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Preparation of bis(diazo) compounds incorporated into butadiyne and thiophene units and generation and characterization of their photoproducts

Fumika Morisaki,[a] Masakuni Kurono,[a] Katsuyuki Hirai[b] and Hideo Tomioka*[a]

[a] *Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie, 514-8507, Japan*

[b] *Instrumental Analysis Facilities, Life Science Research Center, Mie University, Tsu, Mie, 514-8507, Japan*

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(2,6-Dimethyl-4-*tert*-butylphenyl)(2,4,6-tribromophenyl)diazomethane(**1**-N_2) was found to be stable enough to survive under Sonogashira coupling reaction conditions, and aryldiazomethyl substituents were introduced at the 1,4-positions of butadiyne (**4**-2N_2) and the 2,5-positions of thiophene(**5**-2N_2). Irradiation of those bis(diazo) compounds generated bis(carbenes), which were characterized by using ESR and UV/vis spectroscopic techniques in a matrix at low temperature as well as time-resolved UV/vis spectroscopy in solution at room temperature. These studies revealed that both of the bis(carbenes), **4** and **5**, have singlet quinoidal diradical ground states with a very small singlet–triplet energy gap of less than 1 kcal mol^{-1}. A remarkable increase in the lifetime of bis(carbenes), as opposed to that of the monocarbene (**2**), was noted and was interpreted to indicate that bis(carbenes) are thermodynamically stabilized as a result of delocalization of unpaired electrons throughout the π net framework. In spite of the stability, both bis(carbenes) are readily trapped by molecular oxygen to afford bis(ketones). Presumably, the reaction of the upper-lying localized quintet states with oxygen is much faster than that for lower-lying states.

Introduction

Diazo compounds[1] are excellent precursors for carbenes and, hence, have been widely employed to generate and study carbenes[2] because they decompose very efficiently and cleanly upon either heating or irradiation to eliminate nitrogen gas, leaving the carbene. Moreover, the reaction occurs even at very low temperatures in the solid phase, which makes the spectroscopic study of carbenes very easy. However, due to the inherent sensitivity of the diazo functional group to heat, light, acids, and metals, this group is usually introduced at the last step of the synthesis, which sometimes makes the versatility of the group less variable. For instance, a precursor diazo compound cannot always be prepared without restraint.

We found, almost by chance, that a diphenyldiazomethane prepared to generate a persistent triplet carbene[3] is also persistent for a diazo compound and, hence, can be further modified into a more complicated diazo compound while leaving the diazo group intact. For instance, bis(2,4,6-tribromophenyl)-diazomethane survives under Sonogashira coupling reaction[4] conditions, leading to bis(2,6-dibromo-4-trimethylsilylethynyl-phenyl)diazomethane.[5] It is very interesting and important to explore the applicability of this method, as it may open a window to a new route to organic magnetic materials. We report here that a diphenyldiazo unit can be connected by using an oxidative coupling reaction[6] of acetylene to the butadiyne unit, which is then converted to the thiophene ring by the reaction with sodium sulfide.[7] The characterization of bis(carbene) generated from those bis(diazo) compounds is also reported.

Results

Preparation of bis(diazo) compounds

Treatment of 2,6-dimethyl-4-*tert*-butylphenyl)(2,4,6-tribromo-phenyl)diazomethane (**1**-N_2) with trimethylsilylacetylene in the presence of $(Ph_3P)_2PdCl_2$ and CuI at 40 °C for 2 days gave (2,6-dimethyl-4-*tert*-butylphenyl)(2,6-dibromo-4-trimethylsilyl-ethynyphenyl)diazomethane (**2**-N_2) in 63% yield. Deprotection[8] of the TMS group with NaOH proceeded smoothly to give an ethynyl derivative (**3**-N_2) in quantitative yield. Stirring a mixture of **3**-N_2 and CuCl(OH)–TMEDA in CH_2Cl_2 under air for 6 h at room temperature gave a bis(diazo)butadiyne compound (**4**-2N_2) in 94% yield.

The diyne (**4**-2N_2) was treated with $Na_2S{\cdot}9H_2O$ in THF at 50 °C for 20 h to result in the formation of a thiophene derivative (**5**-2N_2) in 60% yield. All the procedures were carried out in the dark, and compounds were purified either by silica gel chromatography at *ca.* 0 °C and/or by GPC. No appreciable decomposition of the diazo group was noted in all cases, at least under the conditions used here.

The results showed that the protected diazo compound is fairly persistent and can be used as a building block to construct a new poly diazo derivative from which a new magnetic system may be derived.

The characterization of the structure of the bis(carbene) expected to be generated upon photolysis of those bis(diazo) precursors is of great importance in view of recent growing interest in spin molecules.[9–12] Thus, the photolysis of **4**-2N_2 and **5**-2N_2 was monitored by UV/vis and ESR spectroscopy.

Spectroscopic studies

ESR studies. Irradiation of monodiazomethane **2**-N_2 in 2-methyltetrahydrofuran (2MTHF) at 77 K gave ESR signals with typical fine structure patterns for unoriented triplet species, *i.e.*, ^{3}**2** (Fig. 1). The signals were analyzed in terms of zero-field splitting (ZFS) parameters to be $D = 0.455\ cm^{-1}$ and $E = 0.0335\ cm^{-1}$. The values were similar with those observed for a series of brominated triplet diphenylcarbenes.[3,13]

Similar irradiation of the bis(diazo) compound (**5**-2N_2) connected by a thiophene ring in 2-MTHF at 70 K gave ESR signals (Fig. 2a) that were completely different from those observed for the corresponding monocarbene, ^{3}**2**. The signals observed from 200 to 400 and around 710 mT were too weak to be unequivocally assigned to a species that is expected to be produced in the photolysis of **5**-2N_2, such as a triplet monocarbene, quinoidal diradical, or quintet bis(carbene). However, a rather strong

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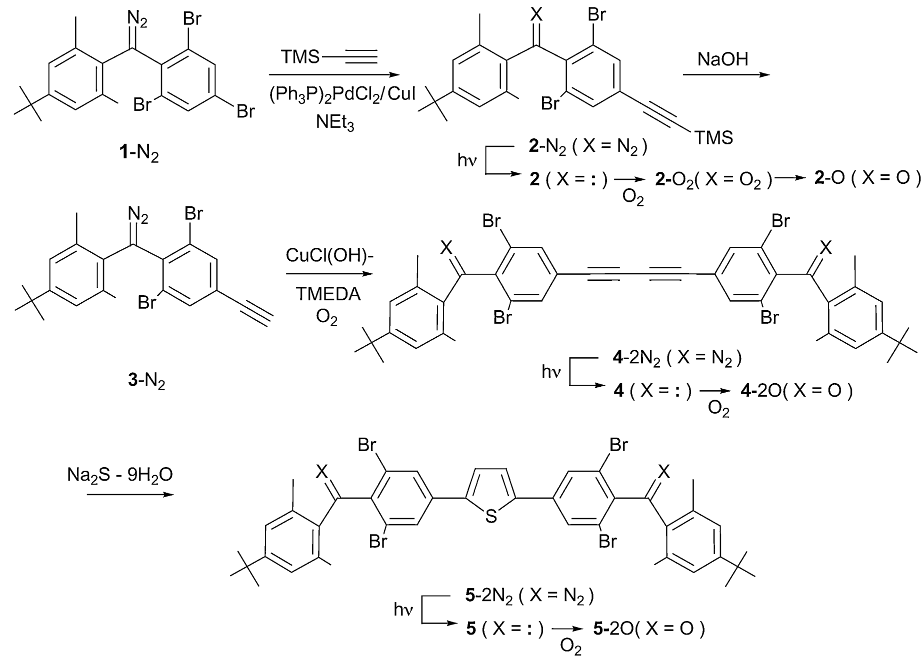


Scheme 1

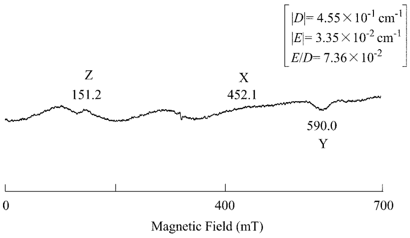


Fig. 1 ESR spectrum obtained by irradiation of monodiazo compound **2**-N$_2$.

signal at 160 mT can be assignable to the $\Delta m_S = 2$ transitions of a triplet species. Usually, this transition in triplet carbene is very weak and often unobserved. Therefore, it is likely that this forbidden transition is due to a triplet state of bis(carbene), that is best represented by its quinoidal diradical form. Cooling the sample to 10 K resulted in a marked decrease of the signal at 160 mT (Fig. 2b), but the signal was regained when the matrix was thawed again to 80 K (Fig. 2c). When the matrix temperature was further raised to 100 K, the shape of the signals around 220 to 400 mT changed rather dramatically to produce a rather well-resolved spectrum along with the increase of the signal due to the forbidden transition (Fig. 2d). These changes in ESR signals upon thawing the matrix are usually interpreted in terms of the geometrical change[13c] of the paramagnetic species as the matrix softens, allowing the carbene to assume a single preferred orientation rather than several slightly distorted orientations dictated by the trapping of the precursor in the frozen matrix. We assigned the new fine structured peaks to a triplet species with $D = 0.180$ cm^{-1} and $E = 0.0121$ cm^{-1}. The observed spectrum was reproduced reasonably well by computer simulation,[14] using these zfs parameters (Fig. 2f).

Recooling the sample to 15 K resulted in a marked decrease in the well-resolved triplet signal at 220 to 400 mT and the forbidden transition at 160 mT (Fig. 2e). Warming the sample to 90 K reproduced the original signals observed at 100 K (Fig. 2f), the intensity of which increased up to 110 K and started to decrease above 110 K. All the signals disappeared irreversibly when the temperature was raised up to 180 K and brought down to 100 K (Fig. 2g).

The decreasing intensity of the spectra at <30 K can make them difficult to observe and clearly shows that the spectra are due to a thermally populated excited state. Actually, the plot of the intensity of the signals at 160 mT *vs.* the temperature from 10–70 K for the diradical before relaxation (Fig. 3a) and from 15–110 K for that after relaxation (Fig. 3b) deviated from the Curie–Weiss law, confirming that the diradical was a singlet ground state with a low-lying excited triplet state.

The temperature dependence of ESR signal intensity for ^{3}**5** indicates that the quinoidal form of bis(carbene) has a singlet ground state. To determine the singlet–triplet energy gap ($\Delta E_{\mathrm{T-S}} = 2J$) of quinoidal bis(carbene), the observed data were analyzed in terms of the Bleaney–Bowers-type thermal distribution (1)[17]

$$I = \frac{C}{T}\,\frac{3\exp(-2J/kT)}{1+3\exp(-2J/kT)} \qquad (1)$$

where I is the intensity of the ESR active triplet state while T, k, and C are the absolute temperature, Boltzman constant, and an arbitrary constant, respectively. Fitting the parameters in eqn. (1) to observed intensity data for thermally populated triplets gave an exchange integral, with J/k values of -117 K ($J = -223$ cal mol^{-1}) and -94 K ($J = -187$ cal mol^{-1}) for nascent and relaxed diradicals, respectively.

Similar irradiation of bis(diazo) compounds connected by butadiyne (**4**-2N$_2$) in 2-MTHF at 70 K gave an ESR spectrum (Fig. 4a) showing a main signal at 257.3 mT. The signals disappeared when the temperature was lowered to 4 K (Fig. 4b) but were reproduced upon thawing up to 80 K (Fig. 4c). The plot of the intensity of the signal at 257 mT *vs.* the temperature from 10–80 K (where the shape of the signals is unchanged) deviated from the Curie–Weiss law (Fig. 5a), again confirming that the diradical was a singlet ground state with a low-lying excited triplet state. When the temperature was raised up to 90 K, a significant change in the spectrum was noted with a shift of main signals to 135.8 mT (Fig. 4d). This is interpreted in terms of the geometrical relaxation of the species accompanied by softening of the matrix.[13c] The intensity of the new signal also decreased as the temperature was lowered but increased upon warming to 110 K (Fig. 4e–f). The signals started to decrease above 110 K and disappeared completely at 200 K (Fig. 4g). The plot of intensity of the signal at 136 mT *vs.* the temperature from 10–110 K, where the shape of the signals is unchanged, deviated from the Curie–Weiss law (Fig. 5b). The nonlinear least-squares

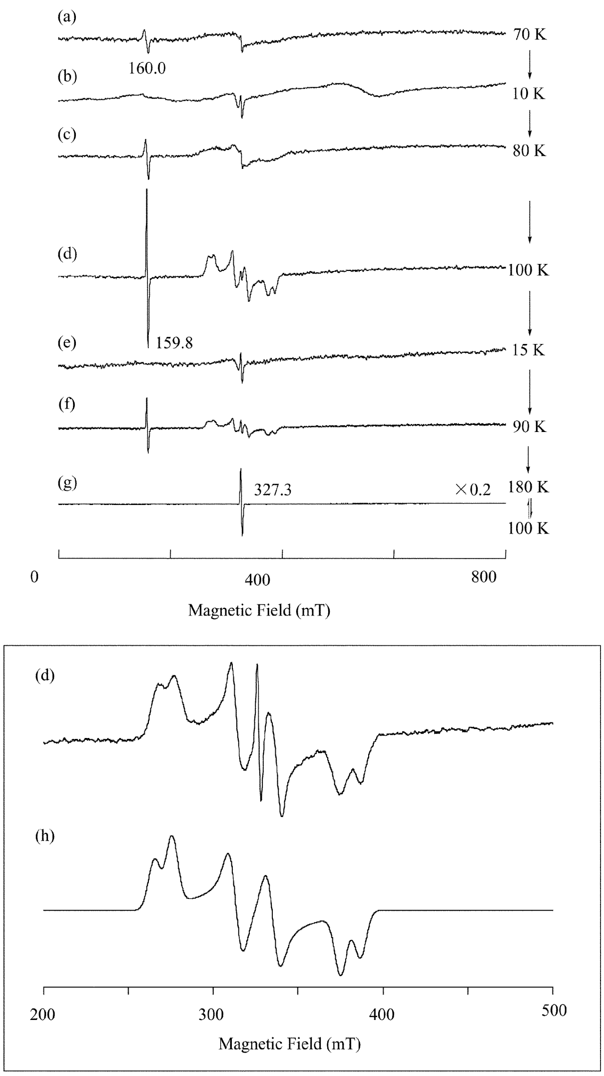


Fig. 2 (a) ESR spectrum obtained by irradiation of bis(diazo) compound **5**-2N_2 in 2-methyltetrahydrofuran at 70 K. (b–e) The same sample observed at 10 K (b), 80 K (c), 100 K (d), 15 K (e), 90 K (f). (g) The same sample taken at 10 K after thawing to 180 K. (h) Simulated spectrum of ^{3}**5** with $S = 1$, $g = 2.000$, $|D/hc| = 0.0566$ cm^{-1}, $|E/hc| = 0.0121$ cm^{-1} and line width of 35 G.

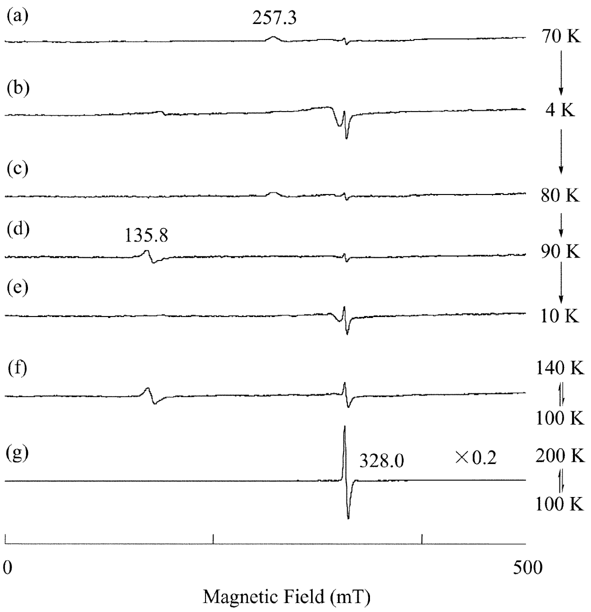


Fig. 4 (a) ESR spectrum obtained by irradiation of bis(diazo) compound **4**-2N_2 in 2-methyltetrahydrofuran at 70 K. (b–g) The same spectra observed at 4 K (b), 80 K(c), 90 K (d), 10 K (e). (f–g) The same spectra taken at 100 K after thawing the matrix to 140 (f) and 200 K (g).

curve fitting of the parameters of eqn. (1) to the data in Fig. 5 yields J/k values of −58 K ($J = -115$ cal mol^{-1}) and −132 K ($J = -262$ cal mol^{-1}) for the nascent and relaxed diradicals, respectively.

UV/Vis spectroscopic study in a matrix at low temperature. Irradiation of **2**-N_2 in a 2-MTHF matrix at 77 K resulted in the rapid disappearance of the original absorption due to **2** and the concurrent growth of sharp and strong absorption bands at 308 and 330 nm with weak bands at 440, 459, and 477 nm (Fig. 6). Characteristic absorption bands usually observed for triplet diarylcarbenes consist of a rather sharp and strong band in the UV region along with weak, broad, and structured bands in the visible region. Since the ESR signals ascribable to triplet carbene are observed under identical conditions, the absorption spectrum can be safely assigned to triplet carbene ^{3}**2**. When the matrix was thawed gradually, the bands became sharper and shifted slightly to shorter wavelengths of 307 and 327 nm. Upon further thawing, the bands started to disappear at around 110 K and completely vanished at around 160 K. This is presumably related to the geometrical changes associated with the softening of the matrix.[13c]

Similar irradiation of **5**-2N_2 in a 2-MTHF matrix at 77 K resulted in the rapid disappearance of the original absorption due to **5**-2N_2 and the concurrent growth of sharp and strong absorption bands at 596 nm along with sharp and weak bands at 548 and 404 nm (Fig. 7). The matrix took on a distinct green color. The bands were found to be thermally quite stable. Thus, when the matrix was thawed gradually, the bands became sharper and shifted slightly to 501, 542, and 589 nm, while the 404 nm band disappeared at around 145 K. This is presumably related to the geometrical changes associated with the softening

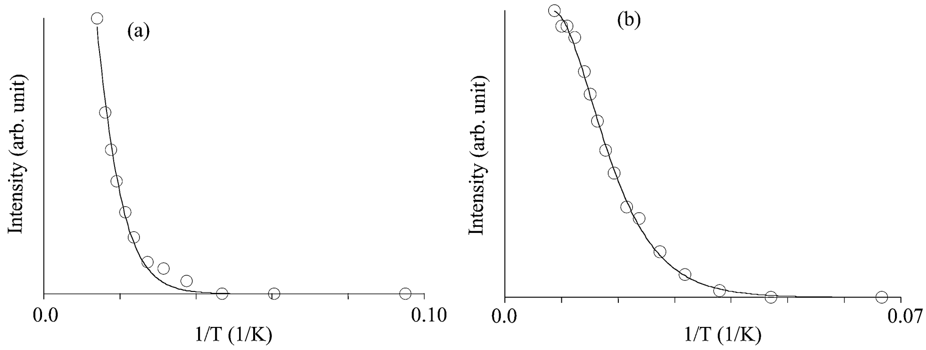


Fig. 3 Plots of the intensities of the ESR signals of thermally populated ^{3}**5** at 160 mT *vs*. reciprocal of temperature (a) before relaxation (10–70 K) and (b) after relaxation (15–110 K).

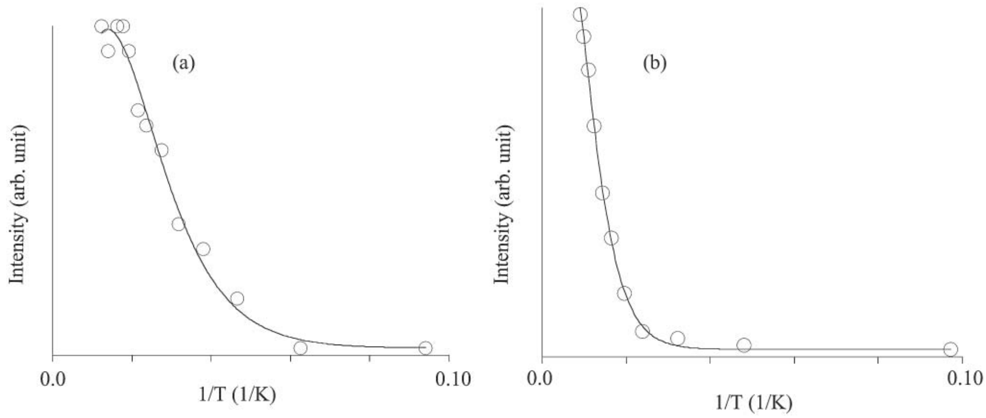


Fig. 5 Plots of the intensities of the ESR signals of thermally populated ^{3}**4** (a) at 267 mT *vs*. reciprocal of temperature (10–80 K) before relaxation and (b) at 136 mT *vs*. reciprocal of temperature (10–110 K) after relaxation.

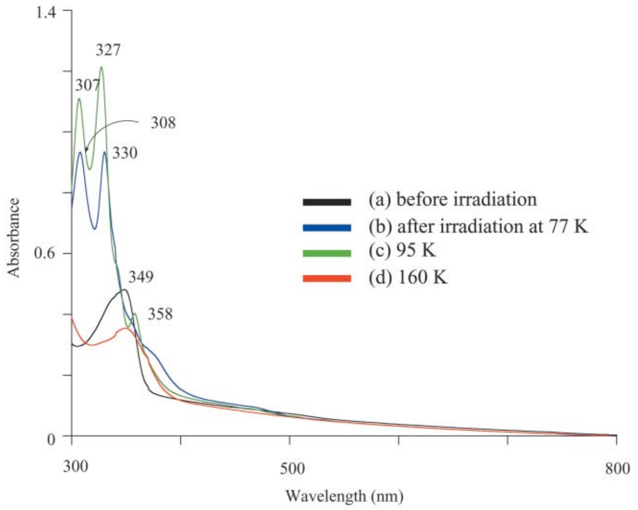


Fig. 6 UV/Vis spectra obtained by irradiation of monodiazo compound **2**-N_2. Spectra of (a) **2**-N_2 in 2-methyltetrahydrofuran at 77 K, (b) the same sample after irradiation ($\lambda > 350$ nm), and (c–d) the same sample after thawing to 95 K (c) and 160 K (d).

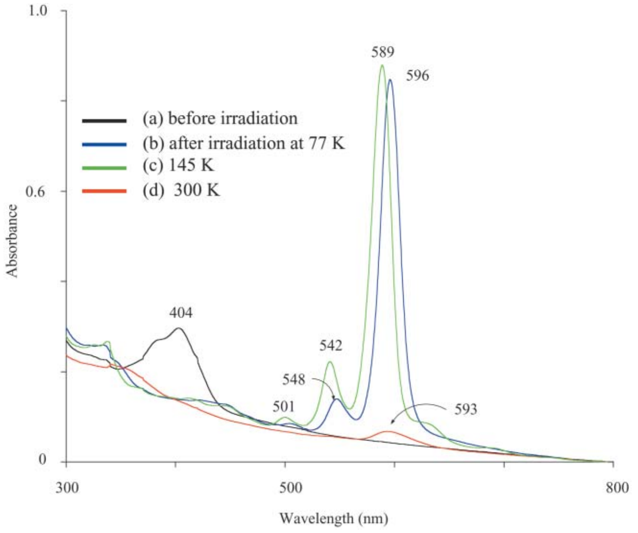


Fig. 7 UV/Vis spectra obtained by irradiation of monodiazo compound **5**-N_2. Spectra of (a) **5**-N_2 in 2-methyltetrahydrofuran at 77 K, (b) the same sample after irradiation ($\lambda > 350$ nm), and (c–d) the same sample after thawing to 145 K (c) and 300 K (d).

of the matrix.[13c] Upon further thawing, the bands started to disappear at around 150 K but did not completely disappear even at 300 K. The anomalous thermal stability of the diradical is noted here.

The bands observed in the photolysis of **5**-$2N_2$ are obviously not ascribable to a mono-carbene but rather to a bis(carbene). The strong absorption bands in the visible regions indicate the presence of the extended π-system.[18] Therefore, the bis(carbene) is likely to exist in a delocalized quinoidal form rather than in a localized one. It is interesting to note here that the bands ascribable to a mono-carbene expected to be generated by elimination of one diazo group were not appreciably detected even at the initial stage of irradiation, suggesting that two nitrogen molecules are likely eliminated following absorption of a single photon.[19]

Similar irradiation of the butadiyne derivative (**4**-$2N_2$) gave essentially identical results. Thus, irradiation in 2-MTHF at 77 K gave a species showing a sharp and strong band at 574 nm along with weak broad bands at 390 and 363 nm (Fig. 8). Upon thawing the matrix, the band shifted slightly to 570 nm at around 145 K, again due to the geometrical changes,[13c] and disappeared irreversibly at around 230 K. Thus, the biscarbene is significantly and thermally more stable than the corresponding mono-carbene but much less stable than the thiophene analogue.

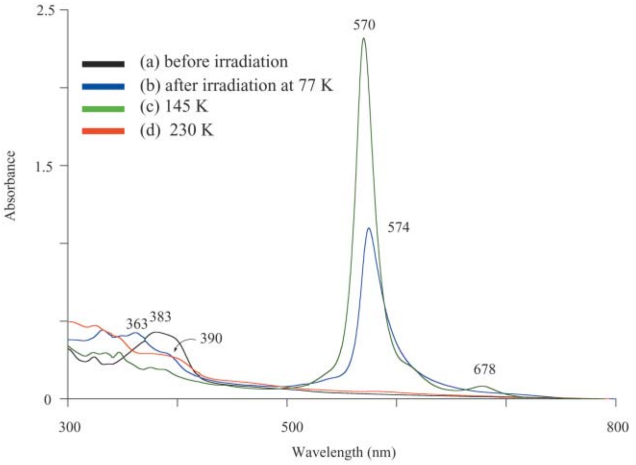


Fig. 8 UV/Vis spectra obtained by irradiation of bis(diazo) compound **4**-$2N_2$. Spectra of (a) **4**-$2N_2$ in 2-methyltetrahydrofuran at 77 K, (b) the same sample after irradiation ($\lambda > 350$ nm), and (c–d) the same sample after thawing to 145 (c) and 230 K (d).

The absorption bands are again completely different from those observed for the corresponding mono-carbene (obtained by irradiation of **2**-N_2 under identical conditions) and, thus, are assignable to bis(carbene). The strong bands in the visible region suggest that this bis(carbene) also exists as a delocalized form.

Time-resolved UV/Vis spectroscopic study in solution at room temperature. In order to know the stability of the present carbenes more accurately, the lifetime was estimated in a degassed benzene solution at room temperature, in which we have measured the lifetime of a series of sterically congested diarylcarbenes.[3]

Laser flash photolysis (LFP) of **2**-N_2 (1×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing a strong absorption at 310 nm, which appeared coincident with the pulse (Fig. 9). On the basis of the low-temperature spectrum, we assigned the transient product to ^{3}**2**. The inset in Fig. 9 shows the decay of ^{3}**2** in the absence of trapping reagents, which is found to be of the second order ($2k/\varepsilon l = 1.27$ s^{-1}). The rough lifetime of ^{3}**2** is estimated in the form of the half-life, $t_{1/2}$, to be 1.3 s.

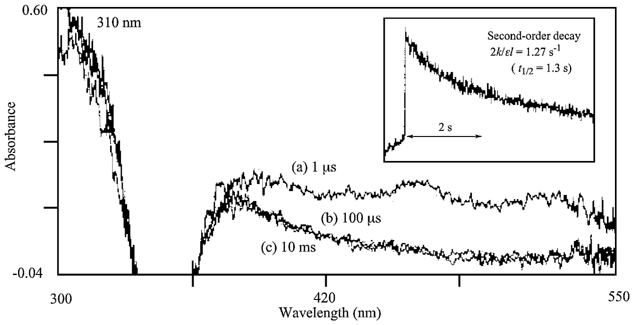


Fig. 9 Absorption of transient products formed during irradiation of monodiazo compound **2**-N_2 in degassed benzene at room temperature recorded (a) 1 μs, (b) 100 μs and (c) 10 ms after excitation. Inset shows the time course of the absorption at 310 nm (oscillogram trace).

Support is lent to this assignment by trapping experiments using oxygen. When LFP was carried out on a non-degassed benzene solution of **2**-N_2, the half-life of ^{3}**2** decreased dramatically, and a broad absorption band with a maximum at 410 nm appeared at the expense of the absorption due to ^{3}**2**. The spent solution was found to contain the corresponding benzophenone (**2**-O) as the main product. It is well documented[20,21] that the diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which are easily observed directly either by matrix isolation or by flash photolysis, and show a broad absorption band centered at 396–450 nm. Thus, the observations can be interpreted to indicate that ^{3}**2** is trapped by oxygen to form the carbonyl oxide (**2**-O_2), which confirms that the transient absorption quenched by oxygen is due to ^{3}**2**.

The apparent build-up rate constant, k_{obs}, of the carbonyl oxide (**2**-O_2) is essentially identical with that of the decay of ^{3}**2**, and k_{obs} is expressed as given in eqn. (2)

$$k_{obs} = k_0 + k_{O_2}\,[O_2] \tag{2}$$

where k_0 represents the rate of decay of ^{3}**2** in the absence of oxygen and k_{O_2} is the quenching rate constant of ^{3}**2** by oxygen. A plot of the observed pseudo-first-order rate constant of the formation of the oxide against $[O_2]$ is linear. From the slope of this plot, k_{O_2} was determined to be 1.1×10^7 M^{-1} s^{-1}, which is approximately 2 orders of magnitude smaller than that observed with the "parent" triplet diphenylcarbene ^{3}DPC ($k_{O_2} = 5.0 \times 10^9$ M^{-1} s^{-1}).[21]

The lifetime of the transient species generated in the photolysis of bis(diazo) compounds was too long to monitor with the laser flash photolysis technique, which has been routinely used for such studies, and a conventional UV/Vis spectroscopic method was more convenient in this case.

As shown in Fig. 10, the UV/Vis spectrum obtained just after brief irradiation of **5**-2N_2 in degassed benzene at 20 °C is essentially the same as that observed in the photolysis in 2-MTHF at 77 K and, hence, attributable to **5**. The absorption bands decayed very slowly; the transient bands did not disappear completely even after 2 h under these conditions.

The decay was analyzed in terms of the combination of the first and second orders. The decay curve was analyzed by Igor using the following equation.

$$\text{O.D.} = A_1\exp(-k_1 t) + 1/(1/A_2 + k_2 t) \tag{3}$$

The decay was fit to a first-order decay ($k_1 = 1.2 \times 10^{-4}$ s^{-1}, $\tau = 139$ min) and the second order ($2k/\varepsilon l = 6.2 \times 10^{-2}$ s^{-1}, $t_{1/2} = 4$ min) in the ratio of 0.21 : 0.31.

The decay rate of the transient bands increased dramatically when the irradiation was carried out in the presence of oxygen. The spent solution was found to include the corresponding diketone **5**-2O as the main product. The observations indicate that the transient species is trapped by oxygen. The quenching rate constant was estimated to be 1.1×10^7 M^{-1} s^{-1}.

The transient absorption bands generated by photolysis of **4**-2N_2 decayed much more quickly than those generated from **5**-2N_2. The irradiation of **4**-2N_2 generated absorption bands that were similar to those observed at low temperature (Fig. 11).

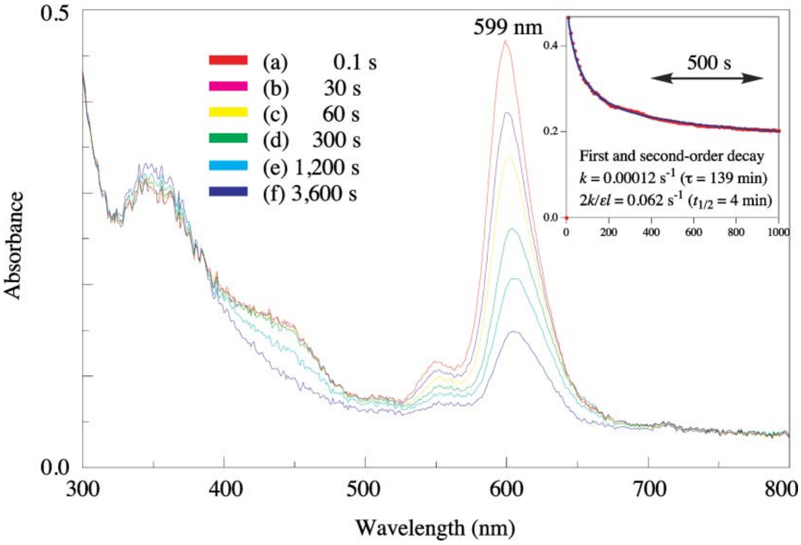


Fig. 10 Absorption of transient products formed during irradiation of monodiazo compound **5**-2N_2 in degassed benzene at room temperature recorded (a) 0.1, (b) 30, (c) 60, (d) 300, (e) 1200 and (f) 3600 s after excitation. Inset shows the time course of the absorption at 599 nm.

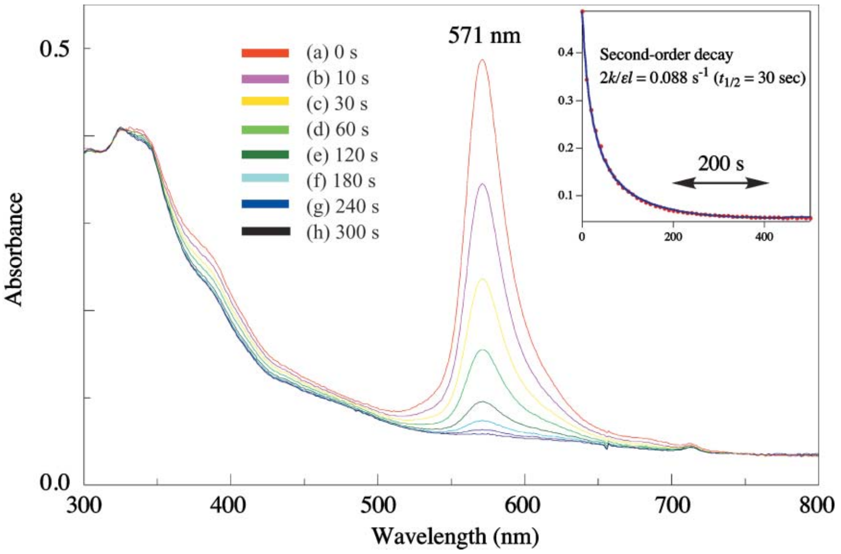


Fig. 11 Absorption of transient products formed during irradiation of bis(diazo) compound **4**-2N_2 in degassed benzene at room temperature recorded (a) immediately, (b) 10, (c) 30, (d) 60, (e) 120, (f) 180, (g) 240 and (h) 300 s after excitation. Inset shows the time course of the absorption at 571 nm.

The absorption bands decayed within 300 s in a second-order manner ($2k/\varepsilon l = 8.8 \times 10^{-2}$ s^{-1}). The half-life was estimated to be 30 s. Again, the transient bands were quenched by oxygen at a rate constant of 7.4×10^6 M^{-1} s^{-1}.

Discussion

Numerous studies have been done to construct high-spin systems built around triplet carbene subunits linked across *m*-phenylene.[11b,22,23] In these systems, the covalent interaction between the triplet centers is topologically prohibited, but communication *via* a shared π-space is possible, thereby generating high-spin states. Considerably less is known about their conjugated cousins, *p*-phenylene poly-carbenes, where spin-pairing between the triplet carbene units leads to lower spin states.[22]

For instance, *p*-phenylenebis(methylene) is predicted to have a singlet ground state of A′ symmetry with a delocalized diradical structure.[24] The lower-lying excited state is computed to be the ^{3}A′ one at about 2 kcal mol^{-1}, and the ^{5}A′quintet state lies at about 27 kcal mol^{-1} above the ^{1}A′ state. Although the ^{3}A′ triplet state was undetected by ESR even at low temperature, probably due to its high reactivity, the species has been generated in an inert gas matrix at 10 K and characterized by the trapping reaction with O_2 and HCl under these conditions.[24] The triplet state of *p*-phenylenebis(phenylmethylene) was detected by ESR and shown to be a thermally populated one lying *ca.* 1 kcal mol^{-1} above the ground state singlet diradical.[16,25]

A series of *p*-phenylenebis(diradicals), in which the local diradical centers are changed from phenylnitrene having a triplet ground state with a σπ singlet lying 18 kcal mol^{-1} high in energy to phenylchlorocarbene having a σ^2 singlet ground state with a triplet lying 7–9 kcal mol^{-1} high in energy, have been generated in an inert gas matrix at low temperature and characterized by IR in combination with theoretical calculations.[22,26] These studies have revealed that all the systems have an ^{1}A′ singlet ground state and that the relative energies between three ^{1}A′ states, singlet, triplet, and quintet, change very little regardless of the nature of the local diradical subunits.

It is to be noted here that the relative energy between those possible multiplicities must be dependent upon the nature of a coupling linker. For instance, in a *p*-phenylene system, maximum bonding occurs for the quinoidal diradicals S_1 and T_1, but this is achieved with loss of aromaticity. The situation must be changed if the linking *p*-phenylene system is replaced with a simple double bond.

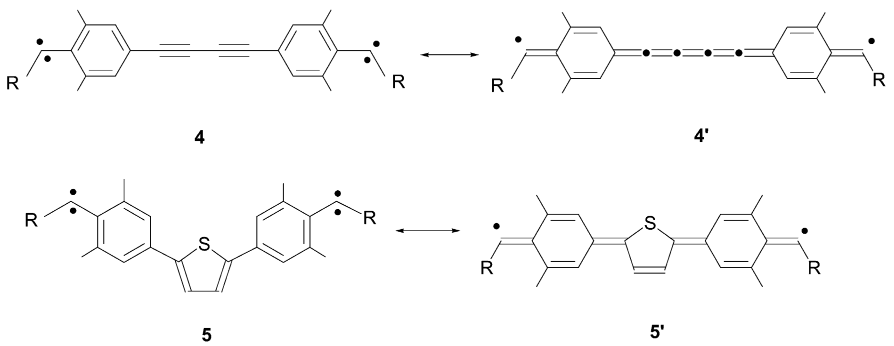
The effect of a coupling linker has been extensively studied, not for the systems with bis(carbene) units,[27] but for those with bis(nitrene) units. For instance, two nitrene centers introduced in conjugative manner into a coupling linker group, such as benzene,[28] biphenyl,[29] stilbene,[30] diphenylbutadiene,[30a,b] diphenyloctatetraene,[30a,b] diphenylacetylene,[31] diphenylbutadiyne,[31] tetraphenylallene,[32] benzophenone and 1,1-diphenylethylene,[33] diphenyl sulfide,[34] azobenzene,[34] and thiophene,[35] have been generated and characterized by ESR; it was revealed that all have a singlet ground state with a delocalized diradical structure having a very small singlet–triplet energy gap of 150 to 600 cal mol^{-1}.

The present findings that two persistent diarylcarbene units introduced either in thiophene or in butadiyne systems have a singlet quinoidal biradical ground state with a very small singlet–triplet energy gap of less than 1 kcal mol^{-1} are in full accord with those from previous observations and predictions.

Most studies on those species have been done simply by using ESR since the measurements have been crucial to characterize those paramagnetic species and successfully employed in many systems, but almost no information is available on the electronic properties and reactivities of those interesting species. In the present study, we have measured the UV/Vis spectra and also revealed their reactivity in solution at room temperature.

Both bis(carbenes), **4** and **5**, feature very sharp and strong absorption bands in the visible region. These features are usually noted for some diradical species incorporated into quinoidal cumulated π conjugating systems.[18] These observations provide further evidence for the contribution of a fully delocalized diradical structure. The surprising thermal stability of the absorption bands is noted. Thus, the bands due to **5** survive even at room temperature. In accord with this, **5** survives for hours in solution at room temperature, being stable enough to be observable by the conventional spectroscopic means. The remarkable increase in the lifetime of biscarbenes **4** and **5**, as opposed to the isolated local diradical system, suggests that the biscarbenes are thermodynamically stabilized as a result of delocalization of unpaired electrons throughout the π net framework.

In spite of their stability, both bis(carbenes) **4** and **5** are readily trapped by oxygen. The quenching rate constants observed for **4** and **5** are very similar to that for the isolated local carbene unit **2**. Moreover, the main oxidation products from both bis(carbenes) are diketones, obviously formed as a result of the interaction of oxygen with the local carbene center rather than with the other



Scheme 2

parts where spin densities must build up. These observations suggest that, although the contribution of extensively delocalized diradical forms is important in bis(carbenes), they still keep their carbenic character toward a typical carbene quencher. Presumably, the reaction of the upper-lying localized quintet states with oxygen is much faster than that of other low-lying states.

Conclusion

The present investigation revealed that sterically congested diphenyldiazomethanes can be used as building blocks to prepare functionalized bis(diazo) compounds. Fairly stable bis(carbenes) with fully delocalized diradical structures are realized by using this method, which enabled us to study the reactivity of these molecules for the first time. Although these molecules are not candidates for practical use in the development of organoferromagnetic materials, they are of considerable importance in understanding the nature of open-shell organic molecules. The present method can be easily extended to construct precursor polydiazo compounds, which can generate high-spin polycarbenes with considerable stability.

Experimental

General methods

Reagents were obtained commercially and used without further purification unless otherwise noted. In the case of experiments, tetrahydrofuran, ether, toluene, dioxane were purified by distillation from sodium/benzophenone and dichloromethane, carbon tetrachloride, triethylamine were from calcium hydride. Gel permeation chromatography (GPC) was performed on a Shodex GPC H-2001 using UV-1570 as a detector, or Shodex GPC H-20025 using UV-970. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL DATUM LTD. JNM-AL300 FT-NMR and were referenced against internal tetramethylsillane on the δ scale in parts per million. Infrared spectra were recorded on a JASCO corporation FT-IR 410 infrared spectrophotometer. UV/Vis spectra were recorded on a JASCO corporation CT-560 UV-vis spectrophotometer on the λ scale in nanometer.

(2,4,6-Tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)methanol. To a mixture of magnesium ribbon (0.8 g, 33 mg atoms) and a crystal of iodine in anhydrous ether (10 mL) was added a solution of 2-bromo-5-*tert*-butyl-*m*-xylene[36] (7.2 g, 30 mmol) in dry ether (15 mL) and the mixture was refluxed overnight under nitrogen atmosphere. After cooling to 0 °C, a solution of 2,4,6-tribromobenzaldehyde[37] (10.3 g, 30 mmol) in dry tetrahydrofuran (25 mL) was added to that Grignard reagent, and the mixture was refluxed for 5 h. Saturated aqueous ammonium chloride was added carefully and the mixture was extracted with ether. The ethereal layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude product which was purified by column chromatography (silica gel, hexane–chloroform = 1 : 1) to give the methanol (2.0 g, 74%) as a white solid: mp 91.5–93.4 °C; ^{1}H-NMR (300 MHz, CDCl$_3$, ppm) δ 7.73 (s, 2H, Ph–H), 6.97 (s, 2H, Ph-H), 6.41 (d, J = 8.82 Hz, 1H, HO–C–H), 2.55 (d, J = 8.82 Hz, 1H, -OH), 2.28 (s, 6H, -Me), 1.29 (s, 9H, -*t*Bu); ^{13}C-NMR (75.5 MHz, CDCl$_3$, ppm) δ 150.4, 139.5, 136.6, 136.0, 133.8, 126.8, 124.8, 121.2, 76.1, 34.1, 31.2, 21.7; MS m/z (relative intensity) 508 (M + 6, 5.0), 506 (M + 4, 14.1), 504 (M + 2, 14.6), 502 (M$^+$, 4.8), 343 (30.2), 57 (100); HRMS calcd for $C_{19}H_{21}OBr_3$ m/z 501.9141, found 501.9136.

(2,4,6-Tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)chloromethane. A solution of the methanol (5.5 g, 11 mmol) in thionyl chloride (20 mL) was stirred at room temperature overnight. Excess thionyl chloride was distilled from the reaction mixture and the mixture was dried under reduced pressure to give the chloromethane (2.0 g, 74%) as a brown semi-solid: ^{1}H-NMR (300 MHz, CDCl$_3$, ppm) δ 7.75 (s, 2H, Ph–H), 6.97 (s, 2H, Ph–H), 6.84 (s, 1H, Cl–C–H), 2.38 (s, 6H, -Me), 1.28 (s, 9H, -*t*Bu); ^{13}C-NMR (75.5 MHz, CDCl$_3$, ppm) δ 150.6, 137.6, 137.2, 136.4, 130.9, 127.2, 125.7, 122.1, 62.0, 34.0, 31.1, 22.8. Since the chloride was found to be unstable, it was used without further purification.

Ethyl *N*-[(2,4,6-tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate. To a heated mixture of ethyl carbamate (13.5 g, 152 mmol) and silver tetrafluoroborate (2.5 g, 13 mmol) in 1,4-dioxane (20 mL) was added a solution of the chloromethane (5.7 g, 11 mmol) in dioxane (30 mL) at 60 °C and the mixture was refluxed overnight. After cooling to room temperature, the mixture was filtered and the filtrate was extracted with chloroform, the organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude product which was purified by column chromatography (silica gel, hexane–dichloromethane = 1 : 1) to give the carbamate (2.0 g, 74%) as a brown solid: mp 101–103 °C; ^{1}H-NMR (300 MHz, CDCl$_3$, ppm) δ 7.71 (s, 2H, Ph–H), 6.96 (s, 2H, Ph–H), 6.39 (d, J = 8.64 Hz, 1H, N–C–H), 5.24 (d, J = 8.64 Hz, 1H, -NH), 4.16 (q, J = 3.03 Hz, 2H, -CH$_2$-), 2.19(s, 6H, -Me), 1.28–1.23 (m, 12H, -*t*Bu + -CH$_3$); ^{13}C-NMR (75.5 MHz, CDCl$_3$, ppm) δ 154.9, 150.6, 137.5, 136.8, 136.3, 132.3, 126.9, 125.0, 120.9, 61.2, 57.9, 34.1, 31.2, 21.3, 14.7; MS m/z (relative intensity) 579 (M + 6, 2.7), 577 (M + 4, 7.8), 575 (M + 2, 7.6), 573 (M$^+$, 2.8), 496 (82.6), 57 (100); HRMS calcd for $C_{22}H_{26}NO_2Br_3$ m/z 572.9512, found 572.9516.

Ethyl *N*-nitroso-*N*-[(2,4,6-tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate. To a stirred solution of the carbamate (4.3 g, 7.5 mmol) in acetic acid (30 mL) and acetic anhydride (40 mL) was added sodium nitrite (10.0 g, 149 mmol) portionwise at 0 °C. After stirring at room temperature overnight, the reaction mixture was poured into ice and extracted with ether. The ethereal layer was washed with water, saturated aqueous sodium carbonate and water again, and the organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give the nitrosocarbamate (6.2 g, 56%) as a brown solid: ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 7.69 (s, 2H, Ph–H), 6.91 (brs, 3H, Ph–H + N–C–H), 4.35 (q, $J = 7.17$ Hz, 2H, -CH_2-), 1.96 (s, 6H, -Me), 1.27 (s, 9H, -*t*Bu), 1.22 (t, $J = 7.17$ Hz, 3H, -CH_3). The nitroso compound was found to be rather unstable and hence used without further purification.

(2,4,6-Tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (1-N_2). To a stirred solution of the nitrosocarbamate (1.4 g, 2.2 mmol) in dry tetrahydrofuran (15 mL) was added potassium *tert*-butoxide (0.5 mg, 4.7 mmol) at −20 °C under argon atmosphere. After stirring overnight, the reaction mixture was poured into ice, extracted with ether, and the ethereal layer was washed with water, dried over anhydrous sodium sulfate, concentrated and dried under reduced pressure to leave a crude product which was purified by column chromatography (alumina, hexane at −20 °C), followed by GPC (chloroform, monitored at 350 nm) to give the diazomethane (0.6 g, 48%) as an orange solid: mp 117.3–118.0 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 7.73 (s, 2H, Ph–H), 7.08 (s, 2H, Ph–H), 2.15 (s, 6H, -Me), 1.30 (s, 9H, -*t*Bu); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm) δ 150.9, 137.3, 135.6, 131.6, 126.0, 125.7, 124.5, 121.1, 63.1, 34.3, 31.3, 21.2; EIMS m/z (relative intensity) 518 (M + 6, 0.6), 516 (M + 4, 1.4), 514 (M + 2, 1.4), 512 (M^+, 0.6), 490(5.5), 488(11.5), 486(8.6), 484(3.2), 227(23.0), 57(100); HRMS Calcd for $C_{19}H_{19}Br_3N_2$ 511.9097; Found m/z 511.9096; IR (NaCl, cm^{-1}) ν 2054.

(2,6-Dibromo-4-trimethylsilylethynylphenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (2-N_2). To a stirred mixture of **1**-N_2 (124.0 mg, 0.24 mmol), bis(triphenylphosphino)palladium dichloride (catalytic amount) and copper iodide (catalytic amount) in dry triethylamine (4 mL) and dry tetrahydrofuran (2 mL) was added trimethylsilylacetylene (100.0 µl, 0.72 mmol) under nitrogen atmosphere. After heating overnight at 35 °C, the reaction mixture was concentrated under reduced pressure, and the residue was dissolved in ether, filtered, and the filtrate was concentrated and dried under reduced pressure to leave a crude product which was purified GPC (chloroform, monitored at 350 nm) to afford **2**-N_2 (95.0 mg, 74%) as an orange viscous liquid: ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 7.66 (s, 2H, Ph–H), 7.07 (s, 2H, Ph–H), 2.14 (s, 6H, -Me), 1.30 (s, 9H, -*t*Bu), 0.24 (s, 9H, -TMS); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm) δ 150.9, 137.4, 136.2, 132.6, 125.9, 124.7, 124.6, 124.3, 101.5, 97.9, 63.7, 34.3, 31.3, 21.1, -0.2. IR (NaCl, cm^{-1}) ν 2054.

(2,6-Dibromo-4-ethynylphenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (3-N_2). To a solution of **2**-N_2 (16.8 mg, 0.03 mmol) in *tert*-butyl alcohol (1 mL) was added 10% aqueous sodium hydroxide (0.3 mL). After stirring overnight at room temperature, the reaction mixture was extracted with ether, the ethereal layer was washed with water, dried over anhydrous sodium sulfate, concentrated and dried under reduced pressure to leave a crude product which was purified by GPC (chloroform, monitored at 350 nm) to afford **3**-N_2 (11.7 mg, 80%) as an orange solid: mp 48.5–49.5.0 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 7.69 (s, 2H, Ph–H), 7.08 (s, 2H, Ph–H), 3.18 (s, 1H, ≡CH), 2.15 (s, 6H, -Me), 1.30 (s, 9H, -*t*Bu); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm) δ 151.0, 137.5, 136.4, 133.1, 125.9, 124.6, 123.2, 80.4, 80.2, 63.7, 34.3, 31.3, 21.1; IR (NaCl, cm^{-1}) ν 2162, 2053.

1,4-Bis{3,5-dibromo-4-(4-*tert*-butyl-2,6-dimethylphenyldiazomethyl)phenyl}butadiyne (4-2N_2). To a solution of **3**-N_2 (10.6 mg, 0.02 mmol) in dichloromethane (2 mL) was added CuCl(OH)·TMEDA (catalytic amount) under oxygen atmosphere. After stirring overnight at room temperature, the reaction mixture was filtered, and the filtrate was concentrated and dried under reduced pressure to leave a crude product which was purified by GPC (chloroform, monitored at 350 nm) to give **4**-2N_2 (6.0 mg, 57%) as an orange viscous liquid: ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 7.71 (s, 4H, Ph–H), 7.09 (s, 4H, Ph–H), 2.16 (s, 12H, -Me), 1.31 (s, 18H, -*t*Bu); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm) δ 151.1, 137.5, 136.6, 133.9, 126.0, 124.55, 124.53, 122.3, 79.7, 76.2, 34.3, 31.3, 21.1; IR (NaCl, cm^{-1}) ν 2139, 2056.

2,5-Bis{3,5-dibromo-4-(4-*tert*-butyl-2,6-dimethylphenyldiazomethyl)phenyl}thiophene (5-2N_2). To a stirred solution of **4**-2N_2 (7 mg, 7.6 µmol) in tetrahydrofuran (2 mL) was added $Na_2S(H_2O)_9$ (7.3 mg, 35 µmol) under nitrogen atmosphere and the mixture was stirred at 50 °C for 20 h. The mixture was concentrated, pored into water, and extracted with ether. The ethereal layer was dried and evaporated under reduced pressure to leave a crude product which was purified by GPC (chloroform, monitored at 350 nm) to give **5**-2N_2 (4.0 mg, 55%) as an orange viscous liquid: ^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ 7.82 (s, 4H, Ph–H), 7.30 (s, 4H, Ph–H), 7.09 (s, 2H, Thiophene-H), 2.20 (s, 12H, -Me), 1.32 (s, 18H, -*t*Bu); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm) δ 150.9, 141.0, 137.4, 135.0, 131.2, 129.9, 126.0, 125.7, 125.5, 124.8, 63.5, 34.3, 31.3, 21.1; IR (NaCl, cm^{-1}) ν 2055.

Irradiation for product analysis. In a typical run, a solution of the diazo compound (**1**, *ca.* 5 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300 W mercury lamp until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated by column chromatography or by preparative TLC and identified by NMR and MS. The following products were isolated and characterized.

Butadiyne-diketone (4-2O). A white solid (90%); mp 312.0–313.4 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.71 (s, 4H), 7.06 (s, 4H), 2.29 (s, 12H), 1.31 (s, 18H); 75.5 MHz ^{13}C NMR ($CDCl_3$) δ 195.6, 155.0, 143.8, 138.7, 136.2, 134.1, 126.8, 124.8, 121.2, 79.5, 77.2, 34.7, 31.0, 22.0; IR (KBr) $\nu_{C=O}$ 1662 cm^{-1}; MS (MALDI-TOF) m/z calcd for $C_{42}H_{37}Br_4O_2$ (M − H^+) 888.9522, found 888.9316.

Thiophene-diketone (5-2O). A pale yellow solid (72%); mp 261.7–263.0 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 4H), 7.38 (s, 2H), 7.06 (s, 4H), 2.32 (s, 12H), 1.32 (s, 18H); 75.5 MHz ^{13}C NMR ($CDCl_3$) δ 196.0, 154.7, 141.6, 141.3, 138.5, 136.8, 134.7, 129.5, 126.6, 126.5, 122.0, 34.7, 31.1, 22.0; IR (KBr) $\nu_{C=O}$ 1672 cm^{-1}; MS (MALDI-TOF) m/z calcd for $C_{42}H_{39}Br_4O_2S$ (M − H^+) 922.9399, found 922.9509.

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M) and the solution was degassed in a quartz cell by three freeze–degas–thaw cycles. The sample was cooled in an optical transmission EPR cavity usually at 77 K and irradiated with a Wacom 500 W Xe lamp using a Pyrex filter. EPR spectra were measured on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter. A JEOL liquid helium transfer system was attached for the low temperature measurement. The temperature was controlled by a 9650 Microprocessor-based Digital Temperature Indicator/Controller, provided the measurements accuracy within ±0.1 K and the control ability within ±0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, the accuracy of the resonance fields determination was within ±0.5 mT.

Low-temperature UV/Vis spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 1704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1 mm path length, and degassed thoroughly by repeated freeze–degas–thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed, under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 300 W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Flash photolysis. All flash measurements were made on a Unisoku TSP-601 flash spectrometer. Three excitation light sources were used depending on the precursor absorption bands and lifetime of the transient species. They were (i) a cylindrical 150 W Xe flash lamp (100 J flash^{-1} with 10 µs pulse duration), (ii) a Quanta-Ray GCR-11 Nd:YAG laser (355 nm pulses of up to 40 mJ pulse^{-1} and 5–6 ns duration; 266 nm pulses of up to 30 mJ pulse^{-1} and 4–5 ns duration), and (iii) a Lamda Physik LEXTRA XeCl excimer laser (308 nm pulses of up to 200 mJ pulse^{-1} and 17 ns duration). The beam shape and size were controlled by a focal length cylindrical lens.

A Hamamatsu 150 W xenon short arc lamp (L 2195) was used as the probe source, and the monitoring beam, guided using an optical fiber scope, was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchro scope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze–degas–thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was flame-sealed under reduced pressure, and the solution was transferred to the quartz cuvette which was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light.

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