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Donor−Acceptor Triazenes: Synthesis, Characterization, and Study of Their Electronic and Thermal Properties

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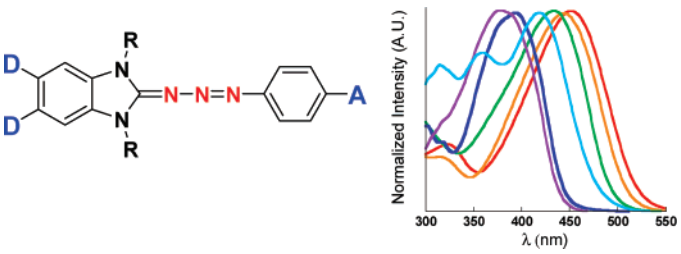

A new class of 1,3-disubstituted-triazenes were synthesized by coupling functionalized benzimidazol-2-ylidenes, as their free N-heterocyclic carbenes or generated in situ from their respective benzimidazolium precursors, to various aryl azides in modest to excellent isolated yields (36−99%). Electron delocalization between the two coupled components was studied using UV−vis spectroscopy, NMR spectroscopy, and X-ray crystallography. Depending on the complementarity of the functional groups on the N-heterocyclic carbenes and the organic azides, the respective triazenes were found to exhibit λ_{max} values ranging between 364 and 450 nm. X-ray crystallography revealed bond alteration patterns in a series of triazenes characteristic of donor−acceptor compounds. Triazene thermal stabilities were studied using thermogravimetric analysis and found to be strongly dependent on the sterics of the benzimidazol-2-ylidene component and the electronics of the azide component. Triazenes possessing bulky N-substituents (e.g., *neo*-pentyl, *tert*-butyl, etc.) were stable in the solid-state to temperatures exceeding 150 °C, whereas analogues with small N-substituents (e.g., methyl) were found to slowly decompose at room temperature. Triazenes featuring electron-rich phenyl azide components decomposed at higher temperatures than their electron-deficient analogues. Products of the thermally induced triazene decomposition reaction were identified as molecular nitrogen and the respective guanidine. Using an isotopically labeled triazene, the mechanism of the decomposition reaction was found to be analogous to the Staudinger reaction.

Introduction

Triazenes are a unique class of polyazo compounds containing three consecutive nitrogen atoms in an acyclic arrangement.[1] Historically, they have found use as DNA alkylating agents in tumor therapy,[2] iodo-masking groups in the synthesis of small[3] and macromolecules,[4] protecting groups for amines and diazonium salts,[5] photoactive substrates,[6] and precursors to various types of compounds of medicinal importance.[7] More recently, triazenes have been used to facilitate coupling of functionalized arenes to passivated Si surfaces for applications in semiconductors and nanoelectronics.[8]

The two most widely utilized methods of synthesizing triazenes[1] are coupling of aryl diazonium salts to amines[9] and addition of organometallic reagents (RMgX, RLi, etc.) to alkyl azides.[10] However, the reagents used in these reactions are

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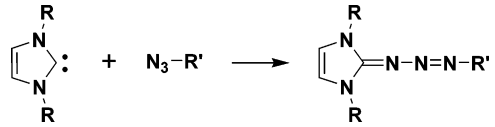

FIGURE 1. Triazene formation via coupling of a N-heterocyclic carbene with an azide.

extremely reactive, and often flammable, which necessitates the use of relatively sophisticated equipment and techniques for safety and success. As a result, the scope of compatible substrates and the range of associated applications for preparing triazenes are restrictive. These limitations warrant the development of new methods for accessing this important class of compound.

Recently, we discovered a new, practical method for preparing triazenes. In our initial communication,[11] we reported that addition of a N-heterocyclic carbene[12] (NHC) to an organic azide afforded a 1,3-disubstituted triazene in excellent yield (see Figure 1).[13] The coupling reaction was found to proceed rapidly at room temperature ($\tau_{1/2} \sim$ minutes) and showed good tolerance toward a broad array of functional groups and structural variations. For example, alkyl, aryl, acyl, and tosylated azides were coupled to imidazol-2-ylidenes with N-substituents ranging in size from relatively small methyl groups to bulky mesityl (1,3,5-trimethylbenzene) groups in 54−94% isolated yields. Since imidazol-2-ylidenes are typically prepared via deprotonation of their more stable and readily accessible imidazolium precursors,[14] we also demonstrated that N-heterocyclic carbenes (NHCs) can be generated in situ from their respective precursors prior to azide coupling.

In many ways, the aforementioned NHC/azide coupling reaction is similar to the Cu-catalyzed [3 + 2] Huisgen[15] cycloaddition reaction between alkynes and azides, now commonly categorized under "click chemistry."[16] Both reactions: (1) provide products in excellent yields, (2) are atom-economical, (3) proceed with relatively high rates, (4) exhibit good functional group tolerance, and (5) utilize a relatively broad range of substrates. Over a short time span, click chemistry has found utility in a multitude of synthetic, biological, and materials applications.[17] Likewise, in an effort to expand this repertoire, we demonstrated that the NHC/azide coupling reaction was useful for the postpolymerization modification of polyolefins containing pendant azido groups.[18]

We have recently launched a program that utilizes NHCs as building blocks for polymer synthesis, with an emphasis on preparing functional materials suitable for use in electronic applications.[19] In addition to the practical advantages discussed above, the NHC/azide coupling reaction has two unique features for this purpose: (1) chemical unsaturation is conserved as reactants are converted to products and (2) the triazeno bridge formed formally conjugates the two organic components to each other (i.e., the imidazole ring and the organic fragment stemming from the azide).

The primary purpose of this study was to explore the feasibility of preparing triazenes that exhibit extensively delo-

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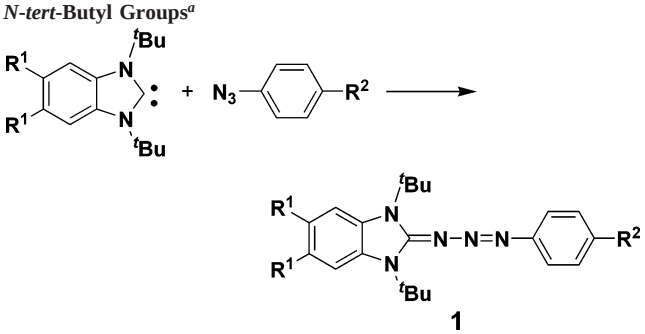
TABLE 1. Synthesis of Donor−Acceptor Triazenes Bearing Bulky *N*-*tert*-Butyl Groups[a]



entry	product	R^1	R^2	yield (%)[b]
1	**1-H-H**	H	H	99
2	**1-H-OCH$_3$**	H	OCH_3	99
3	**1-H-NO$_2$**	H	NO_2	99
4	**1-OCH$_3$-H**	OCH_3	H	99
5	**1-OCH$_3$-OCH$_3$**	OCH_3	OCH_3	99
6	**1-OCH$_3$-NO$_2$**	OCH_3	NO_2	99
7	**1-F-H**	F	H	99
8	**1-F-OCH$_3$**	F	OCH_3	99
9	**1-F-NO$_2$**	F	NO_2	99

[a] General reaction conditions: 1,3-di-*tert*-butyl-benzimidazol-2-ylidene (1.0 equiv) and an organic azide (1.0 equiv), concentration of substrates = 0.1 M, solvent = THF, 23 °C. [b] Isolated yields.

calized structures and examine their potential in preparing robust materials with useful electronic properties. In particular, we describe the synthesis of a variety of "donor−acceptor" triazenes where various benzimidazol-2-ylidenes[20] were coupled to aryl azides possessing complementary functional groups. The extent of electron delocalization was studied using UV−vis spectroscopy, NMR spectroscopy, and X-ray crystallography. The thermal stabilities of the triazene products formed from the NHC/azide coupling reaction were also evaluated and included efforts toward deconvoluting how various steric and electronic features influence this important physical characteristic. Previously, we discovered that at elevated temperatures triazenes obtained from coupling NHCs to organic azides lose molecular nitrogen and afford the respective guanidines.[11] In the well-known Staudinger reaction,[21] the intermediate phosphatriazene formed upon combination of a phosphine with an azide also extrudes molecular nitrogen to form a phosphazene; hence, we also tested whether triazene decomposition proceeded via an analogous mechanism.

A secondary objective of this study was fundamental. The triazeno linkage (C═N−N═N) formed in the NHC/azide reaction bears structural similarities to azine (C═N−N═C) and 1,3-diene (C═C−C═C) linkages, which prompted us to study the electronic properties of four-electron, conjugated π-systems containing three consecutive nitrogen atoms. Previously, Glaser, Euler, and others prepared and studied the electronic and structural properties of donor−acceptor azines by NMR spectroscopy,[22] cyclic voltammetry,[23] and X-ray crystallography for select crystalline materials.[24] It was concluded that electronic communication across the N−N bond was minimal. Hence, while 1,3-dienes are known to exhibit extensively delocalized structures, azines were called effective "conjugation stoppers."[25] However, Clyburne and co-workers demonstrated that azines prepared via coupling of an imidazol-2-ylidene to 9-diazofluorene were extensively delocalized, and under certain conditions exhibited nonlinear optical (NLO) responses.[26]

Results and Discussion

As shown in Table 1, a range of functionalized benzimidazol-2-ylidenes and aryl azides were chosen as coupling partners. Our hypothesis was that if the triazo linkage enabled electronic communication, then bathochromic shifts should be observed by UV−vis spectroscopy as the pendant electron-donating and electron-withdrawing substituents in the resulting triazenes became more complementary. Similarly, successive downfield shifts were also expected in the NMR spectra for the same series of compounds. If quality crystals suitable for X-ray diffraction could be obtained, then distinct changes in the triazo bond length patterns should be observed as a function of the electronic character of the peripheral groups in the solid-state as well.

Triazene Nomenclature. In order to simplify the identification of the triazenes discussed in this study, the following convention was applied: Following the triazene numeric label, which refers to class of benzimidazol-2-ylidene used (with attention directed toward changes in the N-substituents), the first suffix identifies the pendant functional group on the NHC moiety, and the second suffix identifies the pendant functional group on the aryl azide. For example, 1-(1,3-di-*tert*-butyl-benzimidazol-2-ylidene)-3-phenyltriazene was identified as **1-H-H** (see Table 1). Likewise, 1-(1,3-dimethyl-5,6-dimethoxy-benzimidazol-2-ylidene)-3-(*p*-nitrophenyl)triazene was identified as **3-OCH$_3$-NO$_2$** (see Table 3).

Synthesis of Triazenes 1. In general, triazenes **1** were prepared by coupling 1,3-di-*tert*-butyl-benzimidazol-2-ylidene (generated through deprotonation of its corresponding benzimidazolium salt[27] using potassium *tert*-butoxide and then isolated and used as its free NHC) with 1 mol equiv of aryl azide.[28] The reactions were conducted at ambient temperature using tetrahydrofuran (THF) as solvent at 0.1 M substrate concentrations. Depending on the electronics of the azide

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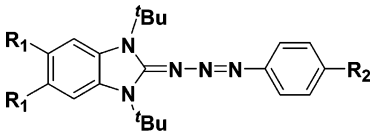
(28) Alternatively, many of the triazenes shown in Table 1 may be prepared by generating the free NHC in situ (from its benzimidazolium salt) in the presence of an equimolar amount of organic azide. However, this approach appears to be limited to substrates which are stable to base. For example, 1-azido-4-nitrobenzene was found to rapidly decompose under strongly basic conditions. Hence, the use of free NHCs (e.g., 1,3-di-*tert*-butyl-benzimidazol-2-ylidene-4,5-dimethoxy-1,3-di-*tert*-butyl-benzimidazol-2-ylidene, and 1,3-di-*tert*-butyl-4,5-difluoro-benzimidazol-2-ylidene) were necessary to form triazenes containing aryl azide moieties (e.g., Table 1: **1-H-NO$_2$**, **1-OCH$_3$-NO$_2$**, and **1-F-NO$_2$**).

TABLE 2. Summary of Key UV−vis Absorbance Data for Triazenes 1[a]



entry	compound	R_1	R_2	λ_{max} (nm)	log (ϵ)[b]
1	**1-H-H**	H	H	364	4.20
2	**1-OCH$_3$-H**	OCH_3	H	372	4.17
3	**1-F-H**	F	H	368	4.16
4	**1-H-OCH$_3$**	H	OCH_3	380	4.12
5	**1-H-NO$_2$**	H	NO_2	440	4.35
6	**1-F-OCH$_3$**	F	OCH_3	383	4.28
7	**1-F-NO$_2$**	F	NO_2	438	4.52
8	**1-OCH$_3$-OCH$_3$**	OCH_3	OCH_3	402	4.41
9	**1- OCH$_3$-NO$_2$**	OCH_3	NO_2	450	4.49

[a] UV−vis spectra were acquired in CH_2Cl_2 at ambient temperature. [b] ϵ is the molar absorptivity with units of L mol^{-1} cm^{-1}.

component, reaction times ranged from minutes (electron-poor azides) to hours (electron-rich azides), as monitored by ^{1}H NMR spectroscopy. To obtain more quantitative information on reaction progress versus time, the bimolecular rate constants of reactions involving 1,3-di-*tert*-butyl-benzimidazol-2-ylidene and a select range of azides with various electronic properties were measured by ^{1}H NMR spectroscopy (THF-d_8, 23 °C). The coupling reaction between the free NHC and an electron-poor azide, 1-azido-4-nitrobenzene, was extremely fast and measured to be 0.215 L·mol^{-1}·s^{-1}. In contrast, the rate constants for coupling the same NHC to relatively more electron-rich azides, phenyl azide and 1-azido-4-methoxybenzene, were relatively slow and found to be 0.003 L·mol^{-1}·s^{-1} and 0.001 L·mol^{-1}·s^{-1}, respectively. Collectively, these observations were consistent with a coupling mechanism that involves nucleophilic attack of a NHC at the terminal nitrogen of an aryl azide. Purification of the products generated from this reaction was straightforward, requiring only filtration of the reaction media through a PTFE filter followed by evaporation of solvent. Using this methodology, triazene products were consistently obtained in excellent (>99%) yields and in high purities. The molecular structures of triazenes **1** shown in Table 1 were confirmed by NMR spectroscopy, UV−vis spectroscopy, and for select crystalline compounds, X-ray crystallography (see below). Mass spectrometry and elemental analyses provided additional support for their structure and purity.

Characterization of 1: UV−vis Absorption Spectroscopy. After the donor−acceptor triazenes shown in Table 1 were synthesized, UV−vis absorption spectroscopy was used to measure the electronic properties of these compounds. As shown in the UV−vis absorption spectra included in Figure 2 and summarized in Table 2, a gradual bathochromic shift in the λ_{max} of the triazene chromophore was observed as the electron-donating/electron-withdrawing character of its peripheral functional groups became more complementary. Close analysis of the data suggested that while electronic communication between the terminal functional group on the benzimidazol-2-ylidene and the azide was observed, the interaction was relatively minor. For example, only 4−8 nm bathochromic shifts were observed in the λ_{max} upon replacing two hydrogens in the benzimidazol-2-ylidene to either methoxy or fluoro groups (i.e., **1-H-H** → **1-OCH$_3$-H** or **1-F-H**; entries 1−3). These observations were in accord with the high degree of bond polarization previously observed in complexes formed between imidazol-2-ylidenes and main group elements[26b,29] and may be rationalized by the strong electron-donating character of the nitrogen atoms present in the imidazole moiety. In contrast, significant effects on λ_{max} were observed when the terminal functional group on the azide coupling partner was varied. For example, replacing a methoxy group with a nitro group resulted in a 60 nm bathochromic shift in the λ_{max} (i.e., **1-H-OCH$_3$** → **1-H-NO$_2$**; entries 4 and 5). Similar spectroscopic changes were observed with triazenes containing electron-poor (i.e., **1-F-OCH$_3$** → **1-F-NO$_2$**, $\Delta\lambda_{max}$ = 55 nm; entries 6 and 7) and electron-rich (i.e., **1-OCH$_3$-OCH$_3$** → **1-OCH$_3$-NO$_2$**, $\Delta\lambda_{max}$ = 48 nm; entries 8 and 9) benzimidazol-2-ylidene components. As expected, triazene **1-OCH$_3$-NO$_2$**, prepared by coupling a highly electron-rich benzimidazol-2-ylidene with a highly electron-deficient azide, exhibited the longest λ_{max} at 450 nm for any of the triazenes studied (entry 9). Collectively, these results suggested that the triazeno linkages (C═N−N═N) were effective in delocalizing electronic charge between complementary NHC and organic azide components.

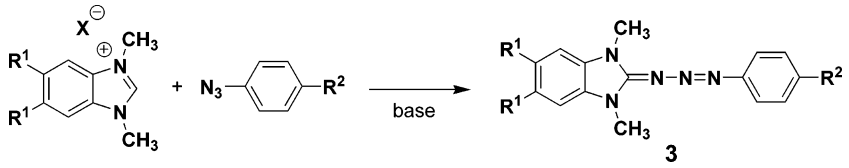
Characterization of 1: NMR Spectroscopy. Next, we turned our attention toward studying the donor−acceptor triazenes (**1**) via ^{1}H and ^{13}C NMR spectroscopy. In general, signals attributed to the arene protons on the azide-containing moieties shifted upfield whereas the benzimidazol-2-ylidene protons shifted downfield upon coupling. This result was consistent with charge transfer from the electron-rich component to the relatively electron-poor component. The magnitude of these shifts were strongly dependent on the nature of the functional group on the azide with a smaller dependency on the pendant functional group on the benzimidazol-2-ylidene, although overall changes were small for all compounds studied (^{1}H NMR: < 0.1 ppm; ^{13}C NMR: < 1.0 ppm). The most pronounced shifts were observed in the series (^{1}H NMR, solvent = $CDCl_3$): **1-OCH$_3$-NO$_2$** (δ = 8.11 ppm, Ar−H ortho to NO_2; 7.50 ppm Ar−H meta to NO_2), **1-H-NO$_2$** (δ = 8.14 ppm; 7.54 ppm), and **1-F-NO$_2$** (δ = 8.18 ppm; 7.58 ppm).

X-ray Crystallography Studies of Triazenes. To obtain additional support for the existence of conjugation through the triazeno linkage and to help quantify the extent to which a dipolar triazene can effectively distribute charge, single-crystal X-ray crystallography was used to study the donor−acceptor triazenes described above. Shown in Figure 3 (top) are two bona fide resonance structures (**A** and **B**) for triazenes flanked by donor (D) and acceptor (A) groups. In our initial investigation, X-ray crystallography revealed that 1-(1,3-dimesityl-imidazol-2-ylidene)-3-benzyl-triazene (**2**), prepared via coupling of 1,3-dimesityl-imidazol-2-ylidene with benzyl azide, exhibited alternating bond lengths consistent with the structure **A** (see Figure 3, bottom).[11] However, we anticipated that the donor−acceptor triazenes (**1**) discussed above would adopt resonance structure **B**, as the pendant electron-withdrawing group on one component was matched with an electron-donating group on the other. More specifically, the single N−N bonds should shorten and the double N═N bonds should elongate as the complementarity of the donor−acceptor groups on the triazenes increased.

Synthesis and Characterization of Triazenes 3. While we were unable to obtain quality crystals suitable for X-ray analysis of the donor−acceptor triazenes **1**, a related series of crystalline analogues (**3**) were obtained by effectively replacing the bulky *N*-*tert*-butyl substituents on the benzimidazol-2-ylidene moieties with smaller *N*-methyl groups. Since benzimidazol-2-ylidenes

(29) Arduengo, A. J.; Calabrese, J. C.; Cowley, A. H.; Dias, H. V. R.; Goerlich, J. R.; Marshall, W. J.; Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151.

TABLE 3. Synthesis and UV−vis Data of Crystalline Triazenes Bearing *N*-Methyl Groups[a]



3

entry	compound	R^1	R^2	yield (%)[b]	λ_{max} (nm)[c]	log (ϵ)[c]	μ_{calc} (D)[d]
1	**3-H-H**	H	H	36	372	4.40	4.29
2	**3-H-NO_2**	H	NO_2	56	444	4.38	10.6
3	**3-OCH_3-H**	OCH_3	H	69	400	4.39	5.39
4	**3-OCH_3-NO_2**	OCH_3	NO_2	74	467	4.22	11.2

[a] General conditions: 1,3-Dimethyl-benzimidazol-2-ylidene (1.00 equiv) was generated in situ in THF (0.2 M) at −30 °C from its respective benzimidazolium salt using potassium *tert*-butoxide (1.05 equiv). The noted organic azide (1.00 equiv) was then added to the resulting reaction mixture. [b] Isolated yield. [c] UV−vis spectra were acquired in CH_2Cl_2 at ambient temperature. ϵ is the molar absorptivity with units of L mol^{-1} cm^{-1}. [d] Calculated using density functional theory; see: ref 33. X = iodide.

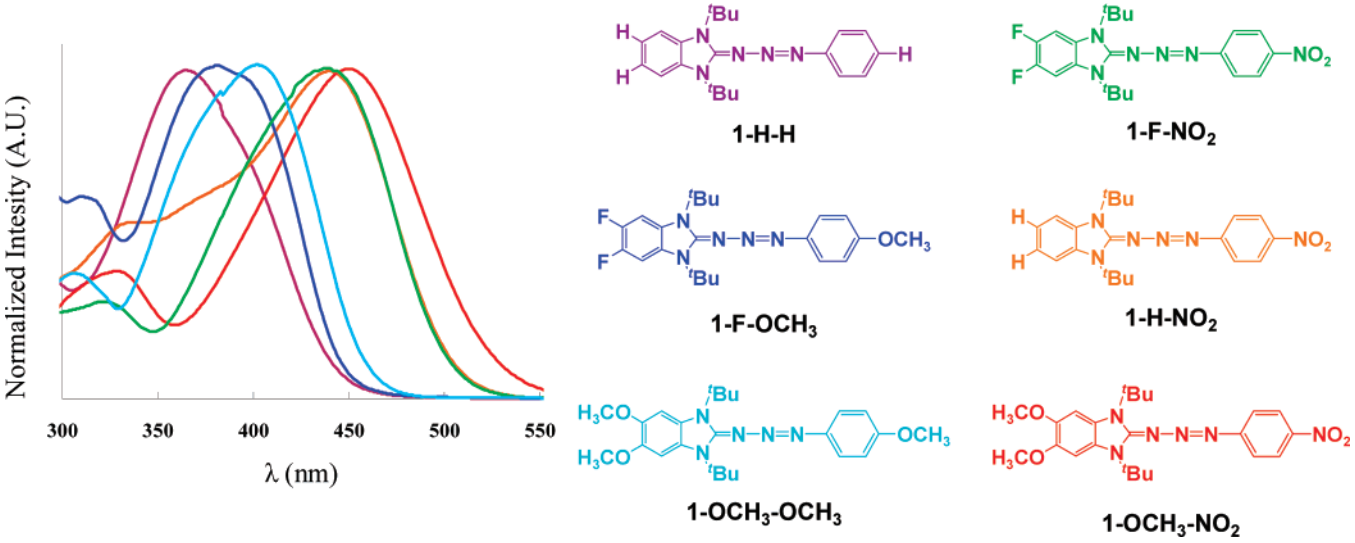
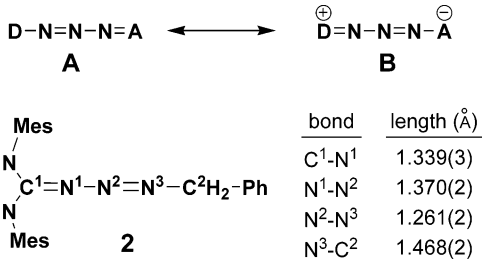


FIGURE 2. UV−vis absorbance spectra (left) color coded with their respective compound (right). Spectra were acquired in CH_2Cl_2 at ambient temperature. For λ_{max} (nm) values, see Table 2.



bond	length (Å)
C^1-N^1	1.339(3)
N^1-N^2	1.370(2)
N^2-N^3	1.261(2)
N^3-C^2	1.468(2)

FIGURE 3. (top) Illustration of two resonance structures for triazenes containing donor (D) and acceptor (A) groups. (bottom) Key bond lengths for 1-(1,3-dimesityl-imidazol-2-ylidene)-3-benzyl-triazene (**2**).[11]

with *N*-methyl groups are known to dimerize to their respective enetetraamines, which oxidize rapidly in the presence of air,[30] NHCs were generated in situ under basic conditions from their known[30] benzimidazolium precursors in the presence of an organic azide. Using this approach, a range of donor−acceptor triazenes **3** were prepared in moderate to good yields (36−74%, see Table 3).[31,32] As shown in the UV−vis absorption spectra (see Figure 4) and summarized in Table 3, the λ_{max} of triazenes **3** in CH_2Cl_2 were found to be nearly identical to their di-*tert*-butyl analogues (**1**), which indicated that the main chromophore was only minimally affected by the differences in steric bulk between these two series of compounds. Notably, the dipole moments (μ) of these compounds, as calculated using density functional theory, correlated with the donor−acceptor groups on their periphery (see Table 3).[33] For example, replacement of the *p*-hydrogen atom on the azide component with a nitro group resulted in a large increase in the calculated dipole, compare: **3-H-H**, 4.29 D vs **3-H-NO_2**, 10.6 D (entries 1 and 2). In contrast, incorporation of electron-donating methoxy groups into the benzimidazol-2-ylidene fragment (i.e., **3-OCH_3-H**) resulted in only a modest increase in the calculated dipole

(30) (a) Wanzlick, H. W.; Buchler, J. W. *Chem. Ber.* **1964**, *97*, 2447. (b) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *Leibigs Ann.* **1997**, 265. (c) Liu, Y.; Lindner, P. E.; Lemal, D. M. *J. Am. Chem. Soc.* **1999**, *121*, 10626.

(31) Since benzimidazol-2-ylidenes with small N-substituents are prone to exist as equilibrium between free NHC and its oxygen-sensitive dimer,[30] these reactions must be conducted with the rigorous exclusion of oxygen.

(32) Unlike their *N*-*tert*-butyl analogues, triazenes **3** were found to exhibit low solubilities in common organic solvents (i.e., THF, toluene, DMF, DMSO, CH_3CN, etc.) and decomposed slowly over several days in solution or in the solid-state (see main text for a more detailed discussion of this phenomenon). These characteristics are partially responsible for the relatively low yields of the reactions summarized in Table 3.

(33) Dipole moments were calculated at the B3LYP (6−31G*) level of density functional theory, as implemented in the Spartan 2004 software package (Wavefunction, Irvine, CA 92612).

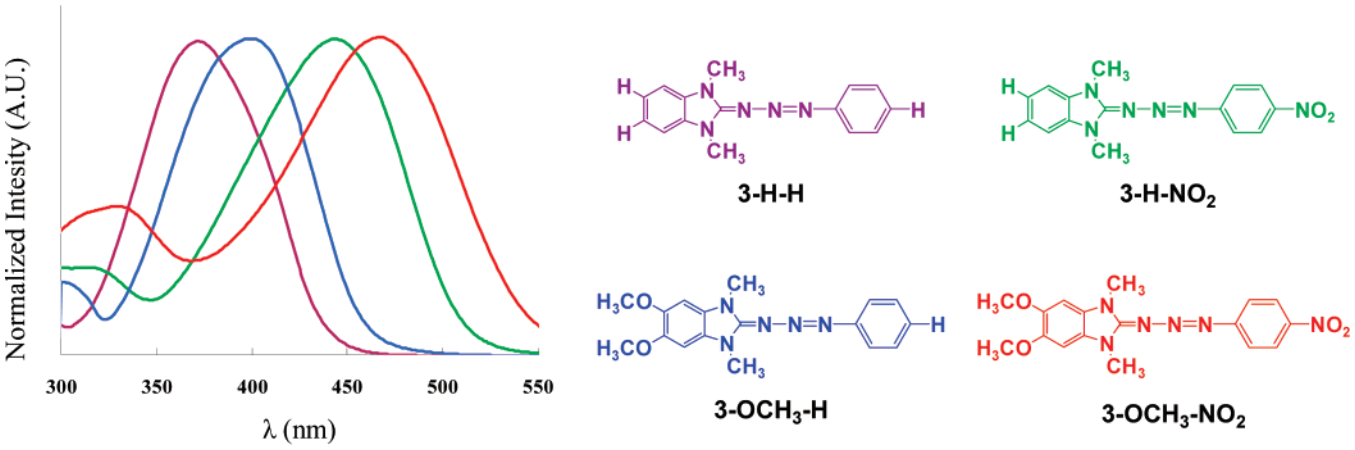


FIGURE 4. UV−vis absorbance spectra (left) color coded with their respective compound (right). Spectra were acquired in CH_2Cl_2 at ambient temperature. For λ_{max} (nm) values, see Table 3.

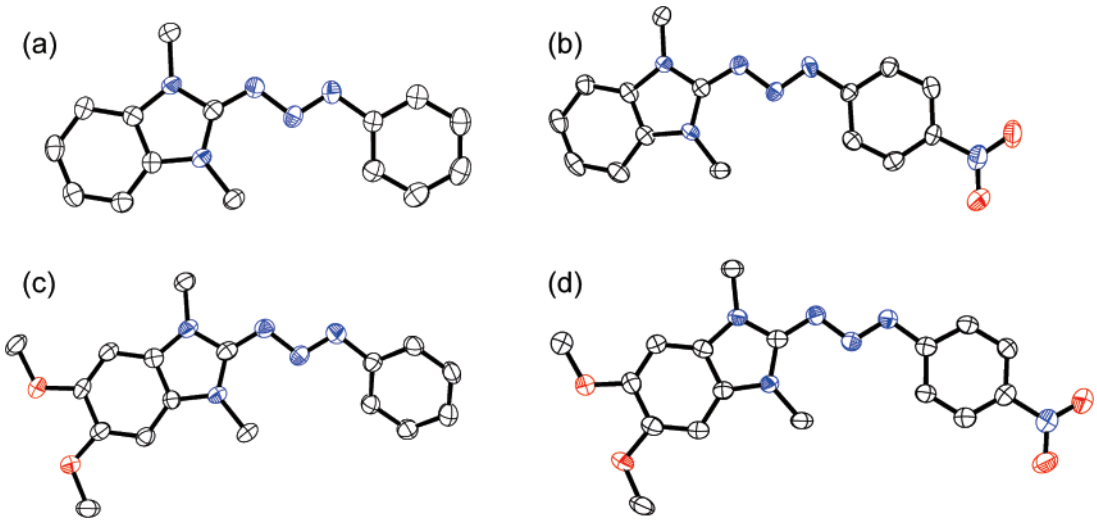
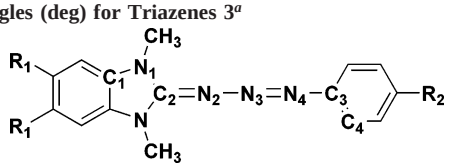


FIGURE 5. ORTEP diagrams for (a) **3-H-H**, (b) **3-H-NO$_2$**, (c) **3-OCH$_3$-H**, (d) **3-OCH$_3$-NO$_2$**. Selected bond lengths (Å) and angles (deg) are summarized in Table 4. Solvent molecules have been removed for clarity.

TABLE 4. Selected Bond Lengths (Å) and Angles (deg) for Triazenes 3[a]



entry	compound	C_1-N_1 (Å)	N_1-C_2 (Å)	C_2-N_2 (Å)	N_2-N_3 (Å)	N_3-N_4 (Å)	N_4-C_3 (Å)	$N_1C_2N_2-N_4C_3C_4$ (deg)[b]
1	**3-H-H**	1.375(4)	1.365(4)	1.329(4)	1.358(3)	1.281(4)	1.423(4)	7.56
2	**3-H-NO$_2$**	1.390(5)	1.360(5)	1.343(5)	1.346(5)	1.285(4)	1.403(5)	0.69
3	**3-OCH$_3$-H**	1.387(4)	1.370(4)	1.339(4)	1.367(4)	1.279(3)	1.430(4)	26.48
4	**3-OCH$_3$-NO$_2$**	1.397(4)	1.360(4)	1.354(4)	1.328(4)	1.287(3)	1.410(4)	1.34

[a] All crystals analyzed were obtained by slow evaporation of concentrated chloroform solutions. [b] Absolute angles between planes defined by $N_1-C_2-N_2$ and $N_4-C_3-C_4$.

(5.39 D) relative to **3-H-H**. This result was in accord with the aforementioned UV−vis spectroscopy data and consistent with the benzimidazol-2-ylidene component showing high polarization. As expected, **3-OCH$_3$-NO$_2$** exhibited the calculated largest dipole of 11.2 D.

Crystals suitable for X-ray analysis were obtained by slow evaporation of saturated chloroform solutions of triazenes **3**. ORTEP diagrams for these structures are shown in Figure 5 with key crystallographic information summarized in Tables 4 (selected bond lengths and angles) and 5 (selected crystal data). Analysis of the data sets revealed that as the complementarity of the pendant electron-donating and electron-withdrawing groups on the periphery of the triazenes improved (i.e., **3-H-H** vs **3-OCH$_3$-NO$_2$**), the C2−N2 and N3−N4 bonds elongated (1.329(4) → 1.354(4) Å and 1.281(4) → 1.287(3) Å, respectively) while the N2−N3 bond shortened (1.358(3) → 1.328(4) Å). Further support for electron delocalization was apparent from the angles between the planes of the two azide and NHC

TABLE 5. Selected Crystal Data for Triazenes 3

	3-H-H	3-H-NO_2	3-OCH_3-H	3-OCH_3-NO_2
CCDC no.	643401	643400	643398	643399
empirical formula	$C_{15}H_{17}N_5O$	$C_{16}H_{15}Cl_3N_6O_2$	$C_{17}H_{21}N_5O_3$	$C_{17}H_{18}N_6O_4$
formula weight	283.34	429.69	343.39	370.37
cryst syst	tetragonal	triclinic	triclinic	monoclinic
space group	*I*-4	*P*-1	*P*-1	*P*21/*c*
a, Å	22.4468(7)	6.7593(3)	7.1500(2)	8.9005(4)
b, Å	22.4468(7)	11.8068(5)	13.9550(3)	7.5544(3)
c, Å	22.4468(7)	12.3651(5)	17.4200(5)	25.4468(12)
α, deg	90°	95.814(3)°	105.406(1)°	90°
β, *δϵγ*	90°	102.092(2)°	90.710(1)°	90.197(2)°
γ, *δϵγ*	90°	100.095(2)°	93.4630(13)°	90°
V, Å^3	2893.5(2)	940.16(7)	1671.89(8)	1710.98(13)
T, K	153(2)	153(2)	153(2)	153(2)
Z	8	2	4	4
D_{calc}, mg/m^3	1.301	1.518	1.364	1.438
cryst size (mm)	0.40 × 0.15 × 0.13	0.40 × 0.10 × 0.08	0.30 × 0.20 × 0.14	0.36 × 0.24 × 0.15
reflections collected	2665	6116	10827	5428
independent reflections	1829	4128	5888	2978
R_1, wR_2 {$I > 2\sigma(I)$}	0.0493, 0.1060	0.0671, 0.1274	0.0563, 0.0922	0.0527, 0.0831
goodness of fit	1.164	1.121	1.059	1.063

components, as defined in Table 4. Triazenes **3-H-NO_2** and **3-OCH_3-NO_2** revealed near perfect planarity between the two components (angles = 0.7 and 1.3°, respectively), a manifestation of good orbital overlap between terminal electron-poor and electron-rich groups. In contrast, triazenes **3-H-H** and **3-H-OCH_3** which possessed relatively mismatched functional groups exhibited angles up to 26.5°. Collectively, these results were consistent with the UV−vis and NMR spectroscopic data discussed above and supported the notion that triazenes **3** possessing complementary functional groups exhibited extensively electron delocalized structures. In concert, the solid-state data suggested structure **B** (see Figure 3, top) was a major resonance contributor in electronically matched, donor−acceptor triazenes.

Evaluation of the Thermal Stabilities of Triazenes: Introduction. During our spectroscopic and crystallographic studies, qualitative observations suggested that triazenes with small N-substituents were relatively unstable in solution and in the solid-state. In contrast, triazenes with large N-substituents were found to be exceptionally stable, even at elevated temperatures (>150 °C) for extended periods of time. In our initial communication, we found that the major product of **2** decomposition was guanidine **4** (R = Mes, R′ = Bn), which formed *via* extrusion of molecular nitrogen at elevated temperatures (>120 °C) (see Figure 6a).[11] To determine if the triazenes synthesized in this study were also susceptible to a similar decomposition process, **3-H-H** was heated to 150 °C in toluene in a pressure vessel. Under these conditions, the respective guanidine (**5**) was observed by ^{1}H NMR spectroscopy and subsequently isolated in 95% yield (see Figure 6b).[34] Supplementary support for the decomposition reaction was obtained from mass spectrometry and elemental analysis. When compared to the triazene starting material (**3-H-H**), the decomposition product (**5**) was 28 Da lower in molecular weight and exhibited a compositional difference consistent with the loss of molecular nitrogen. However, the mechanism for the decomposition reaction was unknown, and we were interested in deconvoluting the key steric and electronic factors governing triazene stability.

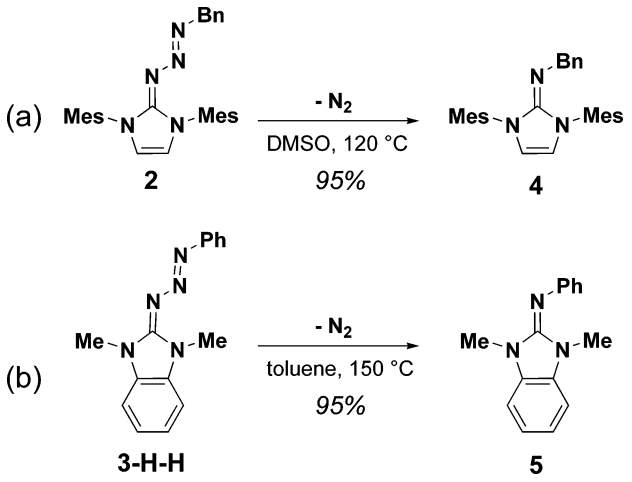
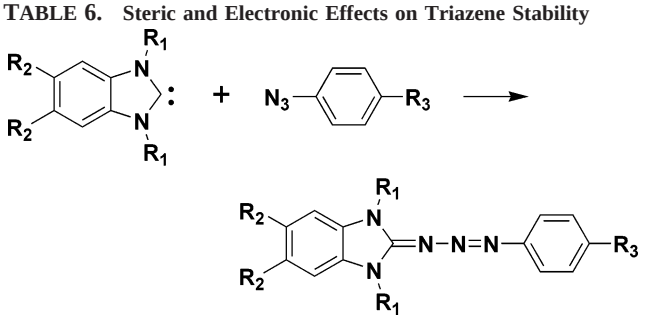


FIGURE 6. Guanidine formation from triazene *via* loss of nitrogen. Bn = benzyl, Mes = 1,3,5-trimethylphenyl, Ph = phenyl. (a) This reaction was reported in ref 11. (b) This work.

Evaluation of the Thermal Stabilities of Triazenes: Thermogravimetric Analysis. In addition to the aforementioned solution-mediated decomposition reactions, triazene stability was also studied in the solid-state. Particular attention was directed toward probing thermal stabilities as a function of triazene size and electronic characteristics. Initial efforts focused on studying how the size of the N-substituent as well as electronics of the benzimidazol-2-ylidene component affected triazene stability. A range of benzimidazol-2-ylidenes with N-substituents ranging in size from methyl to bulky *neo*-pentyl groups were synthesized using known methods[27,35] and coupled to phenyl azide under

(34) Similarly, heating toluene solutions of triazenes **6-H-H** and **6-H-NO_2** (see Table 6) to >150 °C afforded their respective guanidines (**11** and **12**, not shown) in ≥95% yields. This process was conveniently monitored using ^{1}H NMR spectroscopy. For example, the methylene groups (NCH_2) in triazenes **6** exhibit diagnostic chemical shifts at 4.0−4.5 ppm in their ^{1}H NMR spectra; chemical shifts corresponding to the same group in their respective guanidine products were found at 3.5−3.8 ppm. Note that while the thermally-induced triazene decomposition reactions generally afforded high yields (>95%) of guanidine products, a side-reaction was evident. The residual mass was composed of a mixture of products that eluded NMR spectroscopic identification and could not be purified via column chromatography.

TABLE 6. Steric and Electronic Effects on Triazene Stability



entry	triazene	R_1	R_2	R_3	Mp (°C)[a]	T_d (°C)[b]
1	**3-H-H**	Me	H	H	c	93
2	**6-H-H**	*i*Bu	H	H	c	118
3	**1-H-H**	*t*Bu	H	H	100−105	148
4	**7-H-H**	*n*Pn	H	H	126−131	156
5	**1-OCH$_3$-H**	*t*Bu	OCH_3	H	140−142	154
6	**6-H-NO$_2$**	*i*Bu	H	NO_2	128−131	174
7	**6-H-OCH$_3$**	*i*Bu	H	OCH_3	c	139

[a] Melting points (Mp) are uncorrected and were determined under an atmosphere of air. [b] Decomposition temperatures (T_d) determined using thermogravimetric analysis under an atmosphere of nitrogen and defined as the temperature at which 5% mass loss occurred. [c] Melting point was below ambient temperature.

basic conditions using the in situ methodology described above (see Table 6).[36]

After synthesis and characterization, the thermal stabilities of various triazenes were evaluated in the solid-state using thermogravimetric analysis (TGA); results are summarized in Table 6. To ensure that each triazene studied was decomposing in the same phase, melting points were also determined and found to be below the decomposition temperature (T_d) for all compounds studied. In accord with the qualitative assessment noted above, increasing the size of the N-substituent positively influenced triazene stability. For example, while triazenes containing *N*-methyl groups exhibited a T_d = 93 °C (entry 1), they were found to slowly decompose at ambient temperature over time. Comparatively, analogous triazenes with *N-iso*-butyl (**6-H-H**), *N-tert*-butyl (**1-H-H**), or *N-neo*-pentyl (**7**) substituents exhibited T_ds of 118, 148, and 156 °C, respectively (entries 2−4).[34] In contrast, the role of benzimidazol-2-ylidene electronics in influencing triazene thermal stability was found to be relatively minor. For example, **1-H-H** and **1-OCH$_3$-H** were found to exhibit decomposition temperatures (T_ds) of 148 and 154 °C, respectively (entries 3 and 5), which was consistent with the aforementioned UV−vis, NMR, and X-ray spectroscopic data, indicating that donor groups in these positions have only moderate influences on triazene electronics.

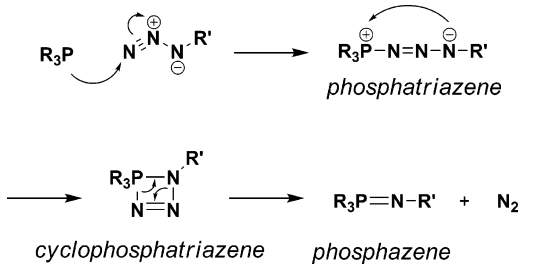


FIGURE 7. Illustration of the Staudinger reaction. Nucleophilic attack of the phosphine on the terminal atom of the organic azide affords an intermediate phosphatriazene. Subsequent intramolecular cyclization leads to an unstable cyclophosphatriazene intermediate that decomposes to a phosphazene and molecular nitrogen.

Next, attention was focused on studying the role of azide electronics. Variation of azide electronics appeared to significantly influence triazene stability. The T_d of **6-H-NO$_2$** which possessed an electron-deficient *p*-nitro substituent was 35 °C higher than an analogue containing a *p*-methoxy substituent (**6-H-OCH$_3$**) (T_ds = 174 and 139 °C, respectively; entries 6 and 7). Collectively, these results suggested that coupling benzimidazol-2-ylidenes possessing bulky N-substituents with electron deficient azides affords triazenes with the highest thermal stabilities.

Mechanistic Investigation of the Triazene Decomposition Reaction. It is well-established that NHCs often function as phosphine analogues.[12,37] Indeed, the NHC/azide coupling reaction to form triazenes and its thermal decomposition products share many similarities with the Staudinger reaction. In the Staudinger reaction, addition of a phosphine to an azide results in formation of a phosphatriazene (see Figure 7).[21] This compound subsequently undergoes intramolecular cyclization to form an unstable four-membered intermediate that rapidly decomposes to a phosphazene, extruding molecular nitrogen in the process. As with the triazenes discussed above, the thermal stabilities of the triazenophosphoranes have been improved through the incorporation of bulky groups.[38]

To confirm that the decomposition mechanism of the triazenes was similar to the Staudinger reaction, a decomposition reaction involving an ^{15}N-labeled triazene was performed. Phenyl azide

(35) (a) Quast, H.; Schmitt, E. *Chem. Ber.* **1968**, *101*, 4012. (b) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267. (c) Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Org. Lett.* **2006**, *8*, 1831. (d) Khramov, D. M.; Boydston, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186. (e) Gehrhus, B.; Hitchcock, P. B.; Pongtavornpinyo, R.; Zhang, L. *Dalton Trans.* **2006**, 1847. (f) Daniele, S.; Drost, C.; Gehrhus, B.; Hawkins, S. M.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G.; Bott, S. G. *J. Chem. Soc., Dalton Trans.* **2001**, *21*, 3179. (g) Myes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366.

(36) Although the spectroscopic signatures of the resulting triazenes were in accord with the aforementioned triazenes, one notable exception was found. Signals attributable to the methylene groups of the *N-iso*-butyl substituents (NCH_2) in triazene **6-H-H** appeared as two doublets at 3.97 ppm and 4.16 ppm in its ^{1}H NMR spectrum (solvent = $CDCl_3$) and were tentatively assigned to cis and trans diazo (N=N) isomers, respectively. While geometric isomers often absorb radiation to differing degrees (see: Hartley, G. S. *J. Chem. Soc.* **1938**, 633 and El Halabieh, R. H.; Mermut, O.; Barrett, C. J. *Pure Appl. Chem.* **2004**, *76*, 1445), triazene **6-H-H** exhibited a single signal at λ_{max} = 367 nm that was similar in shape to the triazenes discussed above (i.e., **1**). This result suggested that the absorption of radiation was concomitant with geometric isomerization (i.e., cis → trans). A similar observation was observed in benzothiazole-based triazenes analogous to **6-H-H** where it was determined that cis → trans isomerization was facilitated with λ = 405 nm radiation (see: Dorsch, H.-T.; Hoffman, H.; Hänsel, R.; Rasch, G.; Fanghänel, E. *J. Prakt. Chem.* **1976**, *318*, 671 and Fanghänel, E; Hänsel, R.; Hohlfeld, J. *J. Prakt. Chem.* **1977**, *319*, 485). Notably, of all the triazenes reported herein, only **6-H-H** and **6-H-Me** exhibited isomers that were clearly resolved at room temperature by ^{1}H NMR spectroscopy. Considering density functional theory calculations at the B3LYP (6−31G**) level of theory suggested that trans **6-H-H** was more stable than its cis isomer by 5.1 kcal/mol, the trans isomer was assumed to dominate in all of the triazenes prepared in this study (DFT calculations were performed using Spartan 2004, Wavefunction, Irvine, CA 92612).

(37) For a direct comparision of N-heterocyclic carbenes with phosphines in various applications, see: (a) Rogers, M. M.; Stahl, S. S. *Top. Organomet. Chem.* **2007**, *21*, 21. (b) Shaughnessy, K. H. *Eur. J. Org. Chem.* **2006**, *71*, 1827. (c) Zuo, G.; Louie, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 2277.

(38) (a) Shalimov, A. A.; Malenko, D. M.; Repina, L. A.; Sinitsa, A. D. Russ. *J. Org. Chem.* **2005**, *75*, 1376. (b) LePichon, L.; Stephan, D. W. *Inorg. Chem.* **2001**, *40*, 3827. (c) Blum, J.; Yona, I.; Tsaroom, S.; Sasson, Y. *J. Org. Chem.* **1979**, *44*, 4178.

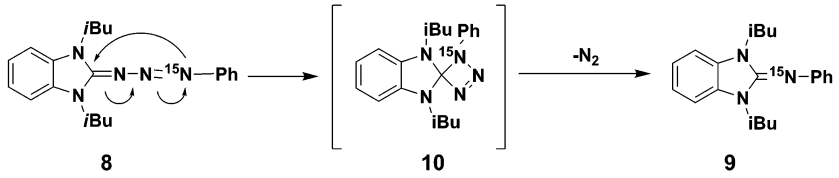


FIGURE 8. Proposed mechanism of thermally induced triazene decomposition based on a ^{15}N-labeling experiment.

containing an isotopically enriched nitrogen atom bonded to the phenyl ring was synthesized using literature protocols from ^{15}N-labeled aniline.[39] After coupling the ^{15}N-labeled azide with 1,3-di-*iso*-butyl-benzimidazol-2-ylidene, the resulting triazene **8** was heated to 170 °C (closed vessel) in toluene at 0.1 M. Guanidine **9** was found as the major product (>95% conversion)[34] by ^{1}H NMR spectroscopy and exhibited a isotopic mass distribution consistent with ^{15}N-labeled azide starting material by mass spectrometry. On the basis of these results, we believe the mechanism to proceed as shown in Figure 8. The nitrogen atom bonded to the phenyl ring attacks the benzimidazol-2-ylidene carbon to form a four-membered intermediate (**10**). Subsequent fragmentation expelled molecular nitrogen to afford the observed guanidine **9**. This mechanism also provides an explanation for increased stability observed with triazenes possessing bulky N-substituents and electron-deficient azide components. The former groups would sterically prevent nucleophilic attack at the electrophilic benzylidene carbon atom while the latter groups would be expected to diminish nucleophilicity of aryl nitrogen atom through resonance.

Conclusions

In summary, we have prepared a novel series of 1,3-disubstituted-triazenes by coupling N-heterocyclic carbenes (NHCs) with various aryl azides. The coupling reactions were accomplished using free NHCs or NHCs generated in situ under basic conditions from their azolium precursors. Modest to excellent isolated yields (36−99%) of triazene product were obtained from these coupling reactions, with typical yields exceeding 95%. The triazenes prepared from this reaction were examined using UV−vis spectroscopy, X-ray crystallography, NMR spectroscopy, and thermogravimetric analysis. Results obtained from the UV−vis spectroscopy experiments suggested that the triazenes exhibited electronically delocalized structures with λ_{max} values ranging between 364 and 450 nm and dependent on the complementarities of the coupled N-heterocyclic carbene and azide components. The electronic properties were dominated by the azide, with minor contributions stemming from the benzimidazol-2-ylidene moiety. Additional support for electronic communication was obtained by X-ray crystallography which revealed bond alteration patterns in the triazeno (C=N−N=N) linkages characteristic of donor−acceptor compounds. Triazene stability was found to be governed by the N-substituents of the benzimidazol-2-ylidene and the electronic nature of the azide component. Notably, a triazene comprised of a benzimidazol-2-ylidene with bulky *N-iso*-butyl groups and a *p*-nitrophenylazide was stable up to 174 °C in the solid-state. The mechanism of decomposition was elucidated using an isotopically labeled azide and found to afford molecular nitrogen and the respective guanidine, in analogy with the Staudinger reaction.

Taken together, these results suggest that the azide−NHC coupling reaction holds tremendous potential for creating materials with high nitrogen contents, delocalized electronic structures, and high thermal stabilities. Recently, we reported[19,35c,d,40] a novel class of bis(NHC)s which feature two diametrically opposed imidazol-2-ylidenes connected to a common arene linker. Combination of this monomer with ditopic bis(azide)s (e.g., 1,4-diazidobenzene) may lead to a novel class of conjugated polymeric materials. Furthermore, compounds exhibiting extensively delocalized structures often leads to molecular polarization, which is a key requirement for creating highly ordered materials. By judiciously combining functionalized azides and NHCs, highly polarized triazenes may find new applications in nonlinear optics. Efforts toward accomplishing these goals as well as exploring the utility of triazenes obtained from the NHC/azide coupling reaction in electronic materials will be reported in due course.

Experimental Section

General Procedure A: Synthesis of Triazenes Using Free N-Heterocyclic Carbenes. After a free N-heterocyclic carbene (1 equiv) was dissolved in THF (approximate concn = 0.3 M), an organic azide (1 equiv) was added in a single portion and the resulting reaction mixture was stirred for up to 8 h at ambient temperature. Solvent was then removed under reduced pressure to yield the desired triazene.

General Procedure B: Synthesis of Triazenes Using N-Heterocyclic Carbenes Generated in Situ from Their Respective Benzimidazolium Salts. Benzimidazolium salt (1 equiv) and potassium *tert*-butoxide (1 equiv) were suspended in THF (approximate concn = 0.2 M) and stirred for 30 min. Afterward, the reaction was cooled to −30 °C, and an organic azide (1 equiv) was added in a single portion. The resulting reaction mixture was then stirred for 24 h at 0 °C and then filtered through a 0.2 μm PTFE membrane. Finally, the solvent was removed under pressure to yield the desired product.

1-Phenyl-3-(1,3-di-*tert*-butyl-benzimidazol-2-ylidene)triazene (1-H-H). Following general procedure A, 1,3-di-*tert*-butyl-benzimidazol-2-ylidene[41] (0.23 g, 1.0 mmol) was treated with phenyl azide (0.12 g, 1.0 mmol) in 3 mL of THF for 2 h to afford 0.35 g of the titled compound as a yellow powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.57−7.54 (m, 2H), 7.34−7.30 (m, 2H), 7.11−7.05 (m, 5H), 1.68 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 161.5, 154.2, 132.1, 128.1, 124.3, 121.7, 121.1, 114.1, 62.0, 30.6. HRMS: $[M + H]^+$ calcd for $C_{21}H_{27}N_5$: 350.2345; found, 350.2349. Anal. calcd for $C_{21}H_{27}N_5$: C, 72.17; H 7.79; N, 20.04; found, C 72.24; H, 7.74; N, 19.95. Mp = 100−105 °C. T_d = 148 °C.

1-(4-Methoxyphenyl)-3-(1,3-di-*tert*-butyl-benzimidazol-2-ylidene)triazene (1-H-OCH$_3$). Following general procedure A, 1,3-di-*tert*-butyl-benzimidazol-2-ylidene[41] (0.23 g, 1.0 mmol) was treated with *p*-methoxyphenyl azide (0.15 g, 1.0 mmol) in 3 mL of THF for 3 h to afford 0.38 g of the titled compound as a yellow powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.58−7.53 (m, 4H),

(39) For additional examples of synthesizing ^{15}N-labeled azides see: Leseticky, L.; Barth, R.; Nemec, I.; Sticha, M.; Tislerova, I. *Czech. J. Phys.* **2003**, *53*, A777.

(40) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073.

(41) See supporting information for the synthesis and characterization of this compound.

7.07−7.04 (m, 2H), 6.90−6.87 (m, 2H), 3.79 (s, 3H), 1.76 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 161.4, 158.1, 145.6, 132.4, 122.3, 120.8, 113.9, 113.8, 61.5, 55.3, 31.0. HRMS: $[M + H]^+$ calcd for $C_{22}H_{30}N_5O$: 380.2450; found, 380.2445.

1-(4-Nitrophenyl)-3-(1,3-di-*tert*-butyl-benzimidazol-2-ylidene)-triazene (1-H-NO$_2$). Following general procedure A, 1,3-di-*tert*-butyl-benzimidazol-2-ylidene[41] (0.23 g, 1.0 mmol) was treated with *p*-nitro-phenyl azide (0.16 g, 1.0 mmol) in 3 mL of THF for 30 min to afford 0.39 g of the titled compound as a red powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 8.14 (d, J = 9.2 Hz, 2H), 7.73 (dd, J = 3.2, 6.4 Hz, 2H), 7.54 (d, J = 9.2 Hz, 2H), 7.22 (dd, J = 3.2, 6.4 Hz, 2H), 1.77 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 160.9, 158.1, 144.0, 131.5, 127.8, 122.5, 120.3, 115.1, 62.9, 31.4. HRMS: $[M + H]^+$ calcd for $C_{21}H_{27}N_6O_2$: 395.2195; found, 395.2198.

1-Phenyl-3-(1,3-di-*tert*-butyl-5,6-dimethoxy-benzimidazol-2-ylidene)triazene (1-OCH$_3$-H). Following general procedure A, 1,3-di-*tert*-butyl-4,5-dimethoxy-benzimidazol-2-ylidene[41] (0.29 g, 1.0 mmol) was treated with phenyl azide (0.12 g, 1.0 mmol) in 3 mL of THF for 2 h to afford 0.41 g of the titled compound as a yellow powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.57−7.55 (m, 2H), 7.31 (t, J = 8 Hz, 2H), 7.17 (s, 2H), 7.14−7.09 (m, 1H), 3.90 (s, 6H), 1.77 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 161.3, 152.1, 144.8, 128.6, 125.9, 125.3, 121.0, 99.6, 61.8, 56.8, 31.3. HRMS: $[M + H]^+$ calcd for $C_{23}H_{32}N_5O_2$: 410.2556; found, 410.2551. Anal. calcd for $C_{23}H_{31}N_5O_2$: C, 67.46; H 7.63; N, 17.10; found, C 67.31; H, 7.64; N, 16.94. Mp = 140−142 °C. T_d = 154 °C.

1-(4-Methoxyphenyl)-3-(1,3-di-*tert*-butyl-5,6-dimethoxy-benzimidazol-2-ylidene)triazene (1-OCH$_3$-OCH$_3$). Following general procedure A, 1,3-di-*tert*-butyl-4,5-dimethoxy-benzimidazol-2-ylidene[41] (0.29 g, 1.0 mmol) was treated with *p*-methoxyphenyl azide (0.15 g, 1.0 mmol) in 3 mL of THF for 2 h to afford 0.44 g of the titled compound as a yellow powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.38 (d, J = 8.8 Hz, 2H), 7.14 (s, 2H), 6.72 (d, J = 8.8 Hz, 2H), 3.89 (s, 6H), 3.79 (s, 3H), 1.76 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 161.4, 157.9, 145.9, 144.5, 126.2, 122.2, 113.9, 99.7, 61.6, 56.8, 55.4, 31.2. HRMS: $[M + H]^+$ calcd for $C_{24}H_{34}N_5O_3$: 440.2662; found, 440.2656. Anal. calcd for $C_{24}H_{33}N_5O_3$: C, 65.58; H 7.57; N, 15.93; found, C 65.48; H, 7.68; N, 15.56.

1-(4-Nitrophenyl)-3-(1,3-di-*tert*-butyl-5,6-dimethoxy-benzimidazol-2-ylidene)triazene (1-OCH$_3$-NO$_2$). Following general procedure A, 1,3-di-*tert*-butyl-4,5-dimethoxy-benzimidazol-2-ylidene[41] (0.29 g, 1.0 mmol) was treated with *p*-nitrophenyl azide (0.16 g, 1.0 mmol) in 3 mL of THF for 30 min to afford 0.45 g of the titled compound as a red powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 8.11 (d, J = 9.2 Hz, 2H), 7.50 (d, J = 9.2 Hz, 2H), 7.23 (s, 2H), 3.91 (s, 6H), 1.58 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 159.8, 158.5, 145.9, 143.6, 125.2, 124.8, 119.9, 99.4, 62.7, 56.6, 31.4. HRMS: $[M + H]^+$ calcd for $C_{23}H_{31}N_6O_4$: 455.2407; found, 455.2408.

1-Phenyl-3-(1,3-di-*tert*-butyl-5,6-difluoro-benzimidazol-2-ylidene)triazene (1-F-H). Following general procedure A, 1,3-di-*tert*-butyl-4,5-fluoro-benzimidazol-2-ylidene[41] (0.27 g, 1.0 mmol) was treated with phenyl azide (0.12 g, 1.0 mmol) in 3 mL of THF for 6 h to afford 0.39 g of the titled compound as a yellow powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.59−7.56 (m, 2H), 7.39 (t, J_{H-F} = 9.2 Hz, 2H), 7.37−7.31 (m, 2H), 7.20−7.15 (m, 1H), 1.73 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 162.3, 151.4, 145.2 (dd, J_{F-C} = 16.4, 243 Hz), 128.7, 127.9 (t, J_{F-C} = 5.93 Hz), 126.4, 121.3, 102.3 (m), 62.3, 30.9. HRMS: $[M + H]^+$ calcd for $C_{21}H_{26}F_2N_5$: 386.2156; found, 386.2155.

1-(4-Methoxyphenyl)-3-(1,3-di-*tert*-butyl-5,6-difluoro-benzimidazol-2-ylidene)triazene (1-F-OCH$_3$). Following general procedure A, 1,3-di-*tert*-butyl-4,5-fluoro-benzimidazol-2-ylidene[41] (0.27 g, 1.0 mmol) was treated with *p*-methoxyphenyl azide (0.15 g, 1.0 mmol) in 3 mL of THF for 8 h to afford 0.42 g of the titled compound as an orange powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7.35 (t, J_{H-F} = 9.2 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.80 (s, 2H), 1.73 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 161.9 (m), 158.7, 145.1 (dd, J_{F-C} = 15.7, 242.7 Hz), 129.3, 128.2 (t, J_{F-C} = 5.9 Hz), 122.6, 114.0, 102.8 (dd, J_{F-C} = 8.9, 15.7 Hz), 62.1, 55.4, 30.9. HRMS: $[M + H]^+$ calcd for $C_{22}H_{28}F_2N_5O$: 416.2262; found, 416.2258.

1-(4-Nitrophenyl)-3-(1,3-di-*tert*-butyl-5,6-difluoro-benzimidazol-2-ylidene)triazene (1-F-NO$_2$). Following general procedure A, 1,3-di-*tert*-butyl-4,5-fluoro-benzimidazol-2-ylidene[41] (0.27 g, 1.0 mmol) was treated with *p*-nitrophenyl azide (0.16 g, 1.0 mmol) in 3 mL of THF for 1 h to afford 0.43 g of the titled compound as a red powder (99% yield). ^{1}H NMR ($CDCl_3$): δ 8.17 (d, J = 9.2 Hz, 2H), 7.59−7.53 (m, 4H), 1.76 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 162.2, 157.3, 146.0 (dd, J_{F-C} = 16.5, 245.7 Hz), 144.7, 127.4, (t, J_{F-C} = 5.9 Hz), 124.8, 120.8, 103.7 (m), 63.3, 31.2. HRMS: $[M + H]^+$ calcd for $C_{21}H_{25}F_2N_6O_2$: 431.2007; found, 431.2007.

1-Phenyl-3-(1,3-dimethyl-benzimidazol-2-ylidene)triazene (3-H-H). Following general procedure B, 1,3-dimethyl-benzimidazolium iodide[35g] (0.28 g, 1.0 mmol) and potassium *tert*-butoxide (0.11 g, 1.0 mmol) were suspended in 5 mL of THF and stirred for 20 min. Afterward, phenyl azide (0.12 g, 1.0 mmol) was added, and the resulting solution was stirred for 24 h at 0 °C. The solution was then diluted with an equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration and then washed with water. After the solvent was removed under reduced pressure, the crude product was triturated with hexanes. Filtration of resulting suspension afforded 0.095 g of the titled compound as a yellow solid (36% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated chloroform solution of the titled compound (CCDC 643401). ^{1}H NMR (CD_2Cl_2): δ 7.58−7.55 (m, 2H), 7.42−7.38 (m, 2H), 7.26−7.17 (m, 5H), 3.81 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 155.2, 152.1, 132.5, 129.2, 127.0, 122.6, 121.8, 108.6, 31.9. HRMS: $[M + H]^+$ calcd for $C_{15}H_{16}N_5$: 266.1406; found, 266.1400.

1-(4-Nitrophenyl)-3-(1,3-dimethyl-benzimidazol-2-ylidene)-triazene (3-H-NO$_2$). Following general procedure B, 1,3-dimethyl-benzimidazolium iodide[35g] (0.28 g, 1.0 mmol) and potassium *tert*-butoxide (0.11 g, 1.0 mmol) were suspended 5 mL of THF and stirred for 20 min. Afterward, *p*-nitrophenyl azide (0.16 g, 1.0 mmol) was added and the resulting solution was stirred for 24 h at 0 °C. The solution was then diluted with equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration, washed with water, and dried under reduced pressure to afford 0.17 g of the titled compound as a red solid (56% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated chloroform solution of the titled compound (CCDC 643400). ^{1}H NMR ($CDCl_3$): δ 7.24 (d, J = 9.2 Hz, 2H), 7.65 (d, J = 9.2 Hz, 2H), 7.31−7.7.25 (m, 4H), 3.89 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 156.5, 145.6, 131.7, 124.9, 123.4, 121.5, 109.1, 31.9. HRMS: $[M + H]^+$ calcd for $C_{15}H_{15}N_6O_2$: 311.1256; found, 311.1260.

1-Phenyl-3-(1,3-dimethyl-5,6-dimethoxy-benzimidazol-2-ylidene)triazene (3-OCH$_3$-H). Following general procedure B, 1,3-dimethyl-5,6-dimethoxy-benzimidazolium iodide[19b] (0.34 g, 1.0 mmol) and potassium *tert*-butoxide (0.11 g, 1.0 mmol) were suspended in 5 mL of THF and stirred for 20 min. Afterward, phenyl azide (0.12 g, 1.0 mmol) was added and the resulting solution was stirred for 24 h at 0 °C. The solution was then diluted with equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration, washed with water, and dried under reduced pressure to afford 0.23 g of the titled compound as a yellow solid (69% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated chloroform solution of the titled compound (CCDC 643398). ^{1}H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.35 (m, 2H), 7.18 (m, 1H), 6.70 (s, 2H), 3.91 (s, 6H), 3.79 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 154.3, 151.5, 146.2, 128.8, 126.4, 125.1, 121.4, 93.9, 56.8, 31.7. HRMS: $[M + H]^+$ calcd for $C_{17}H_{20}N_5O_2$: 326.1617; found, 326.1615.

1-(4-Nitrophenyl)-3-(1,3-dimethyl-5,6-dimethoxy-benzimidazol-2-ylidene)triazene (3-OCH$_3$-NO$_2$). Following general procedure B, 1,3-dimethyl-5,6-dimethoxy-benzimidazolium iodide[19b] (0.21 g, 0.63 mmol) and potassium *tert*-butoxide (0.07 g, 0.63

mmol) were suspended in 5 mL of THF and stirred for 20 min. Afterward, *p*-nitrophenyl azide (0.1 g, 0.63 mmol) was added and the resulting mixture was stirred for 24 h at 0 °C. The reaction mixture was then diluted with an equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration, washed with water, and dried under reduced pressure to afford 0.22 g of the titled compound as a red solid (94% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated chloroform solution of the titled compound (CCDC 643399). ^{1}H NMR (CD_2Cl_2): δ 8.20 (d, J = 9.2 Hz, 2H), 7.59 (m, J = 9.2 Hz, 2H), 6.64 (s, 2H), 6.70 (s, 2H), 3.92 (s, 6H), 3.85 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 157.7, 147.6, 145.2, 125.3, 124.2, 125.1, 121.4, 94.5, 57.1, 32.2. HRMS: $[M + H]^+$ calcd for $C_{17}H_{19}N_6O_4$: 371.1468; found, 371.1468.

1-Phenyl-3-(1,3-di-*iso*-butyl-benzimidazol-2-ylidene)triazene (6-H-H). Following general procedure B, 1,3-di-*iso*-butyl-benzimidazolium tetrafluoroborate[42] (0.32 g, 1.0 mmol) and potassium *tert*-butoxide (0.11 g, 1.0 mmol) were suspended in 10 mL of THF and stirred for 20 min. Afterward, phenyl azide (0.12 g, 1.0 mmol) was added and the resulting mixture was stirred for 24 h at 0 °C. The reaction mixture was then diluted with an equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration, washed with water, and dried under reduced pressure to afford 0.35 g of the titled compound as a yellow oil (99% yield). ^{1}H NMR (CD_2Cl_2): δ 7.58−7.55 (m, 2H), 7.43−7.39 (m, 2H), 7.26−7.20 (m, 5H), 4.16 (d, J = 7.2 Hz, 4H), 2.40 (n, J = 6.4, 7.2 Hz, 2H), 0.97 (d, J = 6.4 Hz, 12H). ^{13}C NMR (CD_2Cl_2): δ 154.7, 152.2, 132.4, 129.1, 126.9, 122.4, 121.7, 109.5, 51.7, 28.4, 20.1. HRMS: $[M + H]^+$ calcd for $C_{21}H_{28}N_5$: 350.2345; found, 350.2342. T_d = 118 °C.

1-Phenyl-3-(1,3-di-*neo*-pentyl-benzimidazol-2-ylidene)triazene (7-H-H). Following general procedure A, 1,3-di-*neo*-pentyl-benzimidazol-2-ylidene[43] (0.26 g, 1.0 mmol) was treated with phenyl azide (0.12 g, 1.0 mmol) in 3 mL of THF for 2 h to afford 0.38 g of the titled compound as a yellow powder (99% yield). ^{1}H NMR (CD_2Cl_2): δ 7.61−7.58 (m, 2), 7.43−7.39 (m, 2H), 7.26−7.16 (m, 5H), 4.35 (br, 4H), 1.04 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 156.2, 152.1, 133.1, 129.2, 126.9, 122.1, 121.8, 110.3, 35.5, 28.2. HRMS: $[M + H]^+$ calcd for $C_{23}H_{32}N_5$: 378.2658; found, 378.2654. Anal. calcd for $C_{23}H_{31}N_5$: C, 73.17; H 8.28; N, 18.55; found, C, 73.07; H, 8.25; N, 18.51. Mp = 126−131 °C. T_d = 156 °C.

1-(4-Nitrophenyl)-3-(1,3-di-*iso*-butyl-benzimidazol-2-ylidene)-triazene (6-H-NO$_2$). Following general procedure B, 1,3-di-*iso*-butyl-benzimidazolium tetrafluoroborate[42] (0.32 g, 1.0 mmol) and potassium *tert*-butoxide (0.11 g, 1.0 mmol) were suspended in 10 mL of THF and stirred for 20 min. Afterward, *p*-nitrophenyl azide (0.16 g, 1.0 mmol) was added and the resulting mixture was stirred for 24 h at 0 °C. The reaction mixture was then diluted with an equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration, washed with water, and dried under reduced pressure to afford 0.39 g of the titled compound as a red solid (99% yield). ^{1}H NMR ($CDCl_3$): δ 8.21 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.25 (br, 4H), 4.19 (d, J = 8.4 Hz, 4H), 2.35 (m, 2H), 0.93 (d, J = 6.5 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 156.7, 154.1, 145.3, 131.6, 124.7, 123.0, 121.4, 109.8, 51.5, 28.1, 20.0. HRMS: $[M + H]^+$ calcd for $C_{21}H_{27}N_6O_2$: 395.2195; found, 395.2198. Mp = 128−131 °C. T_d = 174 °C.

1-(4-Methoxyphenyl)-3-(1,3-di-*iso*-butyl-benzimidazol-2-ylidene)triazene (6-H-OCH$_3$). Following general procedure B, 1,3-di-*iso*-butyl-benzimidazolium tetrafluoroborate[42] (0.32 g, 1.0 mmol) and potassium tert-butoxide (0.11 g, 1.0 mmol) were suspended in 10 mL of THF and stirred for 20 min. Afterward, *p*-methoxyphenyl azide (0.15 g, 1.0 mmol) was added and the resulting mixture was stirred for 24 h at 0 °C. The reaction mixture was then diluted with an equal volume of hexanes which caused solids to precipitate. The crude solids were then collected via filtration, washed with water, and dried under reduced pressure to afford 0.38 g of the titled compound as a yellow oil (99% yield). ^{1}H NMR ($CDCl_3$): δ 7.54 (d, J = 8.8 Hz, 2H), 7.18 (s, 4H), 6.96 (d, J = 8.8 Hz, 2H), 4.13 (d, J = 8.0 Hz, 4H), 3.84 (s, 3H), 2.39 (m, J = 6.4, 6.8 Hz, 2H), 0.97 (d, J = 6.4 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 158.5, 153.9, 145.1, 131.8, 122.5, 121.7, 113.7, 108.7, 55.2, 51.0, 27.7, 19.8. HRMS: $[M + H]^+$ calcd for $C_{22}H_{30}N_5O$: 380.2450; found, 380.2455. T_d = 139 °C.

***N*-Phenyl-1,3-dimethyl-benziminoimidazoline (5).** 1-Phenyl-3-(1,3-dimethyl-benzimidazol-2-ylidene)triazene (**3-H-H**) (0.1 g, 0.38 mmol) was dissolved in 4 mL of toluene and heated to 150 °C for 10 h. After removal of solvent under reduced pressure, 0.09 g of the titled compound was obtained as a yellow oil (99% yield). ^{1}H NMR (CD_2Cl_2): δ 7.28−7.24 (m, 2H), 7.04 (dd, J = 3.0, 5.6 Hz, 2H), 6.94−6.92 (m, 3H), 6.88 (dd, J = 3.0, 5.6 Hz, 2H), 3.22 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 150.5, 146.9, 133.2, 129.0, 122.5, 120.9, 120.5, 106.6, 30.4. HRMS: $[M + H]^+$ calcd for $C_{15}H_{15}N_3$: 238.1344; found, 238.1347.

***N*-Phenyl-1,3-di-*iso*-butyl-benziminoimidazoline (11).** 1-Phenyl-3-(1,3-di-*iso*-butyl-benzimidazol-2-ylidene)triazene (**6-H-H**) (0.1 g, 0.29 mmol) was dissolved in 3 mL of toluene and heated to 170 °C for 10 h. After removal of solvent under reduced pressure, 0.09 g of the titled compound was obtained as a yellow oil (99% yield). ^{1}H NMR (CD_2Cl_2): δ 7.23−7.20 (m, 2H), 6.99−6.96 (m, 2H), 6.89−6.83 (m, 5H), 3.53 (d, J = 7.2 Hz, 4H), 2.11−2.08 (m, 2H), 0.77 (d, J = 6.4 Hz, 12H). ^{13}C NMR (CD_2Cl_2): δ 149.9, 146.1, 133.0, 128.5, 122.6, 120.5, 120.4, 107.5, 49.9, 27.9, 20.1. HRMS: $[M + H]^+$ calcd for $C_{21}H_{28}N_3$: 322.2283; found, 322.2280.

***N*-(4-Nitrophenyl)-1,3-di-*iso*-butyl-benziminoimidazoline (12).** 1-(4-Nitrophenyl)-3-(1,3-di-*iso*-butyl-benzimidazol-2-ylidene)triazene (**6-H-NO$_2$**) (0.15 g, 0.38 mmol) was dissolved in 4 mL of toluene and heated to 180 °C for 10 h. After removal of solvent under reduced pressure, 0.14 g of the titled compound was obtained as a red solid (99% yield). ^{1}H NMR ($CDCl_3$): δ 8.11−8.08 (m, 2H), 7.11 (dd, J = 3.4, 5.6, 2H), 7.03 (dd, J = 3.4, 5.6 Hz, 2H), 6.77−6.74 (m, 2H), 3.64 (d, 15.6 Hz, 4H), 2.12−2.09 (m, 2H), 0.77 (d, J = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 157.1, 148.2, 139.2, 131.6, 125.5, 121.7, 120.3, 108.6, 50.1, 27.5, 19.9. HRMS: $[M + H]^+$ calcd for $C_{21}H_{27}N_4O_2$: 367.2134; found, 367.2132. Anal. calcd for $C_{21}H_{27}N_4O_2$: C, 68.64; H 7.41; N, 15.25; found: C, 68.58; H, 7.20; N, 15.04.

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Supporting Information Available: Additional experimental procedures, kinetic data, computational data, and NMR spectra for all new compounds is available free of charge *via* the Internet at http://pubs.acs.org.

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