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An ESR insight into the thermally activated structural relaxation of the bis(2,4,6-trichlorophenyl)carbene in relation to the molecular mobility of the immediate surroundings

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The dark geometrical relaxation of sterically congested diarylcarbenes under matrix conditions was studied by ESR using bis(2,4,6-trichlorophenyl)carbene as a test molecule. The initial decrease of the parameter *D* has been found to proceed independently from the well-known expansion of the cental carbenic angle. The latter manifested by the reduction of the parameter *E* appears to be in correlation with the molecular mobility of the immediate surroundings probed by the reorientation of the primarily aligned test carbene. The complicated nature of the geometrical relaxation of the test carbene was interpreted in terms of the competition of the release of the congestion at the carbenic center and the restraints imposed by a matrix cage on any geometrical changes of the guest molecule.

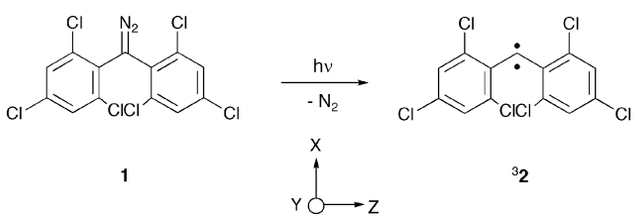
Introduction

Bulky substituents at the *ortho* positions of diphenylcarbene [1–6] have been found to protect a carbenic center from the attack of external reagents, thereby increasing the lifetime of a carbene by many orders of magnitude under ambient conditions. Further research along these lines is expected to provide an opportunity to use persistent triplet carbenes as units in constructing pure organic ferromagnetics.

Strained diarylcarbenes bearing bulky substituents at the *ortho* positions of both phenyl rings generated in a rigid matrix at low temperature tend to undergo structural relaxation upon annealing the matrix. This is usually revealed by ESR studies that show significant decrease in parameters *D* and *E* of zero-field splitting (ZFS).[2–9] The expansion of the valence angle at the carbenic center was shown to be responsible for the observation. The process was classified as irreversible because the starting ESR profiles were never restored upon recooling the matrix.

The issue encountered in the study of thermally activated geometrical relaxation of matrix-isolated molecules is to reveal the relationship between its own structural behavior and the molecular motions of the immediate environment. Concerning the strained diarylcarbenes, the dependence of their structural transitions under matrix conditions on the molecular mobility in the nearest vicinity has yet to be investigated. Since the congestion around the carbenic center is clearly guided by the backbone geometry, it seems reasonable to try to control the protecting ability of *ortho* moieties. In this manner, the tunable structural relaxation of a persistent carbene can be expected to allow the additional extension of its lifetime, for instance, by improving the appropriate medium arrangement.

Assuming that the same driving forces operate during the structural relaxation of the majority of matrix-trapped strained diarylcarbenes, we attempted to examine the aforementioned relationship using a test system. Herein we have chosen the triplet bis(2,4,6-trichlorophenyl)carbene (^{3}**2**, Scheme 1) as a representative target molecule since it exhibits the structural relaxation typical for strained diphenylcarbenes in glassy matrices on the time scale of the steady state ESR technique.[5] We used the reorientation of the molecular framework of the test carbene to judge whether the rearrangement of the immediate surroundings proceeded simultaneously.



Scheme 1 Triplet bis(2,4,6-trichlorophenyl)carbene (^{3}**2**) was generated by photolysis of the corresponding diazo precursor (**1**). The axis convention (X, Y and Z) used in this study is also indicated.

Experimental

General

The starting bis(2,4,6-trichlorophenyl)diazomethane(**1**) was prepared, by essentially the same procedure invented by Zimmerman and Paskovich in 1964,[1] as rather stable yellow–orange crystals.

In a typical experiment about 0.1 ml of the *ca.* 5×10^{-3} M solution of **1** in 2-methyltetrahydrofuran (MTHF) was placed into a quartz tube for ESR measurements and was degassed by three freeze–pump–thaw cycles. The samples were then cooled to 77 K in the cavity of the ESR spectrometer giving a transparent glass. Irradiation was carried out with a high pressure, 150 W mercury lamp at 77 K in the ESR cavity. The 436 nm line, isolated from the emission spectrum by appropriate Toshiba glass filters, was used.

The ESR spectrum of the triplet carbene (^{3}**2**) was measured on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation) at 77 K immediately after irradiation was stopped. The temperature was controlled by a 9650 Microprocessor-based digital temperature indicator/controller, providing accuracy within ±0.1 K and 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.

Results

Preparation of partially ordered samples

In order to visualize the reorientation of the molecular framework of the test carbene, the samples containing partially

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aligned ^{3}**2** were prepared. As a general trend, the molecules of the diazo precursor (**1**) absorb light with a probability depending on the angle between the transition moment within the molecular framework and an electrical vector. Since the latter is naturally ordered perpendicular to the light direction, the molecules whose transition moment lies in the plane, perpendicular to the irradiating beam, undergo photo-fragmentation with the greatest probability. This probability decreases as soon as the angle between the transition moment and the light direction reduces from π/2 to 0.

Thus, irradiation of an ensemble of randomly oriented molecules of the diazo compound **1** with a collimated light beam gives the carbene with a probability depending on the orientation of the molecular framework of the precursor with respect to the light direction. If test carbene ^{3}**2** adopts the starting alignment of the carbon backbone of the diazo precursor **1**, the triplet carbene should exhibit the anisotropy of spatial orientation. Concerning the observed ESR profile, the partial alignment of ^{3}**2** averaged through the sample volume leads to the dependence of the amplitudes of the fine structure components on the angle between the directions of the magnetic field and the irradiating light without changing their resonance fields.

The ESR spectrum of ^{3}**2** immediately from the photolysis of **1** with collimated light at 436 nm satisfies the above suggestion (Fig. 1). The X[10] component exhibits a maximum value at $\phi = \pi/2$ and a minimum one at $\phi = 0$, where ϕ means the angle between the directions of light generating the carbene before ESR measurements, and the magnetic field in the ESR spectrometer cavity. Components Z and Y demonstrate an opposite angle behavior: their amplitudes are of maximum value at $\phi = 0$ with the minimum at $\phi = \pi/2$ (see Scheme 1).

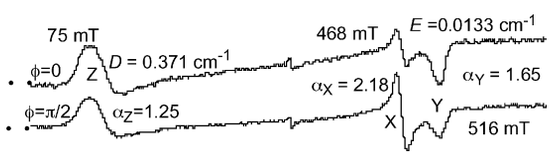


Fig. 1 The ESR profile of ^{3}**2** from photolysis of the diazo precursor **1** in MTHF at 77K. Here and below the upper spectrum in every pair is recorded when the magnetic field is parallel to the primary direction of irradiating light (ϕ = 0, ||), and the lower one when they are perpendicular ($\phi = \pi/2$, ⊥).

Thus, the X component shows a maximum when the principal X-axis of the ZFS tensor coincides with an electrical vector. Since the X-axis adopts the direction of the C=N=N bond as a bisector of the central angle, the transition moment in the diazo precursor is aligned along this bond, similar to that in parent diphenyldiazomethane.[11] Furthermore, the total anisotropy of ^{3}**2** orientation averaged through a sample volume is examined in terms of the ratio of the amplitudes of the X component $a_X = X_{\phi = \pi/2}/X_{\phi=0}$, since it exhibits the greatest starting deviation from unity, compared to a_Z and a_Y. As a result, the behavior of a_X indicates whether the reorientation of the carbenic framework occurs.

The values of a_X (as well as a_Y and a_Z) can be expected to approach unity in response to the gradual loss of the total spatial anisotropy of the trapped test species. Thus, the reorientation kinetics of ^{3}**2** becomes available from the dependence of a_X on the exposure time at a given temperature.

Variable-temperature ESR study

Irradiation of the precursor **1** in MTHF glass at 77 K afforded ^{3}**2** that was identified from the ESR signal with $D = 0.371$ cm^{-1} and $E = 0.0133$ cm^{-1} (Fig. 1). Storage in the dark at 77 K for 4 hours does not change the ESR profile.

Slight heating of the matrix induces the progression of the ESR spectrum. First, after 30 s at 84 K, the Z component shows a remarkable shape modification together with a downfield shift (Fig. 2, spectra a and b). Further standing at the same temperature results in the full displacement of the component Z to the low field side (Fig. 2, spectra c and d).

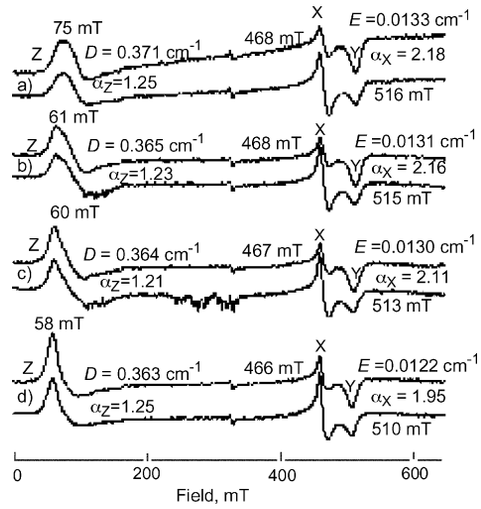


Fig. 2 Expanded portions of ESR spectra of ^{3}**2** illustrating the profile changes at dark storage in MTHF glass: (a) spectra from photolysis of starting diazo compound **1** at 436 nm, 77 K, (b) after 0.5 min at 84 K, (c) after 4 min at 84 K, d) after 10 min at 84 K.

Furthermore, the distance between the components X and Y decreases after 4 minutes at 84 K, demonstrating a sizable reduction of the parameter E (Fig. 2c). Further storage in the dark at 84 K decreases E until it attains a value of 0.0122 cm^{-1} after 10 min. Then, measurable changes in the ESR profile are not observed. Along with the reduction of E, the value of a_X diminishes slightly, showing the partial loss of the initial alignment of the molecular framework of the carbene.

The heating of the sample up to 88 K evokes further reduction of the parameter E (Fig. 3). Simultaneously, the approach of the a_X to unity becomes more pronounced (Fig. 4), clearly demonstrating the reorientation of the molecular framework of trapped ^{3}**2**. Both values attain their limits after standing for 2 min at 94 K ($E_{min} = 0.0106$ cm^{-1} when $a_X = 1$).

It is worth mentioning that, while the intensity of the X components recorded at $\phi = 0$ and $\phi = \pi/2$ gradually approach each other, the same is not true for the Z component. The

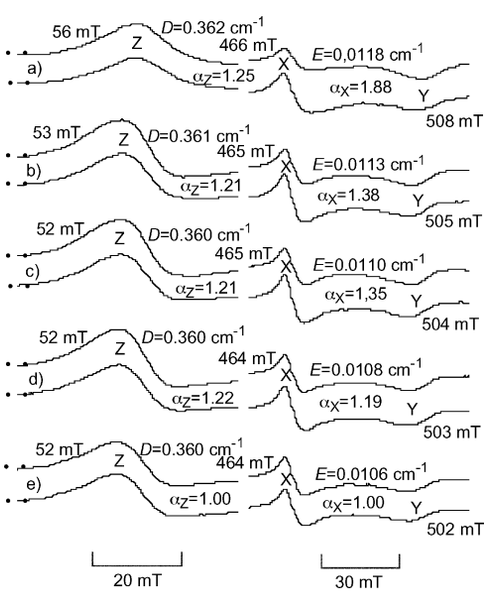


Fig. 3 Expanded portions of the ESR spectra of ^{3}**2** showing the further changes after storage at 84 K in MTHF glass: (a) 88 K, 1 min, (b) 88 K, 5 min, (c) 88 K, 10 min, (d) 90 K, 5 min, (e) 94 K, 2 min.

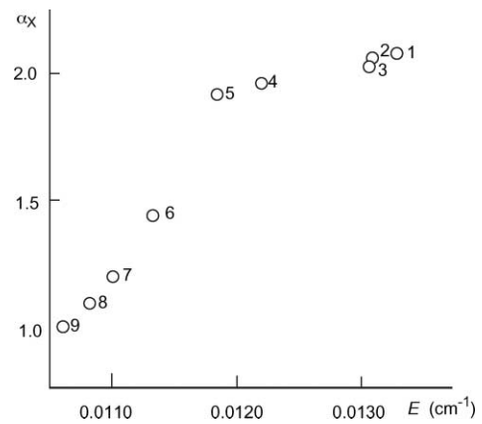


Fig. 4 The reorientation of the trapped ^{3}**2** displayed by the value of a_X *versus* the opening of the central carbenic angle reflected by the parameter E of ZFS at dark storage: (1) from photolysis of **1** at 436 nm, 77 K; (2) 84 K, 0.5 min; (3) 84 K, 5 min; (4) 84 K, 10 min; (5) 88 K, 1 min; (6) 88 K, 5 min; (7) 88 K, 10 min; (8) 90 K, 5 min; (9) 94 K, 2 min.

starting value of $a_Z = 1.25$ retains, within experimental error, up to 90 K (Fig. 2 and 3, a–d) and reduces significantly to 1 only at 94 K (Fig. 3e). As a result, the reorientation of ^{3}**2** exhibits some anisotropy by itself and should be examined more in terms of the rotation around the Z-axis than as random reorientation of the overall molecular framework.

The plot of the values of a_X *versus* the parameter E (Fig. 4) demonstrates two temperature ranges where nearly linear correlation is observed. From 88 K to 94 K, the expansion of the central angle of ^{3}BTC proceeds under more intensive reorientation of the test carbene than at 84 K.

To gain more insight into the structural relaxation mode, the trapped and nonrelaxed ^{3}**2** was exposed to light that was not absorbed either by the carbene or by its precursor. This will give rise to some reorganization of the guest molecule *via* the softening of a matrix due to absorption of the unfiltered IR portion. The ESR spectrum of ^{3}**2** upon mild irradiation at $\lambda > 550$ nm at 77 K (Fig. 5) shows only the downfield shift of the Z component, similar to that at dark storage. However, neither the value of a_X nor the distance between X and Y changes at least after 2 hours of exposure.

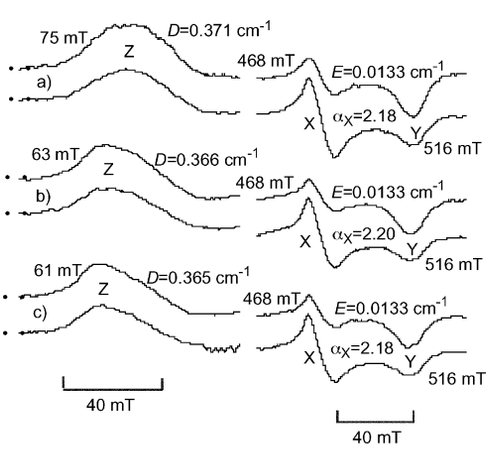


Fig. 5 The expanded portions of the ESR spectra of ^{3}**2** showing the profile changes upon irradiation at $\lambda > 550$ nm ("inactive photon") in MTHF glass at 77 K: (a) spectra from photolysis of 1 at 436 nm, (b) upon irradiation at $\lambda > 550$ nm for 1 h, (c) upon irradiation at $\lambda > 550$ nm for 2 h.

Discussion

The observed dark behavior of the test carbene can be rationalized by taking into account the stepwise nature of its thermally activated structural relaxation. Evidently, the geometrical relaxation pathway of ^{3}**2** passes through several intermediary conformations, presumably accommodated in shallow energy wells conditioned by the host matrix. As a general trend, the thermally activated transitions between them gain the release of steric congestion[6d,c] at the carbenic center but are available as far as they are allowed by the freedom given by the matrix cage.

Photo-fragmentation of the diazo precursor yields ^{3}**2** whose conformation is dictated by the geometry of the starting carbon backbone. Support is lent to this concept by the finding that the starting value of a_X is greater than 2. This provides us with a reason to believe that the overwhelming majority of the triplet species produced in the matrix retain the orientation of the carbon backbone of the precursor diazo molecules. Therefore, motions of the molecular framework during the triplet carbene formation at 77 K are suppressed by rigid surroundings.

The progression of the Z component observed on a short exposure to 84 K or upon "inactive" irradiation originates from the reduction of the parameter D, which occurs independently of E. This seems to arise from the more extensive delocalization of the spin density at the carbenic center with conjugated π-systems. As the parameter E is untouched, the geometrical transition responsible for the reduction of D can be most likely assigned to the twist of phenyl rings towards the plane defined by the carbenic carbon and two adjacent C atoms, *i. e.*, from ^{3}**2A** to ^{3}**2B**, Scheme 2.

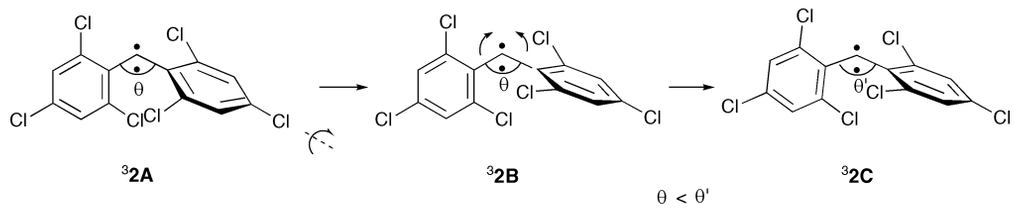
To assign a tentative cause for this transition, the difference in the equilibrium conformation of ^{3}**2** and the carbon backbone of the starting bis(2,4,6-trichlorophenyl)diazomethane (**1**) should be considered in terms of the dihedral angle between phenyl rings (θ_1). The direct X-ray measurements have shown that θ_1 in crystalline **1** is equal to 70.2°.[12] On the other hand, the phenyl rings in the equilibrium geometry of ^{3}**2** is likely to be orthogonal, similar to that for dimesitylcarbene.[7] The theoretical calculations at the DFT(U)B3LYP level of theory on the energy surface of ^{3}**2** as a function of the dihedral angle (θ_1) showed that the angle at the energy-minimum structure is 97.6°.[12] Thus, the twist of both aryl groups leading to further delocalization of the spin density at the carbenic center with π-systems of phenyl rings might be responsible for the reduction of the parameter D.

The twist of aryl groups does not involve the shift of the phenyl rings or the terminal *para* C–Cl portions, unlike the case of expanding the central carbenic angle, and therefore seems to be limited by the lowest matrix cage barriers. Hence, it is available even on shorter annealing or at lower temperatures than other types of relaxation and is not accompanied by profound cage rearrangement.

Consistent with literature reports, we observe the expansion of the central angle at 84 K and at elevated temperatures, *i. e.*, from ^{3}**2B** to ^{3}**2C**, Scheme 2. The reduction of the parameter E occurs along with the approach of a_X to 1. The latter results from the reorientation of the molecular framework of the test carbene. Although a nearly linear type of correlation between two values cannot easily be physically interpreted, the breakpoint in the plot depicted in Fig. 4 presumably originates from the alteration of the driving force of the overall relaxation process.

The first stage observed at 84 K likely occurs mainly due to the release of the congestion at the carbenic center. The mobility of the immediate surroundings seems to be less significant and this is corroborated by only the slight decrease of a_X accompanying the marked reduction of E. The congestion at the carbenic center diminishes as the central angle is opened. In this respect, the limiting value of the parameter E = 0.0122 cm^{-1} satisfies to the reduction of the congestion at the carbenic center to the extent at which it cannot provide further geometrical relaxation.

At this stage, further promotion of the structural changes of ^{3}**2** comes from the molecular mobility of the surroundings. The decisive role of the matrix cage rearrangement for the recovery of the geometrical progression of ^{3}**2** at 88 K is supported by the much faster approach to unity of a_X against the decrease of E



Scheme 2 The initial decrease of the parameter D due to the twist of the phenyl rings is followed by the reduction of the parameter E on extended exposures to the same temperature or under further heating ascribable to the opening of the central carbenic angle.

(Fig. 4). The final value E = 0.0106 cm^{1} measured after the complete reorientation of the molecular framework likely corresponds to the lowest energy geometry of the test carbene.

It is worth noting, that the values of a_X and a_Y approach unity gradually (Fig. 3) as the exposure time is extended or/and temperature is elevated, while a_Z stays unchanged unless temperature achieves 94 K. This provides a reason to consider the reorientation of ^{3}**2** more as a rotation around the Z-axis than as a random reorientation of all molecular axes. The anisotropy of reorientation can be interpreted in terms of the dimensions of the molecule along different molecular axes. Virtually, the Z-axis is parallel to the line, which joins the terminal *para* Cl-atoms. Since the distance between the atoms gives the longest dimension of the molecule of the carbene, the change of the primary orientation of the Z-axis in a matrix cage appears to be most hindered relative to that of the other two axes. Moreover, the opening of the central angle additionally increases the molecular size along the Z-axis.

On the basis of starting and final values of the ZFS parameters of the test carbene, it seems that the effects are too small (D changes by *ca*. 2%, E decreases by *ca*. 20%) to interpret. However, the low shifts in ZFS seem to be very typical for aryl- and diarylcarbenes even in the case of profound geometrical changes. For instance, the differences between the ZFS parameters of rotational isomers of 2-naphthyl(phenyl)-carbene or 2,2′-dinaphthylcarbene are small (3% and 14%, 3% and 13%, respectively).[4,13] Moreover, the ZFS parameters of parent diphenylcarbene obtained by measurement in single crystals and in a glass differ by 1% in D and 10% in E, although the carbene adopts appreciably different geometry in two types of hosts.[14] As a reminder, the data reported earlier support our assignment of the progression of the ZFS parameters of the test carbene observed herein to its actual irreversible geometrical changes. The metastable structures of ^{3}**2** responsible for the stepwise fashion of its geometrical relaxation can be really trapped under matrix conditions. Their lifetime is dependent on the freedom given by a matrix cage to the geometrical transitions of the guest molecule. In addition, the very similar dark ESR profile behaviors were detected earlier for bis(2,4,6-tribromophenyl)carbene,[6d] although the reorientation of the carbene framework was not controlled. The thermally activated geometry changes in the ground triplet state are typical for diarylcarbenes with congestion at the carbenic center but can hardly, if ever, be identified for "parent" diphenylcarbene or its *para*-substituted derivatives.[4,14]

Conclusion

This work presents a detailed insight into the intimate mechanism of the reported thermally activated structural relaxation of sterically congested diarylcarbenes. Under matrix conditions the process under consideration follows a stepwise protocol.

The ESR profile of the carbene ^{3}**2** used as a test species primarily demonstrates the independent decrease of the parameter D, perhaps due to the twist of the phenyl rings to an in-plane conformation of the whole molecule, which is least hindered by the matrix cage. Consistent with earlier reports, the opening of the central carbenic angle is displayed by the reduction of the parameter E on extended exposure to the same temperature or under further heating. The concomitant examination of the reorientation of the molecular framework of the partially ordered test carbene evidences the evolution of the central carbenic angle to be related with the molecular mobility of the immediate surroundings. The appearance of the correlation supports the decisive role of the congestion at the carbenic center as a driving force of the geometrical relaxation at its primary steps.

Furthermore, when the strain is mostly released, the conformational changes of the test carbene come from the profound rearrangement of the matrix cage. The approach used paves the way to guide the geometry relaxation of strained diarylcarbenes varying the arrangement and dynamic behavior of the medium.

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