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AN IRREVERSIBLE STRUCTURAL CHANGE OBSERVED FOR DI-(1-NAPHTHYL)-METHYLENE IN ORGANIC RIGID GLASSES

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The title carbene has been shown by ESR spectroscopy to have bent geometry at the birth from the diazo precursor at low temperatures in organic rigid glasses. An irreversible change into the linear configuration takes place as the media become soft at high temperatures.

The bent vs linear structures of carbenes are the subject of great interest in carbene chemistry. According to the Walsh diagram, a larger angle at the divalent carbon atom is predicted for triplet carbenes.[1] Conjugation with a π system is predicted to favor linear triplets,[2] although the orbital energy for the n-type unpaired electron increases as the π character of the orbital becomes larger. Cyanocarbenes are such examples. Another stereochemical possibility arises when the methylene carries a substituent that does not have axial symmetry. Rotation around the bond between the carbenic carbon and the substituent could give rise to conformations. The presence of syn and anti forms in 1- and 2-naphthylmethylene was first reported by Trozzolo et al. in 1965.[3] We have been intrigued with these stereochemical problems and became interested in the possible dynamic stereochemistry of carbene species.[4] When a carbene is generated in microscopically rigid glasses, it should have the bent geometry and the conformation dictated by those of the precursor. If the thermodynamically most stable geometry and/or conformation of the carbene is different from those at the birth, a structural change would be observed afterward depending on the softness of the media.

When di-(1-naphthyl)diazomethane (**1**)[5] in glassy 2-methyltetrahydrofuran (MTHF) was irradiated with uv light in an ESR cavity at 15 K, a typical set of triplet signals (a) due most probably to di-(1-naphthyl)methylene (**2**) ($D = 0.3157$ cm^{-1} and $E = 0.0109$ cm^{-1})[6] appeared within a few minutes (Figure 1). The signal intensities after the photolysis obeyed the Curie law in the temperature range 15 - 50 K. At about 80 K, another new set of triplet peaks (b) ($D = 0.2609$ cm^{-1} and $E = 0.0051$ cm^{-1}) appeared at the expense of the original peaks (a) which

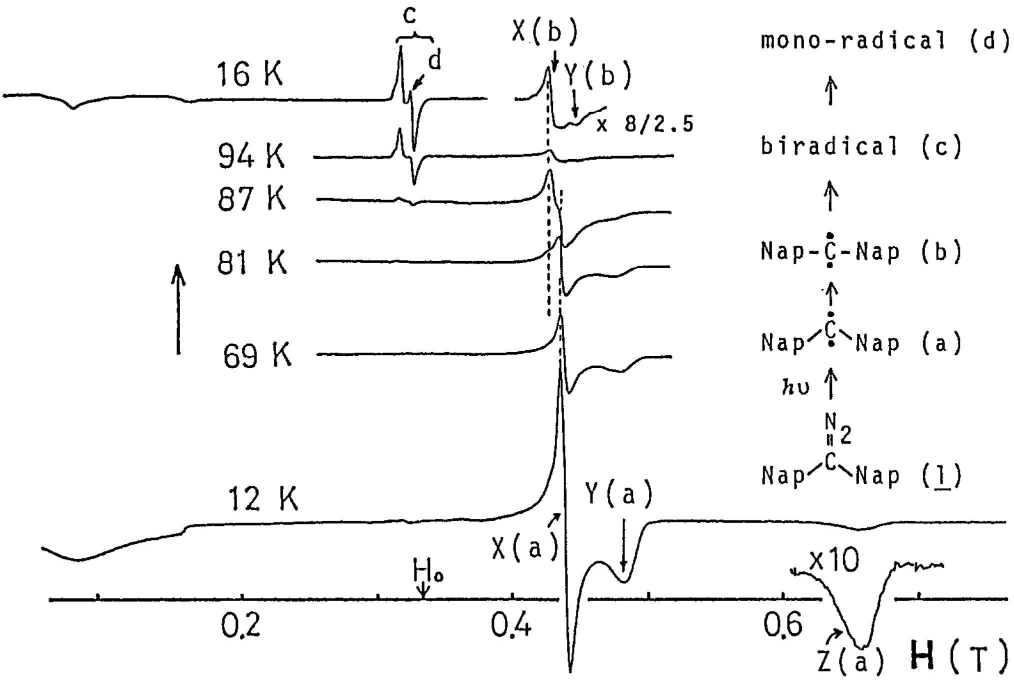


Figure 1. ESR Spectra (X-band) of di-(1-naphthyl)methylene (2) in MTHF at various temperatures.

disappeared rapidly at 87 K. These changes were not reversible; when the sample was cooled down to 16 K, no change took place on signals b except that their intensity increased according to the Curie law (see Figure 1). A third set of triplet signals (c) ($D = 0.0089$ cm^{-1} and $E = 0.00$ cm^{-1}) started to appear at 87 K. Judging from the small D and E values, the last signals are considered not to be due to a monocentric diradical. The triplet signals disappeared immediately at 100 K and were taken over by a signal (d) due to a doublet species.

Similar changes in the ESR spectra of 2 took place in an EPA

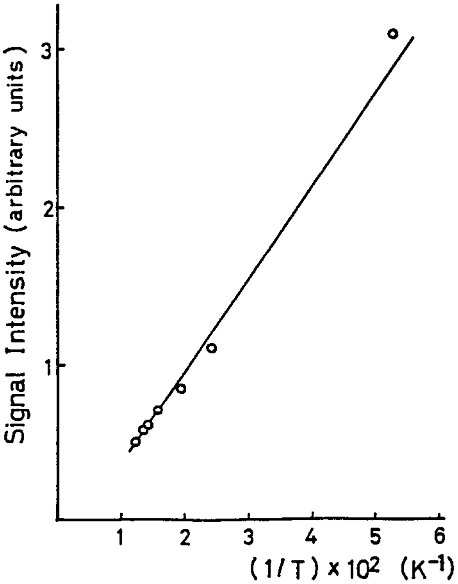
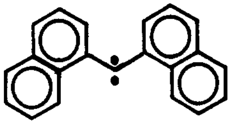
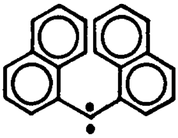
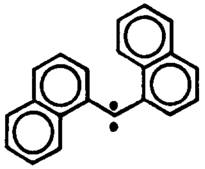
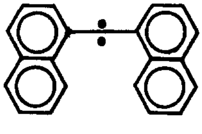


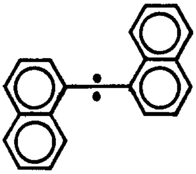
Figure 2. Temperature dependence of the signal intensities due to the X-transition of species 2-a in EPA.

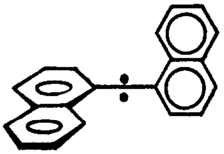

A


B


C


A'(=B')


C'


D'

glass, although at different temperatures. The Curie plots of the signal intensities due to the X-transition of species 2-a are linear (Figure 2). The spectral changes observed in both the organic glasses for 2 are considered to be induced by the softening of the solid media. The importance of the microscopic rigidity of the glasses is supported by an experiment in a third solvent, i.e., Fluorolube; the signals a and b were observed simultaneously as stable species at 30 K.

There are three near planar conformations A - C possible for 2 at its generation by photolysis of 1. The bent carbenes should have very similar zero-field splitting parameters, since the values are practically determined by the one-center dipole-dipole interaction between the n and π spins. In 1-naphthylmethylene, the syn and anti forms have the zfs parameters: $D = 0.4555$, $E = 0.0202$ cm^{-1} and $D = 0.4347$, $E = 0.0208$ cm^{-1}, respectively.[3] In order to estimate the D and E values for conformations A, B and C, these values were calculated based on a dipolar spin-spin interaction model,[7] assuming the planar geometry of the molecules. For structure A, $D = 0.3198$, $E = 0.0150$ cm^{-1}, for B, $D = 0.3006$, $E = 0.0150$ cm^{-1}, and for C, $D = 0.3102$, $E = 0.0178$ cm^{-1}. The observed signals a are consistent with either one of these pairs. However, the observed transformation from signals a through b to c cannot be interpreted in terms of the conformational changes among A - C. The small E value strongly suggests that signal b should be due to the linearized configuration at the divalent carbon atom of 2. The possible structures are A'(=B'), C' and D'. We tentatively assign perpendicular confromation D' of the linear carbene as the origin of signals b which is presumed to be thermodynamically most stable. The calculated D and E values for the linearized structures are in support of this theory. Only the perpendicular conformation (D') can explain the very small E value of the observed signals b; $D = 0.3033$, $E = 0.0199$ cm^{-1} for A'(=B'), $D = 0.3034$, $E = 0.0199$ cm^{-1} for C', and $D = 0.2353$, $E = 0.0001$ cm^{-1} for D'. A precedent for the last structure may be found in di-(9-anthryl)methylene.[2] Finally it remains to be seen which structure the diradical responsible for the triplet signals c should take.[8]

The structural change of triplet di-(1-naphthyl)methylene found in this study will be of use for elaborating the stereochemistry of triplet carbenes and understanding the role of matrices on the stereodynamics of them.

References and Notes

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6) For the D and E parameters given in this paper read $|D/(hc)|$ and $|E/(hc)|$, respectively. They were calculated from the observed resonance frequencies, H_x, H_y and H_z, by using the following equations: $H_x^2 = (H_0 + D - E)(H_0 - 2E)$, $H_y^2 = (H_0 + D + E)(H_0 + 2E)$, and $H_z^2 = (H_0 \pm D)^2 - E^2$.

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8) Diradicals having binaphthyl dimer or dibenzo[a,i]fluorene structures are some of the candidates. Dibenzo[a,i]fluorene itself is one of the pyrolysis products of **1**.[5b]

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