2,3-Dialkynyl-1,4-diazabuta-1,3-dienes as Novel π-Systems: Synthesis, Structure, and Electronic Properties

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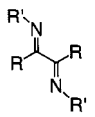
The introduction of alkynyl groups into the 2,3-positions of the 1,4-diazabuta-1,3-diene (DAD) backbone succeeds along two complementary synthetic routes either by condensing triisopropylsilyl-terminated dialkynyl-1,2-diones with primary aromatic amines or by a palladium-mediated alkynylation of bis(imidoyl chlorides). X-ray crystallographic analyses of two dialkynyl DAD derivatives reveals their planar (*E-s-trans-E*) conformations in the solid state. However, the central CC bond of both DAD backbones investigated has a length of 1.491(2) Å, and is therefore too long to indicate efficient delocalization across the DAD core. The UV/Vis spectra of dialkynyl DADs demonstrate that their absorptions in comparison to those of non-alkynyl DADs are bathochromically shifted by more than 40 nm, thereby demonstrating the suitability of the title compounds for developing NIR chromophores. The electron absorption properties of differentially *N,N′*-disubstituted dialkynyl DADs gave no indication for a push-pull effect across the DAD skeleton and suggest the ynimine moiety as the active chromophore of dialkynyl DADs. The electrochemical properties of the title compounds were determined by cyclo- and steady state voltammetry and show that introducing alkynyl groups leads to more easily reducible DAD systems. Again, the perception of dialkynyl DADs as covalently linked, but electronically decoupled ynimine units is corroborated by the redox potential of a differentially *N,N′*-disubstituted dialkynyl DAD. Similar conclusions were drawn from semiempirical MO (PM3) calculations of dialkynyl DADs.

Introduction

N,N′-disubstituted vicinal diimines (1,4-diazabuta-1,3-dienes, DADs) of the general formula **1** have long been studied as versatile building blocks for the construction of four-, five-, and six-membered ring heterocycles,[1] and, in particular, for their excellent coordinating properties towards a variety of transition metal centers.[2] It is with regard to this second aspect that compounds like **1** have recently attracted renewed interest, mainly driven by the discovery that cationic nickel(II) and palladium(II) DAD complexes very efficiently catalyze olefin polymerization reactions.[3] In addition, other CC bond-forming processes mediated by DAD-ligated metal complexes have been documented.[4]

The range of substituents on the internal carbon atoms of the DAD backbone has previously been limited largely to hydrogen, methyl, aryl, and fused areno or cycloalkeno groups. Our interest in transforming small acetylenic building blocks into peripherally peralkynylated Near Infrared chromophores,[5] has led us to consider expanding this range of 2,3-DAD substituents to alkynyl groups as in **2**.[6]



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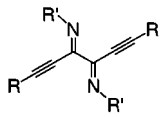

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The 2,3-dialkynyl-1,4-diazabuta-1,3-dienes **2** possess a π-system[7] whose electronic properties are predicted to differ significantly from those of previously investigated, non-acetylenic diazabutadienes. It is reasonable to assume, for example, that in appropriate coordination compounds of **2** the extended π-system of the dialkynyl DAD will allow for charge-transfer interactions between metal and ligand with absorptions of appreciable intensity in the Near Infrared region.[8] Similarly, the electron-withdrawing nature of the acetylenic groups might impart enhanced catalytic activity to metal complexes of **2** in catalytic CC bond-forming processes. In addition, appropriately functionalized alkyne units can serve as rigid yet electronically conducting linking units to assemble several metal binding sites within one molecular entity. Lastly, one or both of the ynimine moieties in **2** can be chemically modified to form heterocyclic ring systems[9] leading to structurally diverse chelating nitrogen ligands[10] and novel (bi-)heterocycles.

Herein we describe two complementary syntheses of the first representatives of **2**, discuss their solid state structures, and disclose details of their electronic properties as studied by electron absorption spectroscopy, ^{13}C-NMR spec-

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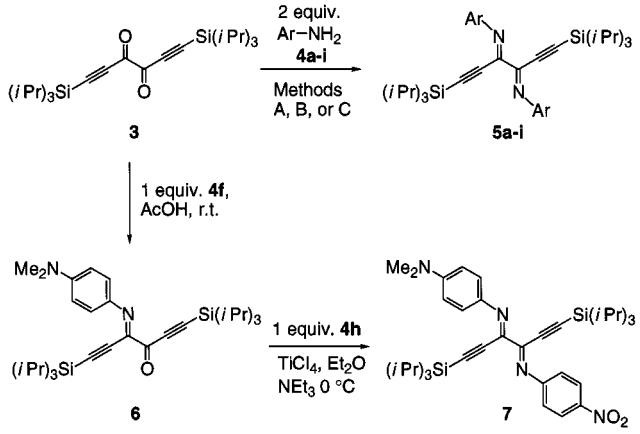
troscopy, and by electrochemical techniques. The results are rationalized by semiempirical calculations.

Results and Discussion

Syntheses

The synthetic methodology leading to dialkynyl diazabutadienes has been communicated in preliminary form.[11,12] Hence, the discussion below will focus only on major points.

Bis(triisopropylsilylethynyl)-1,2-dione **3**, required for the preparation of **2** according to Scheme 1, was recently made available by a convenient copper(I)-mediated direct alkynylation of oxalyl chloride.[13] The bulkiness of the Si(*i*Pr)$_3$ groups[14] turned out to be crucial for the success of the 1,2-condensation with primary aromatic amines,[12] since sterically less demanding terminal alkyne substituents such as phenyl do not suffice to protect the reactive ynone system from dominant nucleophilic 1,4-addition. Hence, a smooth condensation of **3** with the electronically and sterically varied aniline derivatives **4a**−**i** in the presence of Lewis (LiBr, $TiCl_4$) or Brønsted acids (AcOH) was observed furnishing the corresponding dialkynyl diazabutadienes **5a**−**i** in generally satisfactory yields (Scheme 1).



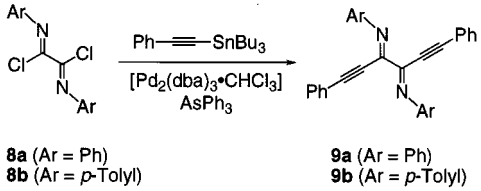
Ar-substituents	a	b	c	d	e	f	g	h	i
	H	4-Me	3,5-Me$_2$	2,6-Me$_2$	2,6-(*i*Pr)$_2$	4-Me$_2$N	4-MeO	4-NO$_2$	4-CF$_3$

Scheme 1. Preparation of dialkynyl diazabutadienes **5** and **7** starting from dialkynyl-1,2-diketone **3**; method A: xylene, cat. LiBr, reflux; method B: glacial acetic acid, reflux; method C: $TiCl_4$, NEt_3, diethyl ether, 0°C

Gratifyingly, imine formation from **3** could be stopped at the β-imino ketone stage using only one equivalent of, for example, the electron-rich aniline derivative **4f** to generate **6** (Scheme 1). Subsequent condensation of **6** with one equivalent of the electron-deficient *p*-nitroaniline **4h** furnished the differentially *N,N′*-disubstituted dialkynyl diazabutadiene **7** in an overall yield of 77%.

Formation of *N,N′*-dialkyl diimines from primary aliphatic amines failed, presumably due to competing desilylation and subsequent decomposition of unprotected **3**. However, condensation reactions with heterosubstituted amines such as hydroxylamine and hydrazines are feasible and further synthetic elaborations of these compounds are currently being performed.[15]

A more general synthetic access[11] to compounds like **2** lies in the palladium-catalyzed alkynylation of bis(imidoyl chlorides) **8**, which can be readily obtained by chlorodehydration of the corresponding oxamides with PCl_5.[16] Hence, reacting **8a** or **8b** with tributyl(2-phenylethynyl)stannane in the presence of catalytic amounts of [$Pd_2(dba)_3 \cdot CHCl_3$]/$AsPh_3$[17] (dba = dibenzylidene acetone) in toluene at 50°C furnished the bis(phenylethynyl) DADs **9a** and **9b** in 50% yield (Scheme 2).[11] Likewise, the triisopropylsilyl-protected DAD **5a** could be prepared in this fashion starting from the corresponding trimethylstannylated triisopropylsilyl acetylene and **8a**. Dialkynyl DADs terminated by the smaller trimethylsilyl group, on the other hand, could not be obtained by this procedure, since the coupling products, although formed, decomposed upon attempted chromatographic purification.



Scheme 2. Preparation of dialkynyl diazabutadienes **9** starting from bis(imidoyl chlorides) **8**

The two synthetic procedures illustrated in Schemes 1 and 2 thus provide complementary entries to dialkynyl diazabutadienes. The presence of geometrical isomers of the DADs shown could not be detected. In general, the dialkynyl DADs are yellow to red (**5f**) crystalline compounds that melt without decomposition. In pure form they are stable to the ambient for extended periods (months), and they are readily soluble in aprotic organic solvents.

Solid-State Structures

Structural information on DADs bearing substitutents at the 2- and 3-positions is relatively scarce.[6a,18] As judged by computational techniques,[19] the global minimum of the parent DAD with hydrogens at the 2,3-positions appears to be a planar *s-trans* conformation with (*E*)-configuration around each of the C=N double bonds, denominated as (*E-s-trans-E*). X-ray crystallographic analyses on *N,N′*-dicyclohexyl-DAD,[20] *N,N′*-di-*tert*-butyl-DAD[21] and *N,N′*-bis(2-methoxymethyl-4,6-di-*tert*-butylphenyl)-DAD[10] seem to confirm this view. Introducing substituents in the 2,3-positions significantly increases the steric burden on the DAD backbone and leads to less symmetrical arrangements as, for example, the (*Z-gauche-Z*) orientation observed in the crystals of 1,2,3,4-tetraphenyl-DAD.[18b] A similar conformation in the solid state was determined for te protonated form of this 2,3-disubstituted DAD.[18a] In such a distorted geometry electronic delocalization across the

DAD backbone is far from ideal and should be severely limited.

Since extensive π electron delocalization within the DAD framework is at the core of the newly designed 2,3-dialkynyl-DADs **2**, an assessment of their structural properties seemed mandatory. We have therefore investigated the solid-state structures of single crystals of **5c** and **9a** by X-ray diffraction (Figures 1 and 2).

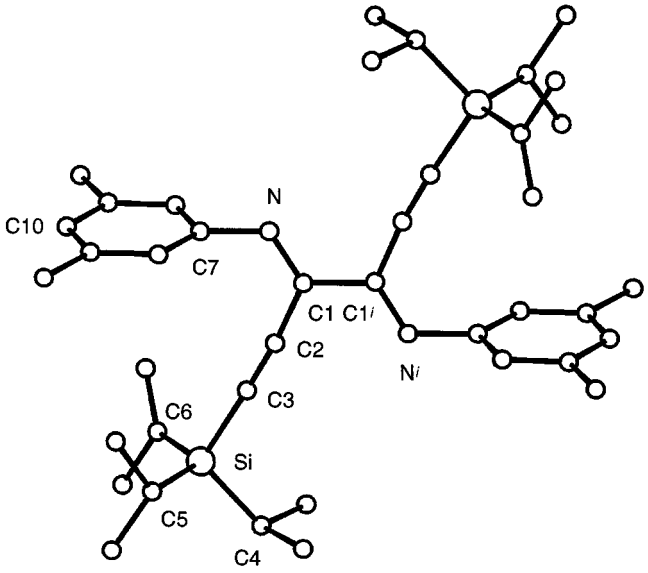


Figure 1. Molecular structure of **5c** in the crystal; selected bond lengths [Å] and angles [°]: C1−C1^i 1.491(2), C1−C2 1.442(3), C1−N 1.272(2), C2−C3 1.196(3), C3−Si 1.847(2), N−C7 1.427(3); N−C1−C1^i 118.3(2), N−C1−C2 124.0(2), C1−C2−C3 174.3(2)

Reassuringly, both compounds adopt an (*E-s-trans-E*) orientation in the crystal and possess molecular C_i symmetry due to a center of inversion located midway between the carbons of the DAD backbones. The DAD moieties of **5c** and **9a** are perfectly planar (cf. Figure 2b) and therefore provide an ideal structural setup for π-electronic delocalization in both directions across the central CC bonds, namely along the DAD backbones and across the 1,5-hexadiyne substructures. In case of **9a**, also the phenyl rings attached to the alkyne units may take part in delocalizing interactions: They are only slightly bent out the plane defined by the DAD, an arrangement that still allows sufficient overlap between the phenyl and the alkyne π-electrons (Figure 2b).

The aryl groups on the nitrogen atoms, on the other hand, are substantially turned out of the DAD plane [e.g. in **9a** by 55.1(1)°] and do not seem to benefit from delocalizing interactions with either the nitrogen lone pair or the DAD system. The alkynyl C2−C3 bonds in **5c** [1.196(3) Å] are slightly longer than those of **9a** [1.185(2) Å] and the triple bonds of the former are slightly more bent [valence angle C1−C2−C3: 174.3(2)°] than in the latter compound [valence angle C1−C2−C3: 175.7(1)°].

While the overall geometries of **5c** and **9a** suggest the presence of significant π-electronic interactions across the entire DAD skeleton, the distance between the internal DAD carbon atoms does not seem to support this view.

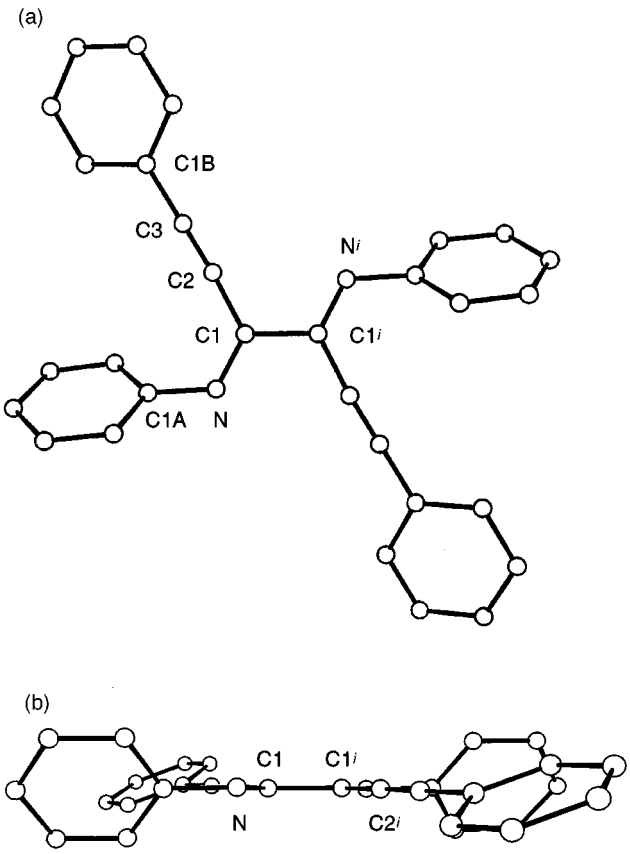


Figure 2. Molecular structure of **9a** in the crystal, (a) top view, (b) side view; selected bond lengths [Å] and angles [°]: C1−C1^i 1.491(2), C1−C2 1.441(2), C1−N 1.282(2), C2−C3 1.185(2), N−C1A 1.417(2); N−C1−C1^i 117.8(1), N−C1−C2 125.2(1), C1−C2−C3 175.7(1)

The C1−C1^i bond lengths amount to 1.491(2) Å in each of the compounds and are therefore significantly larger than the corresponding ones found in the (*E-s-trans-E*) forms of *N,N′*-dicyclohexyl-DAD [1.457(2) Å],[20] *N,N′*-di-*tert*-butyl-DAD [1.467(2) Å],[21] and *N,N′*-bis(2-methoxymethyl-4,6-di-*tert*-butylphenyl)-DAD [1.470(4) Å].[10] In fact, a length of 1.491(2) Å is at the long end of $C_{sp2}-C_{sp2}$ carbon bonds in general, which in average amount to only 1.455 Å.[22] While it might be misleading to assess the degree of electron delocalization on structural grounds alone,[23] the results presented above seem to suggest that π-interactions across the central CC bond of the DAD skeleton are not very efficient and that the dialkynyl-DADs despite their *s-trans* geometry are best represented by two mutually independent ynimine moieties within one molecular framework. This view is in agreement with conclusions drawn previously on uncoordinated DAD molecules.[20]

Electron Absorption and ^{13}C-NMR Spectra

With respect to our interest in using compounds like **2** as building blocks for the construction of NIR-chromophors, an examination of their electron absorption spectra in the UV/Vis region appeared to be worthwhile. In particular, we

sought to assess both, the effect of alkynylation in the 2- and 3-positions of the DAD backbone, and the influence of electronically different *N*-substituents within the molecular framework of **2**.

Generally, the dialkynyl DADs **5a−e** and **5g−i** are intense yellow compounds with longest wavelength absorptions between 360 (**5h**) and 404 nm (**5g**). Increasing the electron-density of the *N*-aryl substituent by alkyl groups leads to a shift of the λ_{max} value from 376 nm (**5a**) to 406 nm (**5e**). This low-energy transition is considerably shifted further to the red when at least one of the *N*-aryl substituents bears a strongly electron-donating dimethylamino group as in the deep red compounds **5f** (λ_{max} = 486 nm) and **7** (λ_{max} = 468 nm). Since the spectral features associated with this substitution pattern are quite pronounced, we have focused largely on Me_2N-derivatives in this study.

The effect of introducing alkynyl groups in to the 2- and 3-positions of the DAD backbone was evaluated by comparing the UV/Vis spectrum of glyoxal-derived *N,N′*-bis(4-dimethylaminophenyl)diimino ethane **10** with that of the correspondingly *N*-substituted dialkynyl DAD **5f** (Figure 3). While **10** shows a longest wavelength absorption maximum at 444 nm (ε = 38400), that of the diacetylenic DAD **5f** is bathochromically shifted by 42 nm to λ_{max} = 486 (ε = 34800). It therefore appears that the extended π-system of the dialkynyl diazabutadienes does manifest itself in the UV/Vis properties of the DADs.

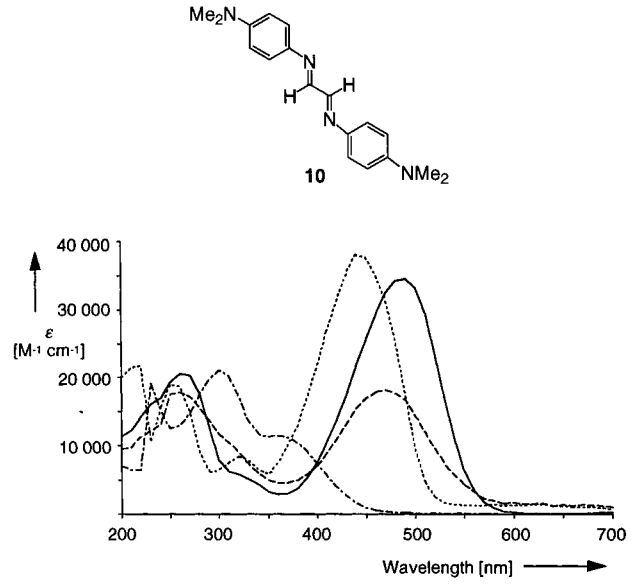


Figure 3. UV/Vis spectra of **5f** (——), **5h** (·−·−·−·), **7** (− − − −), and **10** (------) in CH_2Cl_2 solution

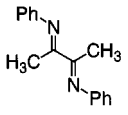
DAD **7** is a potential push-pull-system with electronic interactions across the DAD skeleton. However, comparing the UV/Vis properties of **7** (λ_{max} = 468 nm, ε = 18400) with those of the identically *N,N′*-disubstituted dialkynyl DADs **5f** (λ_{max} = 486 nm, ε = 34800) and **5h** (λ_{max} = 360 nm (sh), ε = 21100) suggests only minimal electronic communication between the two imino moieties across the central CC bond. The longest wavelength absorption of **7** is only marginally shifted hypsochromically compared to that of **5f** and has only half the intensity of the absorption of the latter. No additional bands from intramolecular donor-acceptor interactions between the nitro- and the dimethylamino-substituted half of the molecule can be observed. Likewise, formally replacing one *N*-arylimino group of **5f** by a keto function as in **6** (λ_{max} = 486 nm, ε = 27400) does not lead to a shift of the longest wavelength absorption, but rather to a transition of identical energy with roughly half the intensity of that of **5f**.

The situation is similar when the ^{13}C-NMR chemical shifts of the imino carbon atoms are considered[24]. In case of the symmetrical derivatives **5f** and **5h** the corresponding δ values are 144.6 and 150.5, respectively. If a push-pull mechanism in the "unsymmetrical" DAD derivative **7** was operational, one would expect a more deshielded resonance for the electron-rich imino carbon, and a more shielded resonance for the electron-poor one. The relevant ^{13}C-NMR chemical shifts of **7**, however, are 139.7 for the former and 153.20 for the latter carbon atom, in apparent contrast with the assumption made above.

These findings suggest that the active chromophore within the dialkynyl DADs is the ynimine moiety in one half of the molecule and that the two halves of the DADs behave largely independent from one another. A similar conclusion was drawn from the investigation of the solid-state structures of **5c** and **9a** (vide supra). In view of the fact that the majority of *N,N′*-di-*tert*-butyl DAD molecules was shown to adopt a *gauche* conformation around the central CC bond in the gas phase[25], it may be that the two ynimine moieties of dialkynyl DADs are electronically decoupled by a similar conformational effect in solution. In fact, dipole measurements performed on various DADs point at a non-planar conformation of these molecules in apolar solvents.[26] However, NMR- and IR data seem to indicate a planar *s-trans* conformation of the DAD backbone also in solution.[27,28].

Electrochemical Studies

In an effort to gain further insight into the electronic nature of the dialkynyl diazabutadienes, their redox properties were studied by cyclo- and steady state-voltammetry in CH_2Cl_2 + 0.1 M $[Bu_4N][PF_6]$ and compared to those of the non-alkynyl DAD derivatives **10**, *N,N′*-diphenylbutane-2,3-diimine **11** and *N,N′*-diphenyl-1,2-diphenylethane-1,2-diimine **12** and to those of *N*-phenyl-1,3-diphenylprop-2-ynimine **13**.[29] Generally, most of the acetylenic species investigated exhibit only one irreversible reduction and one irreversible oxidation. Only compounds **5h** could be reversibly reduced. Model compound **11** could be reversibly oxidized. Presumably, the irreversible reductions occur on the



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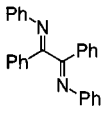

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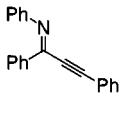

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Table 1. Electrochemical data of selected diazabutadienes[a]

Compound	cyclic voltammetry E^0 [V][b]	ΔE_p[c] [mV]	E_p[d] [V]	steady state voltammetry $E_{1/2}$ [V]	slope[e] [mV]
5a			−1.79	−1.79	107
				+1.35	120
5b			−1.86	−1.85	120
			+1.16	+1.16	113
5f			−1.98	−1.96	108
			+0.25	+0.23[f]	81
			+0.99	+0.98	70
5g			−1.89	−1.87	95
			+0.90	+0.98	100
5h	−1.55	130		−1.59	100
			−1.80	−1.88	95
				−2.27	147
				+1.12	128
5i			−1.61	badly resolved	
7			−1.52	−1.52	120
	−2.09	90		−2.22	72
	+0.40[g]		+1.00	+0.40[f]	68
				+1.05	140
9a			−1.68	−1.69	131
			+1.27	+1.25	95
9b			−1.71	−1.70	116
			+1.06	+1.12	104
10			−2.13	−2.13	155
			+0.31	+0.31[f]	140
11			−2.35		
	+0.60	95		+0.62	75
			+1.00	+1.09	108
12			−2.27		
			+1.08	+1.05	73
13			−2.16[h]		
			−2.37		
			+1.32		

[a] Redox potentials vs. Fc/Fc^+ observed in CH_2Cl_2 + 0.1 M $[Bu_4N][PF_6]$ on glassy carbon. – [b] Formal redox potential $E'^\circ = (E_{pa} + E_{pc})/2$. – [c] At scan rates of 100 mV s^{-1}. – [d] Peak potentials for irreversible reductions and oxidations. – [e] Logarithmic analysis of the wave obtained by plotting E vs. $\log[I/I_{lim} - I]$. – [f] Oxidation of the dimethylamino substituent(s). – [g] Reversible for scan rates > 2 V s^{-1}. – [h] Badly resolved peaks.

DAD core in a single step, as was observed previously for α-diimine derivatives.[30] Analysis of the peak characteristics with scan rate demonstrates that the reduction mechanism involves a reversible one-electron step followed by an irreversible chemical step ($E_{rev}C_{irrec}$-mechanism). The electrochemical data are listed in Table 1 (all values vs. the Ferrocene/Ferrocenyl$^+$ couple).

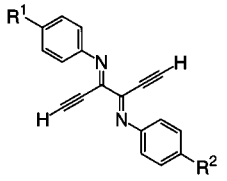
As a general trend, the introduction of alkynyl groups into the DAD backbone leads to compounds that are more easily reduced than non-alkynyl DAD derivatives. For example, the acetylenic DADs **5a** and **9a** are irreversibly reduced at −1.79 V and −1.69 V, respectively, while reduction of the non-alkynyl model compounds **11** and **12** occurs at −2.35 and −2.27 V, respectively. Oxidations of dialkynyl DADs (+1.35 V and +1.25 V for **5a** and **9a**), on the other hand, require higher potentials as is the case for their non-acetylenic counterparts (cf. +1.09 V and +1.05 V for **11** and **12**, respectively). Similarly, substituents on the imino carbon of the electroactive ynimine moiety affect its redox properties. An electron-rich phenyl group as in **13**, for example, leads to reduction potentials of −2.16 and −2.37 V. These values are significantly lower than those of the dialkynyl DADs, in which case the corresponding imino carbon substituent is a second, electron-withdrawing ynimine unit. These findings appear to reflect a general trend arising from the introduction of alkynyl groups into organic molecules,[31] whose origin might lie in the electron-withdrawing nature of the alkynyl substituent and/or in the extension of the π-system associated with additional CC triple bonds. While it is reasonable to assume that reductions of a DAD commonly occur within the N=C−C=N backbone,[30] substituents on the arylimino groups do influence the electrochemical behaviour of the DADs and provide a means to modulate their redox properties. Indeed, plotting the first reduction potentials of **5a**,**b**,**g**−**i** vs. the σ-Hammett constants of the respective *N*-aryl *para*-substituents[32] results in a linear correlation, suggesting that electron-donating *para*-phenyl substituents (**5f**, **5g**) lead to less easily, and electron-withdrawing *para*-phenyl substituents (**5h**, **5i**) lead to more easily reducible DAD systems with respect to simple phenyl-substituted derivatives **5a** and **9a**. The stabilization of additional charge in **5h** is large enough to permit the observation of the only reversible reduction in the series of identically *N*-substituted dialkynyl DADs at −1.55 V. In agreement with previously examined *p*-nitrophenylethynyl derivatives[33] it appears likely that in case of **5h** reduction of the nitrophenyl groups occurs. In addition, irreversible reductions of **5h** are observed at −1.88 V and −2.27 V.

In view of the unexpected electronic absorption data of differentially *N*,*N*′-disubstituted dialkynyl DAD **7** its electrochemical properties are of particular interest (Table 1). A first, irreversible reduction of **7** occurs at −1.52 V. This value is almost identical to that determined for **5h**, but in contrast to this process, the reduction of **7** is not reversible. Evidently, charge stabilization in the radical anion of **7** is not as efficient as in **5h**$^{\bullet-}$, leading to consecutive chemical reactions of the former which presumably involve solvent molecules. Further reduction of the reaction product of **7**$^{\bullet-}$, whose nature was not elucidated, takes place at a potential of −2.22 V and is reversible. Unsymmetrical **7** can also be oxidized at potentials of +0.40 V (oxidation of the Me_2N group, reversible at fast scan rates) and +1.05 V. These values are very close to those of **5f** and therefore suggest that the dimethylaminophenyl-half of **7** dominates the oxidation behaviour of this compound.

It thus appears that in agreement with the UV/Vis and ^{13}C-NMR data of **7**, the two halves of the molecule behave as largely independent units. If the electron-rich part of the molecule would interact strongly with the electron-poor side across the entire molecular skeleton, one would expect the reductions of **7** to occur at potentials between those of **5f** and **5h**. This, however, is clearly not the case. The notion that **7** consists of two electronically largely decoupled molecular halves is further supported by computational techniques (see below).

Computational Study

In an effort to complement some of the experimental results presented above and in order to get a better understanding of the molecular orbitals influencing the electronic properties of the dialkynyl DADs, we have performed semiempirical calculations on model compounds **11** and **14**−**17** (preset (*E*)-configuration around the C=N bonds in all cases) using the PM3 parameter set as implemented in MacSpartan.[34]



14 ($R^1 = R^2 = H$)
15 ($R^1 = R^2 = NO_2$)
16 ($R^1 = R^2 = NH_2$)
17 ($R^1 = NH_2$, $R^2 = NO_2$)

To evaluate the onformational preferences of dialkynyl DADs the dihedral NCCN angle of the DAD backbone of **14** was systematically varied. As can be seen from Figure 4, **14** possesses a global conformational minimum when the angle between the two ynimine moieties is 90°. However, this minimum is rather shallow, and the energy difference between this conformer and the corresponding *s-trans* conformation (dihedral angle 180°) amounts to only 1.50 kcal mol^{-1}. Not unexpectedly, the *s-cis*-conformation of **14** is 2.27 kcal mol^{-1} higher in energy than the global minium. It thus appears that in the ground state of **14** the two ynimine moieties are indeed electronically decoupled. However, at room temperature the more symmetrical *s-cis* and *s-trans* conformers, in which the electronic delocalization across the DAD backbone is maximized, are significantly populated. Similarly, the calculations suggest that the *s-trans* conformations observed in the crystals of **5c** and **9a** (vide supra) are effortlessly induced by crystal packing forces.

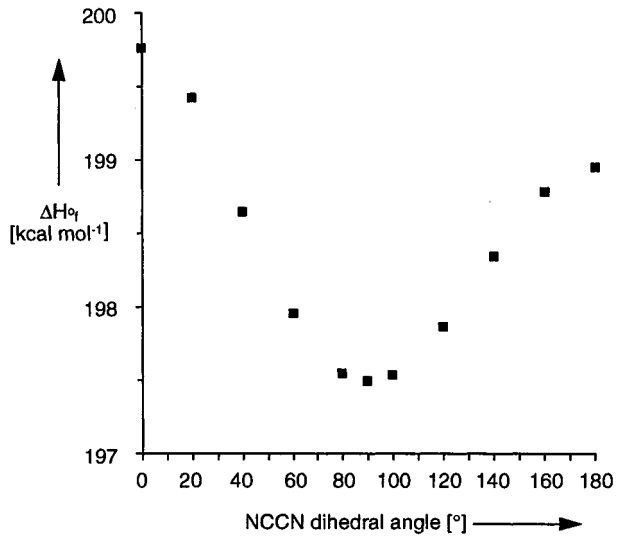


Figure 4. Heats of formation (PM3 data) of **14** upon variations of the N=C−C=N dihedral angle

The redox properties of the dialkynyl DADs as determined by electrochemical measurements are qualitatively reproduced by MO calculations (Table 2). Hence, when comparing the energy of the frontier orbitals of *N,N′*-diphenyl-butane-2,3-diimine **11** with those of **14** it becomes apparent that the LUMO of the latter is significantly stabilized (by 0.52 eV) with respect to that of the former. Alkynylation of the DAD backbone therefore leads to systems that are more easily reduced, in agreement with experimental electrochemical data. Inspection of the shapes of the frontier orbitals of dialkynyl DADs reveals sizeable contributions of the aryl ring atoms to the respective DAD HOMOs and LUMOs. This analysis explains the observed aryl-substituent effects on the redox properties of the dialkynyl DADs. As can be seen from Table 2, introduction of a nitro group leads to a significant stabilization of both the HOMO and the LUMO of **15** (with respect to the frontier orbitals of **14**), whereas the presence of the electron-donating amino group as in **16** raises both frontier orbitals.

Table 2. Heat of formation and energies of the frontier orbitals of selected diazabutadienes as calculated by the PM3 parameter set[a]

	11	**14**	**15**	**16**	**17**
ΔH_f^0 [kcal mol^{-1}]	76.14	198.50	180.77	194.79	187.15
HOMO [eV]	− 9.092	− 9.085	−10.171	− 8.395	− 8.630
LUMO [eV]	− 0.271	− 0.786	− 1.433	− 0.524	− 1.174

[a] DAD dihedral angle restricted to 180°C. Molecular symmetry was used where appropriate.

The energies of the frontier orbital of the differentially aryl substituted dialkynyl DAD **17**, the computational analogon of **7**, on the other hand, are comparable to the LUMO of **15** and the HOMO of **16**. And indeed, a visualization of these orbitals (Figure 5) reveals that the HOMO is centered on the electron-rich half of the molecule, whereas the LUMO has contributions mainly from the electron-poor *N*-aryl-ynimine half. This situation is different from the orbital pictures of the C_i-symmetrical **14** , whose HOMO and LUMO are spread over the entire molecular frame. **15** and **16** on the other hand have their HOMOs centered on the *N*-arylimine moiety, whereas their dialkynyl DAD moieties dominate their respective LUMOs.

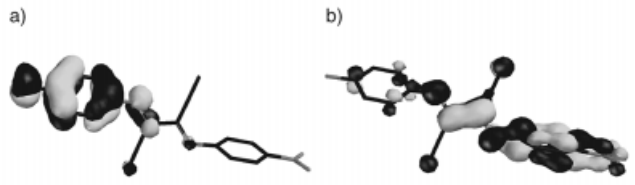


Figure 5. Shape of the frontier orbitals of **17** as calculated by the PM3 parameter set: a) HOMO, b) LUMO

In view of these orbital properties of **17** it is therefore not surprising that the redox behavior of **7** is governed individually and largely independently by the two ynimine halves of the molecule. Clearly, a more in-depth evaluation of the MO properties of dialkynyl DADs at higher levels of theory is warranted to address the question of electronic delocali-

zation within the DAD backbone, and, ultimately, to predict interactions between metal fragments and the dialkynyl DADs.

Conclusion

We have provided two complementary synthetic routes to 2,3-dialkynyl-1,4-diazabuta-1,3-dienes **2** and could establish the structural and some of the electronic properties of these interesting π systems. In general, the electronic features of compounds like **2**, as expressed by their UV/Vis absorption maxima and their electrochemical redox potentials, are significantly different from those of non-alkynyl DADs and are in agreement with the presence of an extended π-system. Similarly, the ease with which dialkynyl DADs can be reduced reflects their pronounced electron accepting properties and should influence the catalytic and the optical behaviour of transition metal complexes with these acetylenic ligand systems. Specifically, the low-lying LUMOs of the dialkynyl DADs should give rise to charge-transfer interactions with electron-rich transition metal centers and lead to sizeable absorptions in the Near Infrared. Particularly suprising was the finding that the ynimine moieties of **2** behave as two covalently connected yet electronically largely decoupled units as judged by X-ray crystallography, UV/Vis spectroscopy, ^{13}C-NMR spectroscopy, electrochemical measurements, and as supported by preliminary semiempirical MO calculations. Hence, the opportunity arises to further desymmetrize the two DAD halves chemically, and to explore them as unsymmetrical ligands to transition metal centers in stereoselective catalysis applications. Work along those lines is under way and the results will be communicated in due course.

Experimental Section

General: Melting points were determined on a Reichert hotstage and are uncorrected. − UV-Vis spectra were recorded on a Hewlett Packard HP 8452 UV-Vis ChemStation spectrometer. − Infrared spectra were obtained as KBr pellets or films on a Perkin-Elmer PE 1600 FT-IR spectrometer. − ^{1}H-NMR spectra were recorded at 300 MHz on a Varian XL 300 or at 250 MHz on a Bruker WM-250. ^{13}C-NMR spectra were measured at 62.9 MHz on a Bruker WM-250 spectrometer, at 90.6 MHz on a Bruker AM 360, or at 75.4 MHz on the Varian spectrometer described above. The degree of carbon substitution was determined by *J*-modulated spin echo experiments. δ values are ppm downfield from internal Me_4Si. − Mass spectra were obtained on a Varian MAT-311 A mass spectrometer at 70 eV. − Elemental analyses were performed on a Foss-Heraeus Vario EL.

Solvents were purified and dried according to standard procedures.[35] Tetrahydrofuran was distilled from sodium benzophenone immediately prior to use. Silica gel (60−200 mesh) for column chromatography was kindly provided by Merck KGaA, Darmstadt. Aniline derivatives **4a−i** are available from commercial suppliers and were distilled or recrystallized prior to use. The non-alkynyl diazabutadienes **10**, **11**, and **12** were prepared from the condensation of glyoxal (**10**), butane-2,3-dione[36] (**11**), or benzil (**12**) with the appropriate aniline derivatives.[1b] *N*-phenyl-1,3-diphenylprop-2-ynimine **13** was synthesized by the palladium-mediated route depicted in Scheme 2 and had spectral properties identical to those previously reported.[29] The bis(imidoyl chlorides) **8a**, **b**[16] and the $[Pd_2(dba)_3{\bullet}CHCl_3]$ complex[37] were obtained by published procedures.

Electrochemical Measurements: Electrochemical studies were carried out in CH_2Cl_2 + 0.1 M $[Bu_4N][PF_6]$ in a classical three electrode cell. The working electrode was a glassy carbon disk, the counter electrode a Pt wire, and the reference electrode an aqueous Ag/AgCl electrode. Measurements were performed by cyclic voltammetry at sweep rates ranging from 10 mV s^{-1} to 10 V s^{-1}, and by steady state voltammetry on a rotating disk electrode using a computerized multipurpose electrochemical device − DACFAMOV, CNRS Microtech, France − connected to an Apple II computer. Under our experimental conditions, the available potential range was −2.10 V to +1.80 V vs. Ag/AgCl. In order to allow comparison with data from previous studies, all potentials are given vs. Ferrocene as an internal standard, which is oxidized at +0.38 V/Ag/AgCl under these conditions.

X-ray Crystal Structure Analysis: Crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of hexane into a CH_2Cl_2 solution of **5c** and **9a**, respectively. Measurements were performed at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator using $Mo_{K\alpha}$ radiation and a ω/2θ scan mode. The structures were solved by direct methods and refined by full-matrix least-squares on *F* with all measured unique reflections. Hydrogens (except isopropyl hydrogens which were included but not refined) were located and refined isotropically. Table 3 summarizes details of the crystal data, the data collection, and the structure refinement. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101698 (for **5c**) and -101699 (for **9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +44-1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Computational Details: The calculations were performed using the semiempirical PM3 parameter set as implemented in MacSpartan Plus, Version 1.1.7, available from Wavefunction Inc., Irvine CA 92612 (USA), mounted on a Power Macintosh 6100. The dihedral angle of the DAD backbone was set to 180° and held constant during the geometry optimizations of **11** and **14−17**. To expedite calculations, molecular symmetry was used whenever possible.

General Procedures for the Preparation of 2,3-Dialkynyl Diazabutadienes Starting from Dialkynyl-1,2-dione (3)[12]

Method A: A mixture of **3**[13] (1 mmol), the corresponding aniline derivative **4** (3 mmol), a catalytic amount of LiBr, and activated molecular sieves was refluxed in dry xylene (25 mL) for several hours. After completion of the reaction (TLC control), the mixture was cooled to room temperature and filtered. Removal of the solvent left a residue which was chromatographed on SiO_2 using hexane/ethyl acetate (20/1).

Method B: To a solution of **3**[13] (1 mmol) in glacial acetic acid (25 mL) was added the corresponding aniline derivative **4** (3 mmol) and the solution was stirred for 30 min at room temperature (**5c**) or refluxed for 2 h (**5d**, **e**). After completion of the reaction (TLC control) the mixture was cooled to room temperature when necessary, poured into water (100 mL), and extracted with diethyl ether. The crude product remaining after drying over Na_2SO_4, filtration, and removal of the solvent was chromatographed on SiO_2 using hexane/ethyl acetate (20:1).

Table 3. Crystallographic data, data collection, and refinement parameters

	5c	**9a**
formula	$C_{40}H_{60}Si_2N_2$	$C_{30}H_{20}N_2$
M_r [g mol^{-1}]	625.11	408.51
colour, habit	yellow prism	yellow prism
crystal size [mm]	0.45 × 0.35 × 0.30	0.40 × 0.30 × 0.25
crystal system	triclinic	monoclinic
space group	*P*1(#2)	*C*2/c (#15)
a [Å]	8.090(2)	20.708(4)
b [Å]	10.325(2)	5.758(1)
c [Å]	12.565(4)	19.646(6)
α [°]	101.74(2)	90.0
β [°]	90.52(2)	103.97(2)
γ [°]	100.34(2)	90.0
V [Å^3]	1009.8(5)	2273(1)
Z	1	4
ρ_{calc} [g cm^{-3}]	1.028	1.193
μ (Mo−*Kα*) [mm^{-1}]	0.115	0.070
F(000)	342	856
independent rflns up to sinθ/λ = 0.66 Å^{-1}	3947	2736
rflns observed [$I \geq 3\sigma(I)$]	3122	1720
refinement method	Full-matrix least squares on *F*	
parameters refined	247	185
R [a]	0.058	0.045
R_w [b]	0.078	0.049

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. − [b] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Method C: To a solution of **3**[13] (1 mmol), the corresponding aniline derivative **4** (3 mmol), and NEt_3 (2 mL) in diethyl ether (50 mL) at 0°C under argon was added an etheral solution (10 mL) of $TiCl_4$ (1 mmol) while cooling with an ice-bath. After completion of the reaction (TLC control) the mixture was filtered through a pad of silica gel and the solvents were removed in vacuo. The crude product was chromatographed on SiO_2 using hexane/ethyl acetate (20:1).

***N,N′*-Diphenyl-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5a):** Yield: 398 mg (70%, method A), yellow solid, m.p. 80−81°C. − IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1} (w) (CH), 2943 (w) (CH), 2863 (s) (CH), 2158 (C≡C), 1585 (s) (C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 nm (9500), 376 nm (4100). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4−7.1 (m, 10 H, C_6H_5), 1.1−0.9 (m, 42 H, CH, CH_3). − ^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 149.03 (C), 148.15 (C), 127.18 (CH), 124.64 (CH), 119.91 (CH), 103.08 (C≡C), 96.73 (C≡C), 17.41 (CH_3), 10.09 (CH). − MS (70 eV); *m/z* (%): 568 (50) [M$^+$], 284 (100) [M$^+$/2]. − $C_{36}H_{52}N_2Si_2$ (568.3669): calcd. C 76.01, H 9.22, N 4.93; found C 75.86, H 9.16, N 4.81.

***N,N′*-Di(p-tolyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5b):** Yield: 388 mg (65%, method A), yellow solid, m.p. 109°C. − IR (KBr): $\tilde{\nu}$ = 2154 cm^{-1} (w, C≡C), 1577 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 nm (16400), 384 nm (9700). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 7 Hz, 4 H), 7.15 (d, *J* = 7 Hz, 4 H), 2.35 (s, 6 H, CH_3), 1.03 [s, 42 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 148.72 (C=N), 147.63 (C), 135.99 (C), 128.96 (CH), 121.75 (CH), 103.96 (C≡C), 98.45 (C≡C), 21.10 ($CH_{3,arom}$), 18.48 (CH_3), 11.20 (CH). − MS (70 eV), *m/z* (%): 596 (60) [M$^+$], 581 (6) [M$^+$ − CH_3], 554 (2) [M$^+$ − *i*Pr], 298 (100) [M$^+$/2]. − $C_{38}H_{56}N_2Si_2$ (596.40): calcd. C 76.46, H 9.46, N 4.70; found C 76.37, H 9.64, N 4.64.

***N,N′*-Bis(3,5-dimethylphenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5c):** Yield: 437 mg (70%, method A); 500 mg (80%, method B); yellow solid, m.p. 131−133°C. − IR (KBr): $\tilde{\nu}$ = 2941 cm^{-1} (w) (CH), 2863 (s) (CH), 2153 (C≡C), 1590 (s) (C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 nm (11600), 386 nm (4700). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (s, 4 H, C_6H_3), 6.81 (s, 2 H, C_6H_3), 2.30 (s, 12 H, CH_3), 1.1 - 0.9 (m, 42 H, CH, CH_3). − ^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 150.32 (C), 148.93 (C), 137.68 (C), 127.20 (CH), 118.32 (CH), 103.54 (C≡C), 97.93 (C≡C), 21.26 (CH), 18.43 (CH_3), 11.10 (CH_3). − MS (70 eV); *m/z* (%): 624 (60) [M$^+$], 312 (100) [M$^+$/2]. − $C_{40}H_{60}N_2Si_2$ (624.4295): calcd. C 76.87, H 9.68, N 4.49; found C 76.71, H 9.68, N 4.23.

***N,N′*-Bis(2,6-dimethylphenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5d):** Yield: 506 mg (81%, method B); yellow solid, m.p. 115−117°C. − IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1} (w) (CH), 2864 (s) (CH), 2155 (C≡C), 1584 (s) (C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 nm (10300), 390 nm (5400). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.1−6.8 (m, 6 H, C_6H_3), 2.11 (s, 12 H, CH_3), 1.0−0.8 (m, 42 H, CH, CH_3). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 151.12 (C), 149.72 (C), 127.73 (CH), 125.16 (C), 123.80 (CH), 103.17 (C≡C), 97.55 (C≡C), 18.29 (CH), 17.73 (CH_3), 10.95 (CH_3). − MS (70 eV); *m/z* (%): 624 (5) [M$^+$], 609 (100) [M$^+$ − CH_3], 312 (96) [M$^+$/2]. − $C_{40}H_{60}N_2Si_2$ (624.4295): calcd. C 76.87, H 9.68, N 4.49; found C 76.76, H 9.64, N 4.46.

***N,N′*-Bis(2,6-diisopropylphenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5e):** Yield: 567 mg (77%, method B); yellow solid, m.p. 128−129°C. − IR (KBr): $\tilde{\nu}$ = 3156 cm^{-1} (w) (CH), 2962 (s) (CH), 2870 (s) (CH), 2161 (C≡C), 1595 (s) (C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 262 nm (18400), 406 nm (1800). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.2−6.9 (m, 6 H, C_6H_3), 2.9−2.8 (m, 4 H, CH), 1.24 (d, 12 H, *J* = 6.9 Hz, CH_3), 1.15 (d, 12 H, *J* = 6.9 Hz, CH_3), 1.0−0.7 (m, 42 H, CH, CH_3). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 151.20 (C), 148.02 (C), 135.11 (C), 124.14 (CH), 122.78 (CH), 103.45 (C≡C), 97.67 (C≡C), 28.55 (CH), 22.77 (CH), 22.68 (CH), 18.24 (CH), 10.89 (CH). − MS (70 eV); *m/z* (%): 737 (5) [M$^+$], 694 (85) [M$^+$ − $CH(CH_3)_2$], 368 (100) [M$^+$/2]. − $C_{48}H_{76}N_2Si_2$ (736.5547): calcd. C 78.19, H 10.39, N 3.80; found C 78.06, H 10.26, N 3.73.

***N,N′*-Di(4-dimethylaminophenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5f):** Yield: 360 mg (55%, method A), red solid, m.p. 196°C. − IR (KBr): $\tilde{\nu}$ = 2147 cm^{-1} (w, C≡C), 1602 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 264 nm (20600), 318 nm (sh, 5800), 486 nm (34700). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 9 Hz, 4 H), 6.68 (d, *J* = 9 Hz, 4 H), 2.99 [s, 12 H, $N(CH_3)_2$], 1.13 [s, 42 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 149.76 (C), 144.60 (C), 139.04 (C=N), 125.71 (CH), 111.68 (CH), 102.69 (C≡C), 100.52 (C≡C), 40.54 ($N(CH_3)_2$), 18.68 (CH_3), 11.40 (CH). − MS (70 eV), *m/z* (%): 654 (100) [M$^+$], 639 (4) [M$^+$ − CH_3], 611 (4) [M$^+$ − *i*Pr], 327 (100) [M$^+$/2]. − $C_{40}H_{62}N_4Si_2$ (654.45): calcd. C 73.34, H 9.54, N 8.55; found C 73.36, H 9.57, N 8.63.

***N,N′*-Di(4-methoxyphenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5g):** Yield: 346 mg (55%, method C), yellow solid, m.p. 99°C. − IR (KBr): $\tilde{\nu}$ = 2144 cm^{-1} (w, C≡C), 1603 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 254 nm (15700), 404 nm (13900). − ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 9 Hz, 4 H), 6.89 (d, *J* = 9 Hz, 4 H), 3.80 (s, 6 H, OCH_3), 1.09 [s, 42 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 158.50 (C), 147.31 (C=N), 142.85 (C), 124.40 (CH), 113.55 (CH), 103.66 (C≡C), 98.97 (C≡C), 55.43 (OCH_3), 18.34 (CH_3), 11.43 (CH). − MS (70 eV), *m/z* (%): 628 (64) [M$^+$], 613 (6) [M$^+$ − CH_3], 585 (4) [M$^+$ − *i*Pr], 314 (100) [M$^+$/2]. − $C_{38}H_{56}N_2O_2Si_2$ (628.39): calcd. C 72.57, H 8.98, N 4.46; found C 72.41, H 8.80, N 4.51.

***N,N′*-Bis(4-nitrophenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5h):** Yield: 395 mg (60%, method A), orange solid, m.p. 166°C. − IR (KBr): $\tilde{\nu}$ = 2144 cm^{-1} (w, C≡C), 1587 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 230 nm (19200), 302 nm (21100), 360 nm (sh, 11400). − ^1H NMR (250.13 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 8.5 Hz, 4 H), 7.22 (d, *J* = 8.5 Hz, 4 H), 0.98 [s, 42 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 156.07 (C=N), 150.52 (C), 145.30 (C), 124.62 (CH), 120.57 (CH), 108.44 (C≡C), 96.36 (C≡C), 18.32 (CH_3), 10.95 (CH). − MS (70 eV), *m/z* (%): 658 (90) [M^+], 615 (6) [M^+ − *i*Pr], 329 (100) [M^+/2], 313 (36) [M^+/2 − O]. − $C_{36}H_{50}N_4O_4Si_2$ (658.34): calcd. C 65.62, H 7.65, N 8.51; found C 65.39, H 7.88, N 8.44.

***N,N′*-Bis(4-trifluormethylphenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (5i):** Yield: 423 mg (60%, method C), yellow solid, m.p. 135°C. − IR (KBr): $\tilde{\nu}$ = 2157 cm^{-1} (w, C≡C), 1599 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 250 nm (16200), 266 nm (sh, 14300), 364 nm (4900). − ^1H NMR (250.13 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.3 Hz, 4 H), 7.20 (d, *J* = 8.3 Hz, 4 H), 0.97 [s, 42 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 153.77 (C), 150.64 (C=N), 127.59 (q, $J_{C,F}$ = 33 Hz, *C*-CF_3), 125.88 (CH), 124.28 (q, $J_{C,F}$ = 271 Hz, CF_3), 120.30 (CH), 106.70 (C≡C), 96.85 (C≡C), 18.30 (CH_3), 11.00 (CH). − MS (70 eV), *m/z* (%): 704 (42) [M^+], 661 (8) [M^+ − *i*Pr], 352 (100) [M^+/2], 309 (16) [M^+/2 − *i*Pr]. − $C_{38}H_{50}N_2F_6Si_2$ (704.34): calcd. C 64.74, H 7.15, N 3.98; found C 64.79, H 7.35, N 3.89.

1,6-Bis(triisopropylsilyl)-4-(4-dimethylaminophenyl)iminohexa-1,5-diyn-3-one (6): Dialkynyl-1,2-diketone **3**[13] was converted with 1 equiv. **4f** under the conditions of method A. Yield: 472 mg (88%), deep red solid, m.p. 78°C. − IR (KBr): $\tilde{\nu}$ = 2150 cm^{-1} (w, C≡C), 2133 (w, C≡C), 1636 (s, C=O), 1610 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 268 nm (12800), 320 nm (sh, 4200), 486 nm (27500). − ^1H NMR (250.13 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9 Hz, 2 H), 6.65 (d, *J* = 9 Hz, 2 H), 3.07 [s, 6 H, N(CH_3)$_2$], 1.16 [s, 21 H, Si(*i*Pr)$_3$], 1.15 [s, 21 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 176.48 (C=O), 151.68 (C) 138.38 (C), 136.69 (C=N), 128.56 (CH), 111.12 (CH), 106.29 (C≡C), 103.65 (C≡C), 99.83 (C≡C), 99.42 (C≡C), 40.15 [N(CH_3)$_2$], 18.58 (CH_3), 11.30 (CH), 11.17 (CH). − MS (70 eV), *m/z* (%): 536 (30) [M^+], 493 (2) [M^+ − *i*Pr], 327 (100). − $C_{32}H_{54}N_2OSi_2$ (536.36): calcd. C 71.59, H 9.77, N 5.22; found C 71.43, H 9.69, N 4.95.

***N*-(4′-Dimethylaminophenyl)-*N′*-(4-nitrophenyl)-1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-diimine (7):** Iminone **6** was reacted with 1 equiv. of the aniline derivative **4h** under the conditions of method C. Yield: 578 mg (88%), deep red solid, m.p. 102°C. − IR (KBr): $\tilde{\nu}$ = 2145 cm^{-1} (w, C≡C), 2136 (w, C≡C), 1604 (s, C=N, NMe_2-half), 1574 (s, C=N, NO_2-half). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 nm (17800), 302 nm (sh, 11500), 468 nm (18400). − ^1H NMR (250.13 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 9 Hz, 2 H), 7.90 (d, *J* = 9 Hz, 2 H), 7.10 (d, *J* = 9 Hz, 2 H), 6.68 (d, *J* = 9 Hz, 2 H), 1.14 [s, 42 H, Si(*i*Pr)$_3$], 0.98 [s, 42 H, Si(*i*Pr)$_3$]. − ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 157.77 (C), 153.20 (C=N, NO_2-half), 150.88 (C), 144.49 (C), 139.74 (C=N, NMe_2-half), 137.51 (C), 127.39 (CH), 124.54 (CH), 120.54 (CH), 111.27 (CH), 105.87 (C≡C), 105.07 (C≡C), 100.03 (C≡C), 97.73 (C≡C), 40.31 (CH_3), 18.62 (CH_3), 18.44 (CH), 11.34 (CH_3), 11.07 (CH). − MS (70 eV), *m/z* (%): 656 (100) [M^+], 613 (2) [M^+ − *i*Pr], 329 (10), 327 (100), 313 (36). − $C_{38}H_{56}N_4O_2Si_2$ (656.39): calcd. C 69.47, H 8.60, N 8.53; found C 69.26, H 8.54, N 8.67.

General Procedure Pd-Mediated Alkynylation of Bis(imidoyl chlorides):[11] A mixture of bis(imidoyl chloride)[16] (1 mmol), alkynylstannane (2 mmol), 10 mol% [$Pd_2(dba)_3 \cdot CHCl_3$] and 45 mol% $AsPh_3$ in 20 mL toluene was heated to 50−85°C for 5 h under argon. After cooling to room temperature, the mixture was filtered through a pad of silica and residual stannane was removed by precipitation with aqueous NaF solution. The organic layer was dried over Na_2SO_4. After filtration and removal of the solvent the residue was chromatographed on SiO_2 using hexane/ethyl acetate 20:1.

***N,N′*-Diphenyl-1,6-diphenylhexa-1,5-diyne-3,4-diimine (9a):** Yield: 204 mg (50%), yellow solid, m.p. 174°C. − IR (KBr): $\tilde{\nu}$ = 2213 cm^{-1} (s, C≡C), 1575 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 nm (31700), 282 nm (sh, 23700), 298 nm (sh, 22400), 376 nm (8400). − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.50−7.20 (m, 20 H). − ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 150.57 (C), 149.84 (C=N), 132.61 (CH), 129.82 (CH), 128.49 (CH), 128.32 (CH), 125.93 (CH), 121.35 (C), 121.02 (CH), 99.73 (C≡C), 82.48 (C≡C). − MS (70 eV), *m/z* (%): 408 (36) [M^+], 204 (100) [M^+/2], 77 (38) [C_6H_5]. − $C_{30}H_{20}N_2$ (408.16): calcd. C 88.20, H 4.94, N 6.86; found C 87.97 H 5.14, N 7.02.

***N,N′*-Di(*p*-tolyl)-1,6-diphenylhexa-1,5-diyne-3,4-diimine (9b):** Yield: 218 mg (50%), orange yellow solid, m.p. 158°C. − IR (KBr): $\tilde{\nu}$ = 2215 cm^{-1} (s, C≡C), 1602 (s, C=N). − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 nm (32100), 288 nm (23900), 392 nm (10100). − ^1H NMR (250 MHz, $CDCl_3$): δ = 7.44−7.22 (m, 18 H), 2.40 (s, 6 H, CH_3). − ^{13}C NMR (90.56 MHz, $CDCl_3$): δ = 149.99 (C=N), 147.71 (C), 136.12 (C), 132.57 (CH), 129.70 (CH), 129.07 (CH), 128.33 (CH), 121.69 (CH), 121.61 (C), 99.25 (C≡C), 82.85 (C≡C), 21.19 (CH_3). − MS (70 eV), *m/z* (%): 436 (36) [M^+], 421 (10) [M^+ − CH_3], 218 (100) [M^+/2], 91 (30) [C_7H_7]. − $C_{32}H_{24}N_2$ (436.19): calcd. C 88.03, H 5.55, N 6.42; found C 87.84 H 5.79, N 6.44.

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