 [N–C(6)=N], 161.9 [N–C(4)=N], 179.7, 180.2 (C=N, C=O). – MS (70 eV), *m*/*z* (%): 451 (5) [M^+], 394 (3) [M^+ – *t*Bu], 374 (4) [M^+ – Ph], 346 (3) [M^+ – PhCO], 311 (5) [$M^+ - (t\text{Bu})_2\text{CN}$], 291 (5), 105 (100) [$PhCO^+$], 103 (27) [$PhCN^+$], 77 (38) [$Ph^+$], 57 (34) [$t\text{Bu}^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 210 nm (4.510), 244 (4.504). – $C_{30}H_{33}N_3O$ (451.6): calcd. C 79.79, H 7.36, N 9.30; found C 79.30, H 7.40, N 9.27.

X-Ray Diffraction Analysis of **4f**[19]: A colorless, column-shaped crystal $C_{30}H_{33}N_3O$ (from diethyl ether), crystal size 0.125 × 0.150 × 0.500 mm^3, was measured at room temperature by using an automatic CAD4 Turbo Diffractometer (Enraf-Nonius) with Mo-K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. 10430 reflexions were collected in the 2-Θ range $4.0 \ll 2\Theta \ll 55.0°$ (scan speed variable; 1.14 to 4.00°/min). Crystal system: Triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.339(2)$, $b = 10.404(2)$, $c = 12.695(3)$ Å, $\alpha = 74.31(3)$, $\beta = 78.49(3)$, $\gamma = 84.66(3)°$; $V = 1287.1(5)$ Å^3; $D_x = 1.165$ g · cm^{-1}. After extinction correction the structure was solved by direct methods (SHELXTL-PLUS program[20]) using 3113 observed reflexions [$F_o > 4.0\sigma(F)$] for the non-hydrogen atoms. After the addition of the hydrogen atoms (coupled with respect to position and temperature parameters to the corresponding carbon atoms), anisotropic refinement led to agreement factors $R = 0.052$ and $R_w = 0.048$ [weighting with $w^{-1} = \sigma^2(F) + 0.0002 \cdot F^2$] [3113 reflections with $I_o > 4.0\sigma(I_o)$, 308 variable parameters, program SHELXTL-PLUS]. In this final refinement an isotropic extinction coefficient χ of 0.0010(3) was obtained. The molecular shape is presented in Figure 1.

Reactions of the N-Lithiated 1,3-Diazabutadienes **7a,b** *with N-Acylimidates*

2,2-Dimethyl-N-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)propanamidine (**7b**): In analogy to ref.[9] 6.86 g (35.0 mmol) of fenchone nitrimine[21] is treated with 3.50 g (35.0 mmol) of 2,2-dimethylpropanamidine. The crude yellow oil is purified by kugelrohr distillation, furnishing **7b** as a colorless liquid; yield 5.46 g of **7b** (67%); b.p. 90°C (oven temp.)/0.02 Torr. – IR (neat): $\tilde{\nu} = 3250$ cm^{-1} (w, NH), 2950 (vs), 2860 (m, CH aliph.), 1685 (vs, C=N), 1595 (s, C=N), 1470 (m), 1450 (m), 1385 (m), 1350 (m), 1325 (s), 1315 (m), 1210 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.18 [s, 9H, $C(CH_3)_3$], 1.24–1.93 (m, 7H, fenchyl CH, CH_2), 7.25 (s, br, 1H, NH). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 17.48$, 23.15 (CH_3), 24.66 (CH_2), 26.32 (CH_3), 28.33 [$C(CH_3)_3$], 33.85 (CH_2), 37.85 [$C(CH_3)_3$], 43.24 (CH_2), 45.94 ($C_{qu.}$), 46.00 (CH), 52.35 ($C_{qu.}$). 181.7, 182.7 (N–C=N, C=N). – MS (70 eV), *m*/*z* (%): 234 (19) [M^+], 194 (15), 149 (23), 107 (35), 81 (100), 67 (83), 57 (69) [$t\text{Bu}^+$]. – $C_{15}H_{26}N_2$ (234.4): calcd. C 76.87, H 11.18, N 11.95; found C 76.70, H 11.29, N 12.35.

General Procedure for the Preparation of **4g–j**: To a solution of the *N*-(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amidine 7 in diethyl ether (60 ml; **4g**: 20 ml) 1 equivalent of *n*-butyllithium (1.6 M solution in *n*-hexane) is slowly added at –78°C. After 5 min, a solution of the *N*-acylimidate **8** in diethyl ether (40 ml, **4g**: 20 ml) is added. After warming to room temp. overnight, the reaction mixture is shaken twice with 0.1 N aqueous HCl and once with satd. aqueous $NaHCO_3$. The organic layer is dried with $MgSO_4$, and the solvent is removed in vacuo. The residue is purified by flash chromatography.

2-tert-Butyl-4,6-diphenyl-6-[(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1-oxa-3,5-diaza-1,3,5-hexatriene (**4g**): From 1.06 g (4.2 mmol) of **7a**[9], 2.5 ml (4.2 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 0.96 g (4.2 mmol) of ethyl *N*-(2,2-dimethylpropanoyl)benzimidate[8] (**8a**) after 36 h and flash chromatography (petroleum ether/diethyl ether, 8:1; $R_f = 0.30$) **4g** is obtained as a yellow oil, which slowly crystallizes to form a colorless solid. Yield 0.75 g (41%), m.p. 153°C. – IR (KBr): $\tilde{\nu} = 3060$ cm^{-1} (w, CH arom.), 2960 (s, CH aliph.), 1710 (s, C=O), 1680 (s, C=N), 1620 (s, C=N), 1590 (vs), 1565 (vs), 1450 (m), 1315 (m), 1285 (m), 1145 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.45$ (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.25 (m, 1H, fenchyl H), 1.34 [s, 9H, $C(CH_3)_3$], 1.46–1.92 (m, 6H, fenchyl CH, CH_2), 7.29–7.51 (m, 6H, *m*/*p*-H), 7.76–7.84 (m, 4H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 16.17$, 22.22 (CH_3), 24.84 (CH_2), 25.76 (CH_3), 27.66 [$C(CH_3)_3$], 33.31 (CH_2), 41.79 [$C(CH_3)_3$], 43.99 (CH_2), 45.57 (CH), 46.62, 53.92 ($C_{qu.}$), 127.8, 128.0, 128.4, 128.6 (*o*/*m*-C), 130.5, 131.3 (*p*-C), 133.2, 135.0 (*i*-C), 157.6 [N–C(4)=N], 161.1 [N–C(6)=N], 186.6 (C=N), 194.6 (C=O). – FD-MS, *m*/*z* (%): 443 (54) [$M^+ + 2H$], 442 (74) [$M^+ + H$], 384 (100) [$M^+ - t\text{Bu}$], 322 (7), 307 (33) [384 – Ph], 291 (28), 286 (17), 192 (25), 139 (19), 86 (25). – UV (diethyl ether): λ_{max} (lg ε) = 209 nm (4.521), 246 (4.495). – $C_{29}H_{35}N_3O$ (441.6): calcd. C 78.87, H 7.99, N 9.52; found C 78.70, H 8.06, N 9.44.

2,4-Di-tert-butyl-6-phenyl-6-[(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1-oxa-3,5-diaza-1,3,5-hexatriene (**4h**). From 2.98 g (11.7 mmol) of **7a**, 7.3 ml (11.7 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 2.50 g (11.7 mmol) of ethyl *N*-(2,2-dimethylpropanoyl)-2,2-dimethylpropanimidate[8] (**8b**) a crude product is obtained after 72 h. Benzonitrile is removed by kugelrohr distillation (ca. 50°C/0.02 Torr). Flash chromatography yields *N*^{2}-*(2,2-dimethylpropanoyl)-2,2-dimethyl-N*^{1}-*(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)propanamidine*[1] (**9b**) as the main product (petroleum ether/diethyl ether, 20:1; $R_f = 0.68$, 1.86 g (50%) light yellow oil). As a second fraction ($R_f = 0.21$), **4h** (colorless solid) is obtained, 0.96 g (19%), m.p. 118°C. – IR (KBr): $\tilde{\nu} = 3060$ cm^{-1} (w, CH arom.), 2950 (s), 2860 (m, CH aliph.), 1670 (vs, C=O), 1640 (vs, C=N), 1610 (vs, C=N), 1570 (w), 1540 (m), 1470 (m), 1435 (m), 1355 (w), 1260 (m), 1165 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.25 [s, 9H, $C(CH_3)_3$], 1.26 [s, 9H, $C(CH_3)_3$], 1.39–2.02 (m, 7H, fenchyl CH, CH_2), 7.31–7.45 (m, 3H, *m*/*p*-H), 7.71 (d, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 16.80$, 23.80 (CH_3), 24.99 (CH_2), 26.85 (CH_3), 27.75, 28.97 [$C(CH_3)_3$], 33.59 (CH_2), 40.56, 41.57 [$C(CH_3)_3$], 43.88 (CH_2), 45.76 (CH), 46.93, 54.27 ($C_{qu.}$), 127.6, 128.3, (*o*/*m*-C), 130.6 (*p*-C), 136.2 (*i*-C), 158.0 [N–C(6)=N], 167.8 [N–C(4)=N], 188.3 (C=N), 192.2 (C=O). – MS (70 eV), *m*/*z* (%): 364 (100) [$M^+ - t$Bu], 281 (35) [364 – *t*BuCN], 238 (32), 230 (46), 216 (18), 199 (20), 135 (39) [$C_9H_{13}N^+$], 105 (56), 103 (45) [$PhCN^+$], 57 (67) [*t*Bu]. – UV (diethyl ether): λ_{max} (lg ε) = 212 nm (4.115), 248 (4.212). – $C_{27}H_{39}N_3O$ (421.6): calcd. C 76.92, H 9.32, N 9.97; found C 76.74, H 9.48, N 10.13.

2,6-Di-tert-butyl-4-phenyl-6-[(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1-oxa-3,5-diaza-1,3,5-hexatriene (**4i**): From 4.85 g (20.7 mmol) of **7b**, 13.0 ml (20.7 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 4.83 g (20.7 mmol) of **8a** hexatriene **4i** is obtained after 48 h and flash chromatography (petroleum ether/diethyl ether, 10:1) as a yellow oil, which crystallizes to form a colorless solid; 1.19 g (14%), m.p. 88°C ($R_f = 0.22$). The main fraction consists of *N*^{2}-*(2,2-dimethylpropanoyl)-N*^{1}-*(1,3,3-trimethylbicyclo-[2.2.1]hept-2-ylidene)benzamidine*[1] (**9a**) ($R_f = 0.60$), 4.77 g (68%), yellowish oil. – IR (KBr): $\tilde{\nu} = 3050$ cm^{-1} (w, CH arom.), 2940 (s, CH aliph.), 1720 (s, C=O), 1680 (s, C=N), 1600 (s), 1565 (vs), 1470 (m), 1450 (m), 1280 (m), 1260 (m), 1160 (s), 1130 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.19$ (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.27 [s, 9H, $C(CH_3)_3$], 1.28 [s, 9H, $C(CH_3)_3$], 1.32 to 1.79 (m, 7H, fenchyl CH, CH_2), 7.28–7.37 (m, 3H, *m*/*p*-H), 7.68 (m, 2H, *o*-H). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 16.36$, 21.52 (CH_3), 24.74 (CH_2), 25.79 (CH_3), 27.50, 29.25 [$C(CH_3)_3$], 33.15 (CH_2), 39.03, 41.61 [$C(CH_3)_3$], 43.94 (CH_2), 45.36 (CH), 46.18, 52.49 ($C_{qu.}$), 127.9, 128.3 (*o*/*m*-C), 130.3 (*p*-C), 133.6 (*i*-C), 156.9 [N–C(4)=N], 171.8 [N–C(6)=N], 181.7 (C=N), 194.5 (C=O). – MS (70 eV), *m*/*z* (%): 421 (0.7) [M^+], 406 (1.5) [$M^+ - CH_3$], 364 (100) [$M^+ - t$Bu], 238 (10), 135 (24) [$C_9H_{13}N^+$], 103 (46) [$PhCN^+$], 57 (64) [tBu$^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 217 nm (4.147), 246 (4.176). – $C_{27}H_{39}N_3O$ (421.6): calcd. C 76.92, H 9.32, N 9.97; found C 76.70, H 9.26, N 9.87.

2,4,6-Tri-tert-butyl-6-[(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)amino]-1-oxa-3,5-diaza-1,3,5-hexatriene (**4j**): From 4.68 g (20.0 mmol) of **7b**, 12.5 ml (20.0 mmol) of *n*-butyllithium (1.6 M solution in *n*-hexane), and 4.26 g (20.0 mmol) of **8b** compound **4j** is obtained after 48 h and flash chromatography (petroleum ether/diethyl ether, 10:1) as a yellow oil ($R_f = 0.24$), which crystallizes at low temperature to form a colorless solid; 0.23 g (2.9%), m.p. 47°C. The main fraction consists of *N*^{2}-*(2,2-dimethylpropanoyl)-2,2-dimethyl-N*^{1}-*(1,3,3-trimethylbicyclo[2.2.1]hept-2-ylidene)propanamidine* (**9b**) ($R_f = 0.73$), 5.02 g (79%), yellow oil. – IR (KBr): $\tilde{\nu} = 2960$ cm^{-1} (s), 2860 (m, CH aliph.), 1710 (s, C=O), 1675 (s, C=N), 1610 (vs, C=N), 1475 (m), 1385 (w), 1355 (m), 1260 (m), 1165 (m), 1110 (m), 1015 (m). – ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.07$ (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.19 [s, 9H, $C(CH_3)_3$], 1.20 (s, 9H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.33-1.97 (m, 7H, fenchyl CH, CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 16.99$, 23.66 (CH_3), 25.09 (CH_2), 26.60 (CH_3), 27.76, 29.14, 29.35 [$C(CH_3)_3$], 34.33 (CH_2), 39.36, 40.67, 40.98 [$C(CH_3)_3$], 43.76 (CH_2), 45.39 (CH), 46.45, 53.07 ($C_{qu.}$), 165.8 (N–C=N), 167.1 (N–C=N), 182.7 (C=N), 190.5 (C=O). – MS (70 eV), *m*/*z* (%): 401 (7) [M^+], 386 (2) [$M^+ - CH_3$], 344 (100) [$M^+ - t$Bu], 261 (12) [344 – *t*BuCN], 218 (16), 150 (16) [$C_{10}H_{16}N^+$], 135 (17) [150 – CH_3], 85 (20) [tBuCO$^+$], 84 (43) [tBuCNH$^+$], 57 (82) [tBu$^+$]. – UV (diethyl ether): λ_{max} (lg ε) = 214 nm (3.911). – $C_{25}H_{43}N_3O$ (401.6): calcd. C 74.76, H 10.79, N 10.42; found C 74.49, H 10.85, N 10.34.

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