X-ray Crystal Structure Study of Sterically Congested Diphenyldiazomethanes

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X-ray crystallographic structures were determined for five diphenyldiazomethanes (DDMs) with various *ortho* substituents, namely, bis(2,4,6-trichlorophenyl)diazomethane, bis(2,4,6-tribromophenyl)diazomethane, bis(4-*tert*-butyl-2,6-dibromophenyl)diazomethane, (4-*tert*-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)diazomethane, and [4-*tert*-butyl-2,6-bis(trifluoromethyl)phenyl](4-*tert*-butyl-2,6-dibromophenyl)diazomethane, and for bis(4-bromophenyl)diazomethane, a DDM with no *ortho* substituents. The correlation between the structural parameters, the ESR zero-field splitting (ZFS) parameters and the lifetimes of the triplet diphenylcarbenes (DPCs) generated from these diazo compounds was examined. It is noted that as *ortho* substituents are introduced onto the phenyl rings of the DDMs, the interplanar angle between the two phenyl rings increases, while the angle of the diazo carbon changes very little. DDM **6**-N_2, from which the longest-lived triplet carbene is generated, is shown to have the largest interplanar angle of the DDMs examined. The bond distances between the aromatic carbons and the *ortho* substituents as well as the van der Waals radii of the substituents were also examined. These studies do not provide a quantitative correlation between the structural parameters of the precursor DDMs and the ZFS parameters and lifetimes of their photoproducts, triplet DPCs, but show how steric shielding of the *ortho* substituents affects the structures and stabilities of triplet DPCs.

The stabilization of triplet carbenes has emerged as a challenging target[1] since the recent syntheses of stable singlet carbenes ruled out the long-standing view that carbenes are not stable enough to be isolated on a macroscopic scale at room temperature.[2,3] Recent growing interest in triplet carbenes as potential organic ferromagnets[4] adds practical meaning to the project.

The stabilization of a triplet carbene has been shown to be better accomplished by steric protection than by electronic effects.[5] The latter strategy does stabilize the singlet state, but, at the same time (due to the conjugation involved) raises questions with respect to the electronic configuration of the resulting species, that is, whether it is a "pure" carbene (a one-centered diradical) or not.[5,6] On the other hand, a bulky group, when introduced near to the carbene center, is capable of protecting it from external reagents, thus kinetically stabilizing the carbene. At the same time, such groups tend to increase the angle at the divalent center simply because of steric congestion. This geometric factor tends to stabilize the carbene thermodynamically because the wider the angle, the more stable the triplet state becomes relative to the singlet.[7−10]

In order to generate persistent triplet carbenes, a series of diphenylcarbenes (DPCs) with *ortho* substituents such as chlorine,[11] bromine,[12] methyl,[13] and trifluoromethyl groups[14] as kinetic protectors have been generated and characterized. Although these carbenes are fairly stable for triplet carbenes, they are still not stable enough to be isolated and crystallized for X-ray crystallographic analysis.[15] Therefore, we could not obtain direct information on how the kinetic protectors shield the carbene center from external reagents.

DPCs can be conveniently generated from the corresponding DDMs, which lose nitrogen very cleanly and efficiently upon photoexcitation. The structures of the DPCs are thus thought to be affected to some extent by those of the precursors. In this respect, it might be useful to determine the structures of the precursor diazomethanes by X-ray diffraction. Thus, we decided to determine the crystal structures of a series of DDMs and systematically examine their structural parameters.

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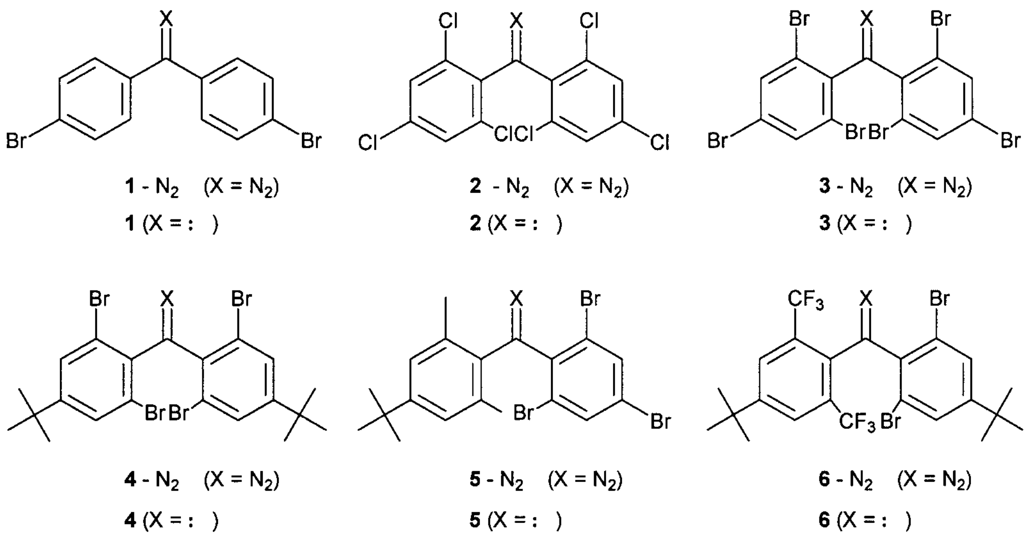


Scheme 1. Structures of diphenyldiazomethanes and diphenylcarbenes

Five diphenyldiazomethanes were used in this study, namely, bis(2,4,6-trichlorophenyl)diazomethane (**2**-N_2), bis(2,4,6-tribromophenyl)diazomethane (**3**-N_2), bis(4-*tert*-butyl-2,6-dibromophenyl)diazomethane (**4**-N_2), (4-*tert*-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)diazomethane (**5**-N_2), and [4-*tert*-butyl-2,6-bis(trifluoromethyl)phenyl](4-*tert*-butyl-2,6-dibromophenyl)diazomethane (**6**-N_2), from which fairly persistent triplet diphenylcarbenes can be generated. As a reference compound, a diphenyldiazomethane with no *ortho* substituents, that is, bis(4-bromophenyl)diazomethane (**1**-N_2), was also studied (see Scheme 1). The correlation between the structural parameters obtained for the precursor molecules, the ESR zero-field splitting (ZFS) parameters and the lifetimes of the triplet diphenylcarbenes generated from these diazo compounds was examined.

Results and Discussion

Crystals suitable for X-ray analysis were obtained for the six diphenyldiazomethanes. The ORTEP views of compounds **1**-N_2 to **3**-N_2 and **4**-N_2 to **6**-N_2 are shown in Figures 1 and 2, respectively. The selected bond angles and bond lengths of the main frameworks of the DDMs are listed in Table 1, where θ is the diazo carbon C−C−C angle and ω is the interplanar angle between the two phenyl rings, while d_1 and d_2 are the C−C distances between the aromatic and diazo carbons and d_3 and d_4 are the distances between $C-N^1$ and N^1-N^2, respectively (see Scheme 2). The bond lengths (C−X) between the *ortho* carbon atoms and the *ortho* substituents are listed in Table 2 along with the van der Waals radii of the substituents.

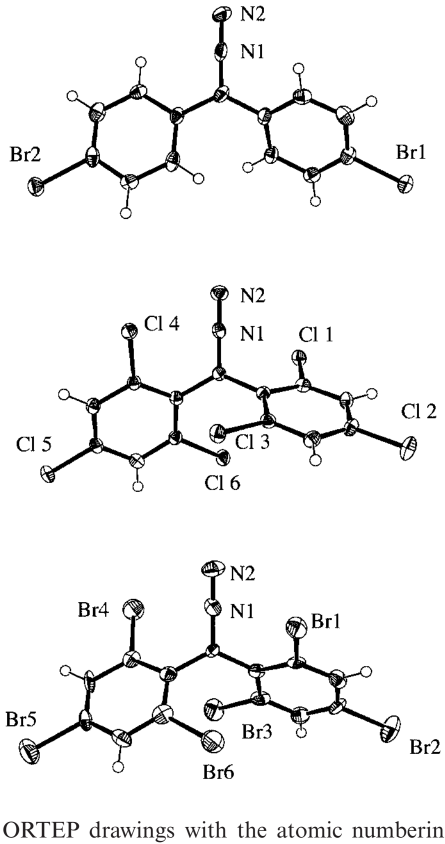


Figure 1. ORTEP drawings with the atomic numbering of bis(4-bromophenyl)diazomethane (**1**-N_2), bis(2,4,6-trichlorophenyl)diazomethane (**2**-N_2), and bis(2,4,6-tribromophenyl)diazomethane (**3**-N_2). The thermal ellipsoids for the non-hydrogen atoms are drawn at 50% probability[22]

The structural and kinetic data for the triplet diphenylcarbenes $^3\mathbf{1}-^3\mathbf{6}$, generated from the diazo precursors, are summarized in Table 3. These are the ESR zero-field

Table 1. Selected bond lengths and angles for diphenyldiazomethanes **1**-N_2 to **6**-N_2

Diazo compounds	θ Ar−C−Ar′ [°]	Interplanar angle ω C12−C11−C21−C22 [°]	d_1 Ar−C [Å]	d_2 C−Ar′ [Å]	d_3 C=N_2 [Å]	d_4 N=N [Å]
1-N_2	126.9(8)	45.6(8)	1.48(1)	1.45(1)	1.29(1)	1.14(1)
2-N_2	127.2(2)	70.2(2)	1.469(2)	1.478(2)	1.307(3)	1.138(3)
3-N_2	127.0(1)	70(1)	1.48(1)	1.48(1)	1.29(1)	1.29(1)
4-N_2	126.9(4)	67.9(5)	1.473(5)	1.460(5)	1.318(5)	1.129(5)
5-N_2	126.0(1)	65(1)	1.47(3)[a]	1.47(3)[a]	1.32(3)	1.12(3)
6-N_2	127.8(4)	80.8(4)	1.471(6)[b]	1.471(6)[b]	1.312(6)	1.152(6)

[a] Ar = 4-*tert*-butyl-2,6-dimethylphenyl, Ar′ = 2,4,6-tribromophenyl. [b] Ar = 4-*tert*-butyl-2,6-bis(trifluoromethyl)phenyl, Ar′ = 4-*tert*-butyl-6-dibromophenyl.

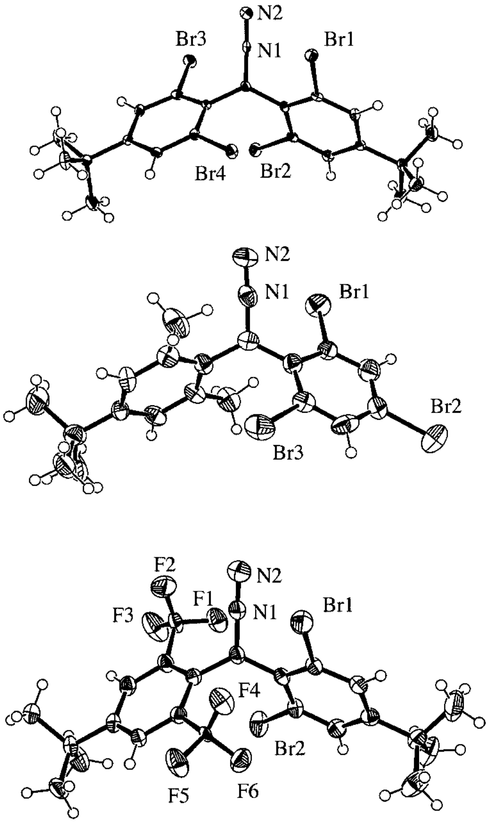
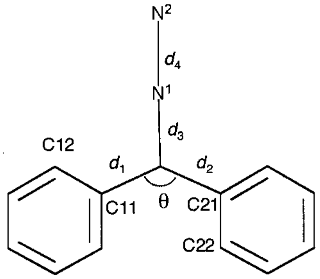


Figure 2. ORTEP drawings with the atomic numbering of bis(4-*tert*-butyl-2,6-dibromophenyl)diazomethane (**4**-N_2), (4-*tert*-butyl-2,6-dimethylphenyl)(2,4,6-tribromophenyl)diazomethane (**5**-N_2), and [4-*tert*-butyl-2,6-bis(trifluoromethyl)phenyl](4-*tert*-butyl-2,6-dibromophenyl)diazomethane (**6**-N_2). The thermal ellipsoids for the non-hydrogen atoms are drawn at 50% probability[22]



Scheme 2

splitting (ZFS) parameters and the lifetimes (or half-lives) of the triplet DPCs measured in a degassed benzene solution at room temperature.

The zero-field splitting (ZFS) parameters D and E give us information on the molecular and electronic structures of the triplet carbenes.[16] The D value is related to the separation between the unpaired electrons. The E value, on the other hand, when weighed by D (i.e., E/D), is a measure of the deviation from the axial symmetry. For diarylcarbenes, this value will thus depend on the magnitude of the central C−C−C angle. Put more simply, the more the two electrons are delocalized through the conjugated π-system of the carbenes, the smaller the value of the repulsive interaction D will be. On the other hand, increasing the bond angle at the carbene center leads to a higher p-orbital contribution and a smaller value of E. Although the values of D and E depend on the electronic distribution within the carbenes, it has been shown that there is a good correlation between the E/D ratio and the bond angle at the divalent carbon atom. The lifetimes (or half-lives) of the triplet DPCs, on the other hand, provide direct information about their stability.

The most prominent structural difference between the DDMs with no *ortho* substituents (**1**-N_2), and those bearing *ortho* substituents (**2**-N_2 to **6**-N_2), in the main framework is the interplanar angle (ω) between the two phenyl rings. Thus, in **1**-N_2, this angle is 45.6°, while the angles in **2**-N_2 to **6**-N_2 are in the range of 70 to 80.8°. There is very little difference in the diazo carbon angles (θ) for **1**-N_2 to **6**-N_2, which suggests that the steric repulsion between the *ortho* substituents is mitigated by rotation of the phenyl ring around the C(=N_2)−C(Ar) bond rather than by increasing the diazo carbon C−C−C angle. In this way, the procarbenic diazo carbon is shielded more effectively from external reagents by the protector substituents.

This situation is likely to be maintained after the loss of nitrogen upon photoexcitation. Thus, the stability of the ^{3}DPCs is dramatically increased once substituents are intro-

Table 2. Distances between the *ortho* carbon atoms and the *ortho* substituents (X) for the diphenyldiazomethanes

Diazo compounds	*ortho* substituents (X)	C−X [Å]	van der Waals radius of X [Å]
1-N_2	H	0.95	1.0
2-N_2	Cl	1.74	1.75
3-N_2	Br	1.86−1.90	1.85
4-N_2	Br	1.88−1.90	1.85
5-N_2	Br	1.89−1.90	1.85
	CH_3	1.50−1.51(C−C)	2.0
6-N_2	Br	1.89−1.90	1.85
	CF_3	1.60−1.61(C−C)	2.7

Table 3. ESR zero-field splitting parameters and half-lives (lifetimes) of triplet diphenylcarbenes **1**−**6**

Triplet carbenes	D[a] [cm^{-1}]	E[a] [cm^{-1}]	E/D	$t_{1/2}(\tau)$[b] [s]	Ref.
1	0.388	0.0195	0.0502	0.000002	This work
2	0.364	0.0115	0.0317	0.018	11
3	0.396 (0.368)	0.0295 (0.00026)	0.0745 (0.0007)	1	12
4	0.397 (0.442)	0.0311 (≈ 0)	0.0784 (≈ 0)	16	12
5	0.432	0.033	0.077	0.55	12
6	0.376 (0.377)	0.0249 (0.0252)	0.066 (0.0667)	(530)	14

[a] Measured in 2-methyltetrahydrofuran matrix at 77 K. The values in parentheses are those measured in 3-methylpentane at 77 K. [b] In degassed benzene at 20°C. The lifetime (τ) is shown only for carbenes decaying by first-order kinetics while the half-life ($t_{1/2}$) is shown for those decaying by second-order kinetics.

duced at the *ortho* positions of the phenyl rings. Furthermore, **6**-N_2, from which the longest-lived triplet DPC of the DDMs employed is generated, also has the largest interplanar angle (ω = 80.8°). This suggests that the interplanar angle may be useful to estimate the stability of triplet DPCs. However, although the angles of the other *ortho*-substituted DDMs (**3**-N_2 to **5**-N_2) are smaller than that of **6**-N_2, they are similar to each other. Nevertheless, the lifetimes of the corresponding carbenes (^{3}**2** to ^{3}**5**) vary quite significantly (from 18 ms to 16 s). Thus, the interplanar angle can be used simply as a very rough measure of stability. Note here that the correlation of this angle with the ESR ZFS parameters, the D and E values, is very poor. There is very little difference in the other structural parameters of the DDMs regardless of the nature of the *ortho* substituents.

The data in Table 2 are more intriguing. The differences in the bond lengths (C−X) and van der Waals radii of the DDMs appear to correlate relatively well with the stability of the corresponding triplet DPCs, and certainly better than the correlation of the angles α and ω. Thus it is generally true that as both values increase, the lifetimes of the corresponding DPCs also increase. In other words, the procarbenic diazo carbon is better shielded from external reagents as larger substituents (with larger van der Waals radii)[17] are introduced further away from the *ortho* carbon.

It is interesting to compare the structure of **3**-N_2 with that of **4**-N_2 since the corresponding triplet carbenes generated from them showed marked differences in stability. The half-life of bis(2,4,6-tribromophenyl)carbene (^{3}**3**) is 1 s, while that of bis(4-*tert*-butyl-2,6-dibromophenyl)carbene (^{3}**4**) is 16 s; this suggests that substituents at the *para* position exert quite a significant effect on the stability of triplet DPCs. However, there is no significant difference in the structural parameters of the two precursor DDMs. This is in accord with the intuition that *para* substituents exert little steric effect on the remote diazo carbon. It is also consistent with the ESR analyses of the triplet carbenes generated from them. The ZFS parameters observed for the ^{3}**3** and ^{3}**4** are essentially the same, which suggests that they have almost identical structures.

Thus, the significant increase in the lifetime of the triplet diphenylcarbene ^{3}**4**, relative to ^{3}**3**, on introduction of the *tert*-butyl group at the *para* position cannot be ascribed to structural changes in the carbene itself but to the suppression of the decay path caused by the build up significant spin density at the *para* position.[12c]

When two of the four *o*-bromine groups are replaced with a methyl group, that is, on going from **4**-N_2 to **5**-N_2, a slight decrease in the interplanar angle is observed, while the structural parameters of the main framework change little. The decrease in the interplanar angle suggests that the interactions between the two *o*-methyl and two *o*-bromine groups are not as severe as that between the four *o*-bromine groups.

There may be several reasons for this. For instance, the bromine group is spherically symmetrical, and, therefore, it interacts not depending on the direction. On the other hand, in the case of the methyl group, a hydrogen atom bound to carbon is only conically symmetrical, and the interaction potential of this hydrogen atom with another atom will depend on the particular point on the carbon−hydrogen bond at which the other atom approaches. Therefore, methyl groups can minimize their interaction potential by simply rotating. The electronic repulsion between two adjacent substituents should also be more significant for electronegative bromine groups than for neutral methyl groups. Note also that the C(aromatic)−C(methyl) bond length is ca. 1.5 Å, which is significantly shorter than those of C−Br (ca. 1.9 Å) and C−Cl (1.74 Å).

The effects of two different substituents on the structures and lifetimes of triplet diphenylcarbenes are not straightforward. The structure of triplet carbene ^{3}**5**, as deduced from the ZFS parameters, is largely influenced by the bromophenyl substituent, while the kinetic behavior at room temperature is affected by the methyl groups, which are potentially reactive towards triplet carbenes.[12c]

A rather significant increase in the interplanar angle is observed when the two methyl groups in **5**-N_2 are replaced with two trifluoromethyl groups, that is, on going from **5**-N_2 to **6**-N_2. This increase clearly reflects a much more severe steric compression in **6**-N_2 than in **5**-N_2. Even though the C(aromatic)−C(trifluoromethyl) bond length is significantly shorter (1.6 Å) than that of C−Br (1.9 Å),[17] the van der Waals radius of the trifluoromethyl group is much larger than those of the methyl and bromine groups. Therefore, the phenyl rings are forced to rotate around the $C(=N_2)-C(Ar)$ bond to relieve the compression, which results in a larger interplanar angle. This motion results in more effective shielding of the procarbenic carbon. Triplet DPC ^{3}**6**, generated from **6**-N_2, is found to survive for several hours in solution at room temperature with a half-life of nearly 10 min.[14b]

However, the ZFS parameters do not reflect the difference in stability. The E/D value for ^{3}**6** in a soft matrix, in which the carbene assumes the most stable geometry, is significant and larger than that for ^{3}**4**, where E is essentially zero. This suggests that ^{3}**4** is essentially linear, while ^{3}**6** is still bent.

Note also that when the matrix containing ^{3}**4** was warmed, the x and y lines of the spectrum moved closer together, resulting in an essentially zero E value. This can be interpreted as being a result of the geometrical change that is often observed in sterically congested carbenes.[18] The substantial reduction in the E value upon annealing the matrix indicates that the carbene relaxes to a structure with an expanded C−C−C angle, presumably to gain relief from steric compression. Thus, when a carbene is formed at a low temperature, it should have a bent geometry with a conformation dictated by that of the precursor. Even if the thermodynamically most stable geometry and/or conformation of the carbene are different from those of the initially formed carbene, the rigidity of the matrix prevents it from assuming its minimum energy structure. However, when the matrix is softened upon annealing, the carbene can relax to a more stable geometry depending on the softness of the media. The fine-structure constants observed for ^{3}**4** in a softer matrix, that is, in 3-methylpentane (3-MP),[19] were essentially the same as those observed for the relaxed carbenes even at 77 K, and the spectrum did not change upon annealing in this case.

In marked contrast, only a slight change in the ESR signals of ^{3}**6** was observed upon annealing the matrix, although the steric compression in ^{3}**6** was expected to be much more severe than that in ^{3}**4** due to the bulkiness of the trifluoromethyl groups relative to the bromine atoms.

We do not know the exact reason for this rather unexpected behavior. The spectroscopic features provide no evidence for a significant interaction between the carbene center and the substituents. It may be, then, that two kinds of substituents with significantly different natures might perturb the electronic configurations of the carbenes and/or that there may be a spatial interaction between the two *ortho* substituents on the different phenyl rings.

Conclusions

Information on how the structures and stabilities of triplet DPCs are affected by kinetic protector *ortho* substituents, based on the crystallographic structural features of their precursor DDMs, suggest that the interplanar angle between the two phenyl rings in DDMs is the most prominent parameter reflecting the steric congestion around the carbenic carbon. This angle increased as larger *ortho* substituents were introduced onto the phenyl rings of the DDMs. Although the present studies do not provide a quantitative correlation between the structural parameters of the precursor DDMs and the ZFS parameters and lifetimes of their photoproducts, triplet DPCs, they do show how steric shielding of the *ortho* substituents affects the structures and stabilities of triplet DPCs.

Experimental Section

All the sterically congested DDMs (**2**-N_2,[11,20] **3**-N_2,[12] **4**-N_2,[12] **5**-N_2,[12] and **6**-N_2[14]) were prepared from the corresponding diarylmethanols by way of carbamates and were purified by column chromatography followed by GPC. Detailed procedures have been reported elsewhere. Bis(4-bromophenyl)diazomethane (**1**-N_2) was prepared[21] by the conventional method.

The crystal data and details of the experimental conditions are listed in Table 1.[22] The intensity data were collected on a Rigaku RAXIS-RAPID imaging plate area-detector with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.7107$ Å) at a temperature of −150 °C (23 °C for **5**-N_2) using the cold-nitrogen gas-flow method. The structures were solved by a direct method using SIR92[23] and refined by the full matrix least-squares method.[24] All of the non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C−H 0.96 Å, C−C−H 109.5° or 120°) and were refined isotropically using a rigid model. All of the calculations were performed using the CrystalStructure crystallographic software package.[25] Crystallographic parameters and refinement data are summarized in Table 4.

ESR spectra were recorded on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation). DDMs were dissolved in 2-methyltetrahydrofuran (10^{-3} M), and the solutions were degassed in a quartz cell by three freeze−degas−thaw cycles. The samples were cooled in an optical transmission EPR cavity at 77 K and irradiated with a Wacom 500 W Xe or Hg lamp using a Pyrex filter.

For the kinetic measurements of the decay of the triplet carbenes, solutions of the DDMs (10^{-4} M) in benzene were placed in a long-necked Pyrex tube and degassed using a minimum of four

Table 4. Crystal data, experimental conditions, and details of refinements for diphenyldiazomethanes **1**-N_2 to **6**-N_2

	1-N_2	**2**-N_2	**3**-N_2	**4**-N_2	**5**-N_2	**6**-N_2
Formula	$C_{13}H_8Br_2N_2$	$C_{13}H_4Cl_6N_2$	$C_{13}H_4Br_6N_2$	$C_{21}H_{22}Br_4N_2$	$C_{19}H_{19}Br_3N_2$	$C_{23}H_{22}Br_2F_6N_2$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/a$	$P\bar{1}$
Temp. [°C]	−150	−150	−150	−150	23	−150
a [Å]	16.737(2)	9.6654(4)	9.8960(4)	13.903(1)	11.003(2)	9.184(3)
b [Å]	3.9499(6)	12.7318(6)	13.1882(7)	10.0514(4)	15.818(1)	10.953(3)
c [Å]	19.678(3)	12.2145(6)	12.6620(6)	17.499(1)	11.116(1)	12.877(5)
α [deg]	90	90	90	90	90	108.39(1)
β [deg]	113.771(9)	91.0891(9)	92.1188(7)	112.584(4)	93.906(3)	94.43(2)
γ [deg]	90	90	90	90	90	98.54(2)
V [Å^3]	1190.5(3)	1502.8(1)	1651.4(1)	2257.7(2)	1930.2(3)	1204.8(7)
Z	4	4	4	4	4	2
d_{calcd} [mg·m^{-3}]	1.964	1.772	2.685	1.830	1.772	1.654
μ(Mo-Kα) [cm^{-1}]	68.05	11.32	146.23	71.60	62.92	34.34
Crystal dimens. [mm]	0.80 × 0.30 × 0.10	0.50 × 0.30 × 0.30	0.70 × 0.70 × 0.50	0.40 × 0.65 × 0.30	0.50 × 0.50 × 0.50	0.40 × 0.40 × 0.40
No. of meas. reflns.	6719	11279	14563	20659	16935	11346
$2\theta_{\mathrm{max}}$ [deg]	55.0	55.0	55.0	55.0	55.0	55.0
No. of unique reflns.	2377	3443	3777	5100	4422	5365
No. of retained reflns.	2034	3130	2177	3798	2051	3706
No. of variables	163	195	195	267	237	320
$R1$	0.078	0.039	0.045	0.024	0.073	0.050
$wR2$	0.139	0.081	0.080	0.040	0.124	0.085
GOF	1.38	0.60	0.74	1.02	1.16	0.95
Residual electron density						
max [e·Å^{-3}]	2.28	0.60	1.02	0.69	2.36	0.86
min [e·Å^{-3}]	−1.59	−0.49	−1.04	−0.45	−0.71	−0.79

freeze−degas−thaw cycles at a pressure near 10^{-5} Torr immediately prior to flashing. All flash measurements were made on a Unisoku TSP-601 flash spectrometer with a Lamda Physik LEXTRA XeCl excimer laser (308 nm pulses of up to 200 mJ·pulse^{-1} and 17 ns duration).

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