

## Geometric Isomerism in Quinolymethylenes

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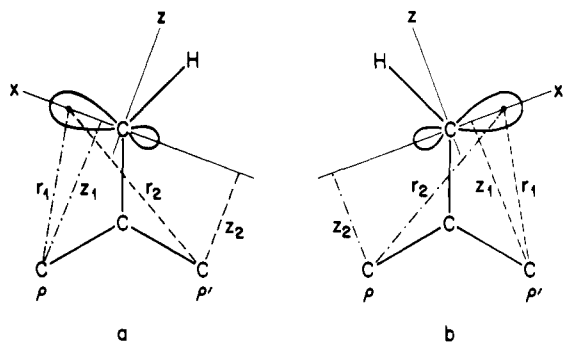
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**Abstract:** Triplet EPR spectra have been observed for four isomers of quinolymethylene. These divalent-carbon species were generated by photodecomposition of 3-, 4-, and 8-quinolyldiazomethane and of 5,6-benzopyridotriazole at cryogenic temperatures in frozen solutions. For each of the three quinolymethylenes derived from diazomethanes the EPR spectra indicate the presence of two similar but nonidentical triplets, which are assigned to the two rotameric structures with different orientations of the carbene proton. In contrast, the photolysis of 5,6-benzopyridotriazole in methyltetrahydrofuran gave rise to only one triplet as dictated by the fixed position of the proton in the precursor although in other solvents two triplets are observed. The zero-field parameters of all the quinolymethylenes are quite similar to those of the naphthylmethylenes leading to the surprising conclusion that a nitrogen in close proximity to the divalent carbon does not have a substantial effect on the  $\pi$  spin distribution of these methylenes.

Triplet carbenes whose divalent carbon atom is substituted with an  $sp^2$  hybridized carbon atom may exist in two rotameric forms which are stable at sufficiently low temperatures. In favorable cases the EPR spectra of these carbenes exhibit two sets of triplet signals with slightly different zero-field splitting parameters indicating the presence of two similar but nonidentical species. This phenomenon of "geometric isomerism" was first observed for 1- and 2-naphthylmethylene.<sup>1</sup> More recently we discovered isomerism for vinylmethylene<sup>2,3</sup> and carbalkoxycarbenes,<sup>4</sup> which show more substantial differences in the EPR species of the isomers. The observation of geometric isomers requires different orientations of the localized  $\sigma$  spin relative to the delocalized  $\pi$  spin. This, in turn, requires a nonlinear carbene whose  $\pi$  spin density distribution is unsymmetric relative to the bond attaching the substituent to the divalent carbon. For most triplet carbenes, the angle at the divalent carbon is near  $140^\circ$ , which places approximately two thirds of the  $\sigma$  spin density in the larger lobe and one third in the smaller lobe.<sup>1</sup> The zero-field splitting parameter  $D$  depends on the dipolar spin-spin interaction of the two electrons as viewed along the  $z$  axis.

$$D \propto \left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle \quad (1)$$

where  $r$  is the distance between  $\sigma$  and  $\pi$  electrons,  $z$  is the component of  $r$  along the  $z$  axis, and the brackets imply an average over the electronic wave function. For carbenes with unsymmetric  $\pi$  spin density distributions the spin-spin interaction of  $\sigma$  and  $\pi$  electrons will be different for the two planar orientations of the carbene. With spin densities  $\rho$  and  $\rho'$  at the respective  $\beta$  positions,



the contribution to  $D$  from these interactions may be approximated using a point dipole as

$$D_a \propto \rho \left( \frac{r_1^2 - 3z_1^2}{r_1^5} \right) + \rho' \left( \frac{r_2^2 - 3z_2^2}{r_2^5} \right) \quad (2)$$

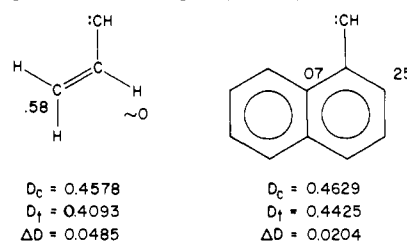
Rotation around the carbon-carbon axis interchanges  $\rho$  and  $\rho'$  so that

$$D_b \propto \rho' \left( \frac{r_1^2 - 3z_1^2}{r_1^5} \right) + \rho \left( \frac{r_2^2 - 3z_2^2}{r_2^5} \right) \quad (3)$$

The difference in the  $D$  values of the two isomers is

$$\Delta D \propto (\rho - \rho') \left[ \left( \frac{r_1^2 - 3z_1^2}{r_1^5} \right) - \left( \frac{r_2^2 - 3z_2^2}{r_2^5} \right) \right] \quad (4)$$

Accordingly, pairs of isomers which have larger differences in the  $\pi$  spin densities (vinylmethylene) are expected to show larger  $D$  value differences than pairs with smaller differences in the respective  $\pi$  spin densities (naphthylmethylene).



Equation 4 is strictly valid only for pairs of rotomers with identical bond angles and bond lengths. Actually, the zero-field splitting parameters for several pairs of geometric isomers<sup>1-4</sup> indicate small differences in the ratio  $E/D$  which could reflect differences in the angle at the divalent carbon. Nevertheless, the differences in  $E/D$  for pairs of isomers are sufficiently small so that any changes in the angle are also small. Accordingly, eq 4 provides a good estimate of the actual difference in  $D$ .

The introduction of a nitrogen atom into the aromatic skeleton of naphthylmethylene may affect the pairs of geometric isomers in two ways. In general, the presence of the nitrogen atom may change the  $\pi$  spin density distribution in the molecule and, thereby, affect the relative magnitude of the zero-field-splitting parameters. More importantly, however, there may be specific interactions between the nitrogen lone pair and the nonbonding orbitals of the divalent carbon center. For an isomer with a suitable orientation of the two key moieties this interaction may affect the singlet-triplet splitting. In recent years several groups have evaluated the effect of heteroatom substitution on the singlet-triplet splitting of methylene.<sup>5-8</sup> From these studies, two principal mechanisms

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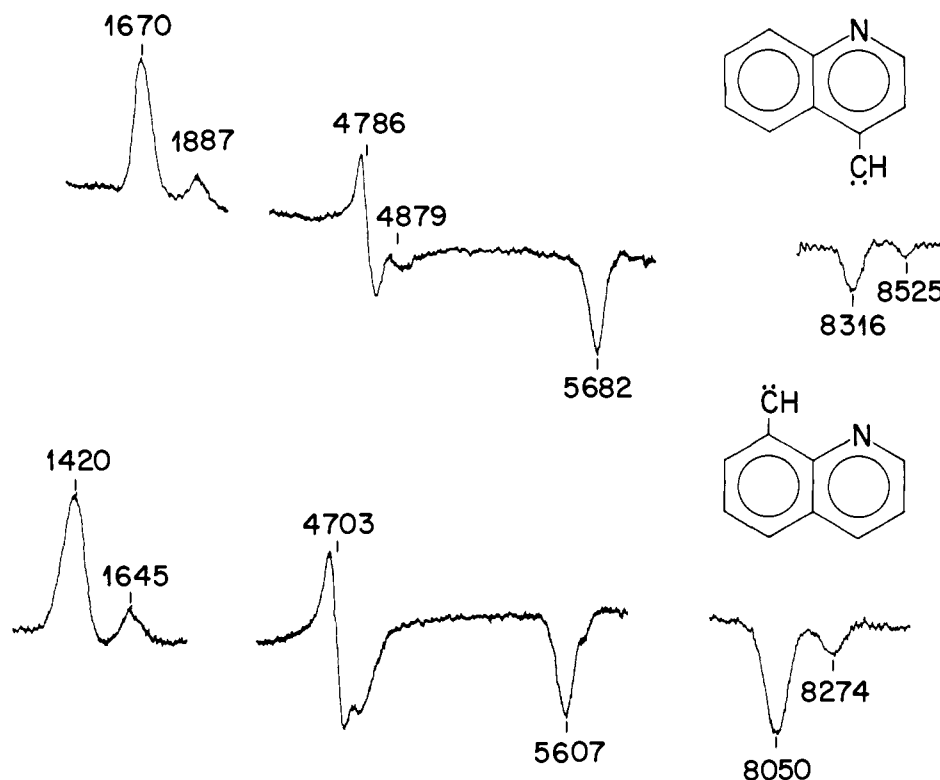
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**Figure 1.** EPR spectra of 4-quinolylmethylene in ethanol and 8-quinolylmethylene in methylcyclohexane at 6 K. Fields are given in G;  $h\nu/g\beta = 3305.3$  G (top) and 3303.9 G (bottom).

emerged by which appropriate substituents can stabilize the singlet relative to the triplet state. These mechanisms involve either the donation of out-of-plane lone pairs into the (unoccupied)  $\pi$  orbital of the divalent carbon<sup>6,8</sup> or the inductive withdrawal of  $\sigma$  electron density from the carbenic center by electronegative substituents.<sup>5,7</sup>

Recent theoretical studies also revealed that the geometries of singlet and triplet states may be different in features other than the bond angle at the divalent carbon. For example, the singlet state of carboxyhydrocarbene was found to have an energy minimum for a perpendicular arrangement of the carboxy group relative to the plane of the carbenic center.<sup>9</sup> In contrast, the triplet state was found to have minima for planar configurations,<sup>9</sup> in full agreement with the structures derived from EPR spectroscopic data for carbalkoxycarbenes.<sup>4</sup>

In the light of these considerations several quinolylmethylenes (QM) may be of interest, especially the 2 and the 8 isomers. These species offer different orientations of the nitrogen atom relative to the carbene center, which may both permit a direct interaction between nitrogen lone pairs and carbenic  $\sigma$  orbital. In addition to these, we selected the 3 and the 4 isomers, one as an isomer with a minimal conjugative effect, the other one to assess the conjugative effect of the nitrogen atom.

### Experimental Section

The four isomeric quinolylmethylenes were prepared from the corresponding aldehydes; 3- and 4-quinolinecarboxaldehyde were purchased from Aldrich Chemical Co. whereas 2- and 8-quinolinecarboxaldehyde were prepared according to the procedures of Monti<sup>10</sup> and of Rodionov and Berkengeim,<sup>11</sup> respectively.

Three of the quinoline carboxaldehydes, the 3, 4, and 8 isomers, were converted to the corresponding tosylhydrazones by reaction with equimolar amounts of tosylhydrazine. The 3- and 8-tosylhydrazones, mp 175 and 60 °C, respectively, were prepared in methanol solution<sup>12</sup> whereas

the 4-tosylhydrazone, mp 55 °C, could only be prepared from a slurry of the reactants in diethyl ether.<sup>13</sup>

3- and 4-quinolylidiazomethane were prepared from the corresponding tosylhydrazones by reaction with sodium methoxide in dry pyridine at 60–65 °C.<sup>14</sup> The reaction mixtures were poured over ice, the diazo compounds extracted with petroleum ether, and the solvent removed in vacuo. 8-Quinolylidiazomethane was generated from the corresponding tosylhydrazone by reaction with sodium hydride in 2-(2-methoxyethoxy)ethanol at 65 °C.<sup>12</sup> After cooling, water was added, the diazo compound extracted with pentane, and the solvent removed in vacuo.

For 2-quinolylmethylene, 5,6-benzopyridotriazole<sup>15</sup> was a more viable precursor than the diazo compound in analogy to the generation of 2-pyridylmethylene from pyridotriazole.<sup>16</sup> 2-Quinolinecarboxaldehyde, a 20% solution in pyridine, was converted to the hydrazone by reaction with a 95% aqueous solution of hydrazine.<sup>15</sup> The hydrazone was oxidized by treating it in ether solution with freshly prepared silver oxide for 18 h.<sup>15,17</sup>

The quinolylmethylenes were generated by UV irradiation (Osram 200 W high-pressure mercury lamp) of the diazo compounds or of 5,6-benzopyridotriazole in hydrocarbon or fluorocarbon glasses at liquid helium temperatures.

The EPR spectra were obtained by using a Varian E-15 EPR spectrometer equipped with an Air Products LTD-3-110 liquid helium transfer system.

### Results and Discussion

The photolysis of 3-, 4-, and 8-quinolylidiazomethane and of 5,6-benzopyridotriazole at liquid helium temperatures gave rise to EPR spectra (Figures 1 and 2) characteristic for derivatives of triplet methylene with zero-field-splitting parameters (Tables I and II) quite similar to those of the naphthylmethylenes (NM). In order to properly evaluate the effect of the incorporated nitrogen atom on the structure and properties of the carbene it is important to consider these data in the light of an appropriate standard. We

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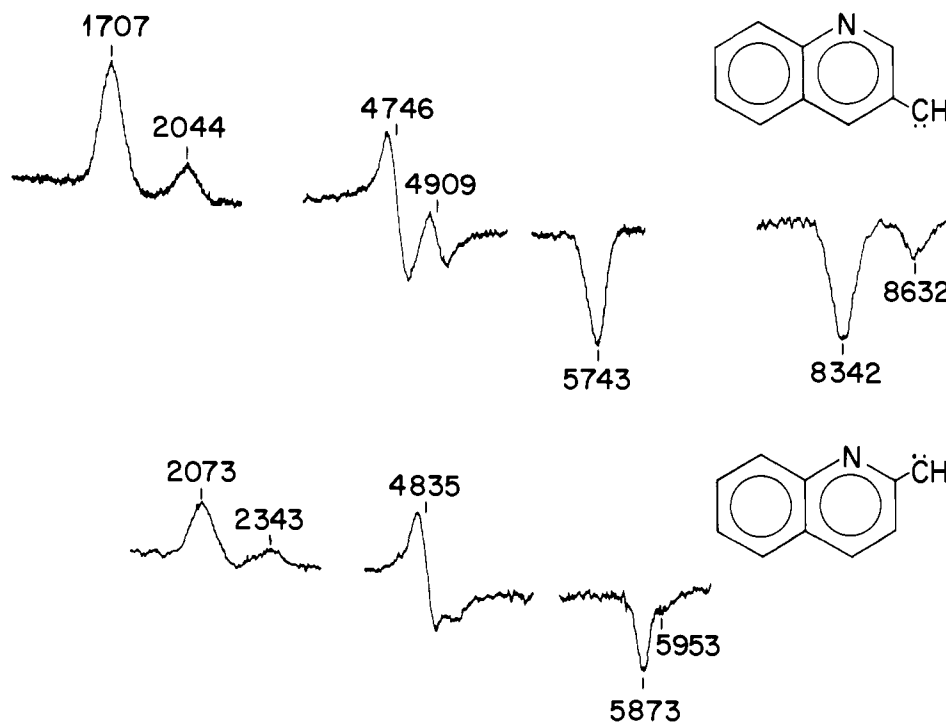
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

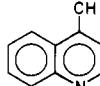
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**Figure 2.** EPR spectra of 3-quinolylmethylene in methylcyclohexane and 2-quinolylmethylene in propylene carbonate at 6 K. Fields are given in G;  $h\nu/g\beta = 3305.1$  G (top) and 3304.0 G (bottom).

**Table I.** Zero Field Splittings of 1-Naphthylmethylenes and Quinolyl Analoga<sup>a</sup>

			
	(1-naphthyl)-methylene	(8-quinolyl)-methylene	(4-quinolyl)-methylene
trans	D 0.4629 E 0.0201	0.4641 0.0225	0.4865 0.0207
cis	D 0.4425 E 0.0221	0.4434 0.0225	0.4666 0.0219

<sup>a</sup> Measured in methylcyclohexane glass at 6 K.

note that the  $\pi$  spin density of the 1-naphthylmethylenes is more efficiently delocalized than is that of the 2-naphthylmethylenes. Accordingly, the  $D$  values of the 1-naphthylmethylenes are smaller than those of the 2 isomers. Therefore, it appears appropriate to compare 4- and 8-quinolylmethylenes with 1-naphthylmethylene (Table I) whereas 2- and 3-quinolylmethylenes should be compared with 2-naphthylmethylene (Table II).

**Analoga of 1-Naphthylmethylene.** The photolysis of 8-quinolyldiazomethane produces an EPR spectrum indicating the formation of two triplets quite similar to the 1-naphthylmethylenes. These are assigned logically to the isomeric 8-quinolylmethylenes. The  $D$  values of the two pairs of isomers are identical within experimental error (Table I). This finding indicates that the introduction of a tertiary nitrogen in the 8-position of the 1-NM's does not affect appreciably the  $\pi$  spin density distribution in these species.

Minor differences between the two pairs of isomers include the  $E$  value of *trans*-8-QM which is noticeably larger than that of *trans*-1-NM and different *cis/trans* isomer ratios. The 1-NM's have an isomer ratio close to unity whereas the 8-QM's show a pronounced preference for the *cis* isomer. One may be tempted to explain this observation as evidence for a preferred conformation of the precursor diazo compound. However, previous experience shows that the isomer ratios of carbenes at liquid helium temperatures do not correspond to the conformer ratio of the precursor in fluid solution. For example, at 5 K *cis*-carbomethoxycarbene

predominates over the *trans* isomer by a factor of five,<sup>4</sup> whereas NMR studies have shown that in fluid solution the two rotomers of the precursor are present in nearly equal amounts.<sup>18</sup>

The photolysis of 4-quinolyldiazomethane gives rise to an EPR spectrum which, once again, indicates the presence of two triplet species. The isomeric 4-quinolylmethylenes have slightly higher  $D$  values than the pair of 1-naphthylmethylenes but the difference between the isomers remains unchanged as do the  $E$  values. The observed changes in  $D$  are similar in magnitude to that caused by the introduction of a nitrogen atom in the 4-position of phenylmethylene.<sup>17</sup> However, as in the case of the 8-quinolylmethylenes, the changes in  $D$  do not indicate any dramatic redistribution of the  $\pi$  spin density upon incorporation of a nitrogen into 1-naphthylmethylene.

This conclusion is supported by calculations of the  $\pi$  spin density of 1-NM and 4- and 8-QM which indicate nearly identical spin distributions for all these species. In contrast to 8-QM, there is significant spin density at the nitrogen atom of 4-QM and the increase in  $D$  may be attributed to spin-orbit effects due to the larger nuclear mass of the nitrogen.

Having ruled out any substantial influence of the incorporated nitrogen on the spin density distribution, we examined its potential influence on the relative energies of singlet and triplet states, which may be revealed by the temperature dependence of the EPR intensity. Ground state triplets follow the Curie law

$$\chi = c/T \quad (5)$$

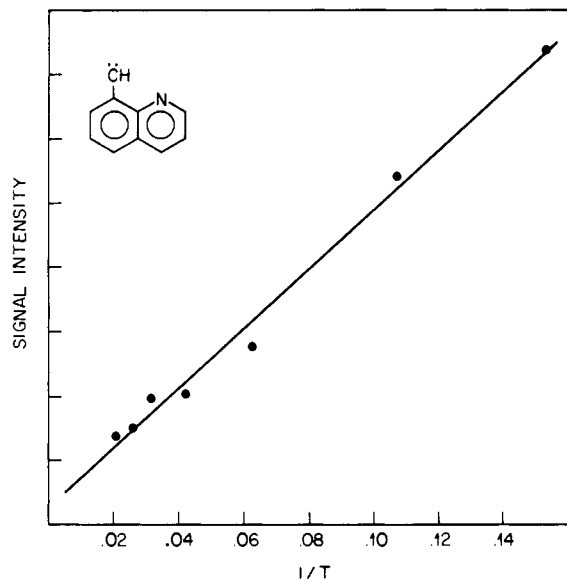
i.e., the signal intensity is inversely proportional to the temperature. On the other hand, if the triplet lies closely above the singlet so that it can be populated thermally, the temperature dependence of the EPR intensity would reflect the thermal activation of the paramagnetic state<sup>19</sup>

$$\chi = \frac{c}{T} \left( \frac{3e^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}} \right) \quad (6)$$

Of course, no EPR spectrum is expected if the singlet lies substantially below the triplet.

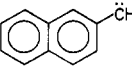
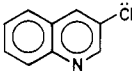
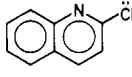
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**Figure 3.** Signal intensity of the  $x$  line of the cis isomer of 8-quinolylmethylene vs.  $1/T$ . Experimental results are shown as circles; the line represents the best linear least-squares fit of the data.

**Table II.** Zero Field Splittings of 2-Naphthylmethylenes and Quinolyl Analoga

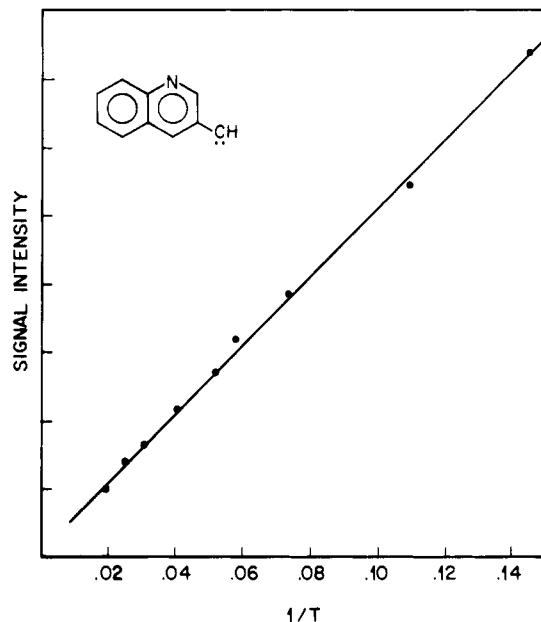
				
		(2-naphthyl)- methylene <sup>(a)</sup>	(3-quinolyl)- methylene <sup>(b)</sup>	(2-quinolyl)- methylene <sup>(c)</sup>
cis	D	0.4926	0.4975	0.5313
	E	0.0209	0.0202	0.0246
trans	D	0.4711	0.4702	0.5038
	E	0.0243	0.0245	0.0251

<sup>a</sup> Measured in benzophenone powder at 4 K.<sup>1</sup> <sup>b</sup> Measured in methylcyclohexane glass at 6 K. <sup>c</sup> Measured in propylene carbonate glass at 6 K.

For 8-quinolylmethylene the EPR signal intensity could be followed conveniently in the range 5–40 K. In this temperature range, the signal intensity was found to be inversely proportional to the temperature (e.g., Figure 3). These results allow the same conclusion that was derived previously for 1-naphthylmethylene, that 8-quinolylmethylenes either have triplet ground states or that their triplet states lie at most a few calories higher than the corresponding singlet states. However, we emphasize that these results do not rule out changes in the singlet–triplet splitting. They merely show that the singlet state is not stabilized to the extent that the ordering of states is reversed.

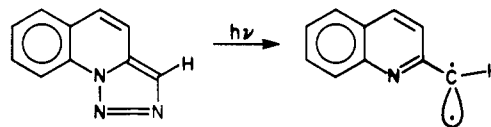
**Analoga of 2-Naphthylmethylenes.** The photolysis of 3-quinolyldiazomethane in a methylcyclohexane glass at cryogenic temperatures generates an EPR spectrum compatible with the presence of two rotameric quinolylmethylenes. The zero-field splitting parameters are only slightly different from those of the 2-naphthylmethylenes, once again indicating only minor changes in the spin density distribution upon incorporation of the nitrogen atom. As in the case of the previously discussed quinolylmethylenes, the two isomers are not present in comparable quantities; in this case, the trans isomer was found to predominate (Figure 2).

The last quinolylmethylene to be discussed, the 2 isomer, is generated from a triazole, the cyclic isomer of 2-quinolyldiazomethane which contains the hydrogen atom in a fixed position whereas the diazo compounds in each case have two rotomers. The irradiation of the 5,6-benzopyridotriazole in a methyltetrahydrofuran glass at 5 K produced an EPR spectrum showing a single isomer with zero-field splittings,  $D = 0.5039 \text{ cm}^{-1}$  and  $E$



**Figure 4.** Signal intensity of the  $x$  line of the trans isomer of 3-quinolylmethylene vs.  $1/T$ . Experimental results are shown as circles; the line represents the best linear least-squares fit of the data.

$= 0.0248 \text{ cm}^{-1}$ . This triplet is identified on the basis of a comparison with 2-naphthylmethylene and with 2-pyridylmethylene.



Of the 2-naphthylmethylenes, the trans isomer has a slightly smaller  $D$  value and a substantially larger  $E$  value than the cis isomer. A similar trend is found in the 3-quinolylmethylenes. On the other hand, the presence of the nitrogen atom in 2-pyridylmethylene raises its  $D$  value by an increment of  $\sim 0.02 \text{ cm}^{-1}$  relative to that of phenylmethylene (vide supra). These considerations suggest that the observed triplet is *trans*-2-quinolylmethylene, the isomer corresponding to the geometry of the precursor (even though its  $D$  value is larger than that of either 2-naphthylmethylene isomer).

This assignment is confirmed by photolysis of the triazole in different glasses, e.g., propylene carbonate, which produced two triplets. The major isomer is identical with that obtained in methyltetrahydrofuran; the minor one has the expected larger  $D$  value ( $0.5313 \text{ cm}^{-1}$ ) but an unexpectedly high  $E$  value ( $0.0246 \text{ cm}^{-1}$ ). The  $D$  values of these isomers indicate that even when the nitrogen is in close proximity to the carbene center there are only small changes in the  $\pi$  spin distribution. The relatively large  $E$  value of the minor (cis) isomer is reminiscent of a similar observation for *trans*-8-quinolylmethylene (vide supra).

As in the case of 1-NM and its quinolyl analogues, calculations of the  $\pi$  spin density for 2-NM and 2- and 3-QM yield nearly identical spin distributions in these carbenes. The results for 2-QM are analogous to those of 4-QM in that there is substantial spin density at the nitrogen and the increase in  $D$  may be attributed to spin–orbit effects.

The temperature dependence of the EPR intensities (cf. Figure 4) indicated that both 2- and 3-quinolylmethylenes either have triplet ground states or their triplet states lie within a few calories of the ground states. We emphasize once again that these results are not incompatible with changes in the singlet–triplet splitting; they merely indicate that the singlet states are not stabilized to the extent that the ordering of states is reversed.

**Geometric Isomerization of Divalent Carbon Species.** The generation of a single, well-defined isomer (*trans*-2-QM) from a cyclic precursor such as the triazole may provide the opportunity to investigate the potential isomerization of such a species. The

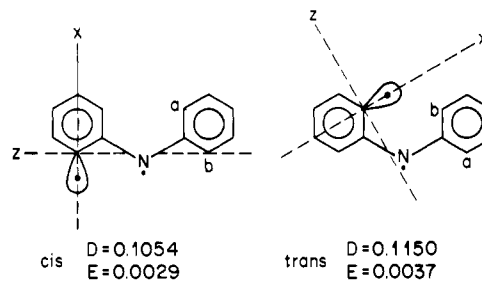
interconversion of a pair of isomers can be achieved by inversion of the divalent carbon or by rotation around the carbon-carbon bond. The corresponding barrier heights are of obvious interest. Theoretical studies have indicated an inversion barrier of  $\sim 9$  kcal/mol for vinylmethylene<sup>20</sup> and a rotational barrier of  $\sim 5$  kcal/mol for carbohydroxycarbene.<sup>9</sup> If these barriers are at all representative, the thermal isomerization of most carbenes would be quite unlikely considering the low barriers to decay encountered for many triplet methylenes.

Of course, the rotation barriers depend on the bond order of the carbon-carbon junction; they should be lowest for carbenes with localized  $\pi$  spin and have high values for fully delocalized carbenes. Accordingly, the carbalkoxycarbenes ( $\rho_1 = 0.85$ ) should have lower barriers to rotation than vinylmethylene ( $\rho_1 = 0.58$ ), whose barrier should lie close to that of substituted allyl radicals (10 kcal/mol).<sup>21,22</sup>

The potential isomerization of *trans*-2-quinolylmethylene was studied by monitoring the signal intensities of the  $z$  lines before and after warming a sample to 40 K and keeping it at that temperature for varying periods of time. At these conditions, the decay of the *trans* isomer is moderately fast but no conversion to the *cis* isomer was evident. Of course, the observation of the *cis* isomer during the photolysis of 5,6-benzopyridotriazole in propylene carbonate requires that an isomerization has occurred but it is not clear what species or state is involved. We may well be dealing with a light-induced isomerization which is suppressed in more rigid matrices.

One example of a light-induced *cis*-*trans* isomerization of a carbene/biradical has been studied in some detail.<sup>23</sup> The photolysis of *N*-phenylbenzotriazole produces *cis*-phenyliminocyclohexadienyldiene which upon continued irradiation is converted to the corresponding *trans* isomer. In the temperature range 104–124 K, the *cis* isomer decays with an activation energy of  $\sim 5$  kcal/mol without evidence of any conversion to the *trans* isomer. In this context we note that the original assignment of the isomers<sup>23</sup> is inconsistent with the method of generation and with the generally accepted model accounting for the  $D$  value differences. The *cis* isomer is the likely primary product because it resembles the geometry of the triazole more closely. Likewise, the *cis* isomer should have a *lower*  $D$  value than the *trans* isomer.

This follows from a consideration of the  $\pi$  spin density pattern and its contribution to  $D$ . The overall magnitude of the  $D$  values is dominated by the one-center interaction at the divalent carbon atom. In addition, both isomers have an identical (small) negative



contribution to  $D$  due to the spin density on the nitrogen and nearly identical contributions due to the spin density at one ortho phenyl position (denoted a). The difference in  $D$  can be ascribed chiefly to the  $\pi$  spin density in the other ortho position (denoted b) because of a substantially different orientation relative to the divalent carbon. For the *trans* isomer the contribution from position b is positive ( $r^2 > 3z^2$ ; cf eq 1) whereas the *cis* isomer has a negative contribution ( $r^2 < 3z^2$ ) from that position. Accordingly, the *cis* isomer is assigned the lower  $D$  value.

Regardless of the assignment of the isomers it is not clear which structural feature is responsible for the remarkable difference of their stability. As for *trans*-2-quinolylmethylene its potential photochemical isomerization awaits careful evaluation.

### Conclusion

The EPR results presented in this paper identify the quinolylmethylenes as fine examples of geometric isomerism in divalent carbon species. The data also show that the incorporation of a nitrogen atom into the parent naphthylmethylenes, in close proximity to the divalent carbon, does not alter the ordering of the lowest singlet and triplet states and causes only minor changes in the  $\pi$  spin density distribution. This small effect of the lone pair electrons on the zero-field splitting parameters is in sharp contrast to the changes of as much as 9% which have been observed due to charge transfer with solvent in other triplets.<sup>24,25</sup> The failure to affect the ordering of states may be due to unfavorable steric factors. It is quite possible that there is a lack of appreciable overlap in either the three-center (2-QM) or the four-center arrangement (8-QM) of the nitrogen relative to the divalent carbon. The study of a substrate with a five-center arrangement of the nitrogen and the carbene moiety, a logical extension of the work reported here, is being pursued.

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