JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 104, NUMBER 26 DECEMBER 29, 1982

Spin-Density Distribution and Geometric Isomerism in Triplet Carbenes

Richard S. Hutton* and Heinz D. Roth*

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.

Received February 19, 1982

Abstract: Zero-field splitting parameters, D, have been calculated for a series of triplet carbenes substituted with a single aromatic moiety. The dipolar spin–spin interaction between the localized σ spin and the delocalized π spin is evaluated on the basis of a point-spin model. The π spin densities used are those calculated for the parent π radicals on the basis of a modification of the McLachlan method. The results show excellent agreement with experimentally determined zero-field splitting parameters. Specifically, the D value difference between geometric isomers is reproduced quite well. The calculations indicate that the potential isomers of 2- and 3-pyridylmethylene have nearly identical D values so that their EPR spectra would not be resolved.

A characteristic of benzenoid aromatic systems is their ability to delocalize the spin of an unpaired electron in the π orbital of a π radical or of a carbene. The determination of the spin distribution in these systems is a problem of considerable interest. In both π radicals and carbenes the delocalization manifests itself in the hyperfine couplings (hfc) for the nuclei of the aromatic moiety. For radicals, hyperfine couplng constants of nuclei such as ^{1}H or ^{19}F are determined routinely from the splitting pattern of the EPR spectrum since the line width is usually smaller than the typical hfc. For carbenes, the line widths in the triplet EPR spectrum are usually much greater than the proton hfc and it is necessary to use ENDOR techniques to determine these splittings. For triplet carbenes the reduced spin density at the divalent carbon atom is also reflected in the zero-field splitting (zfs) parameters. The magnitude of the zfs parameter D is largely determined by the spin–spin dipolar interaction of the two electrons at the divalent carbon atom. Accordingly, the fraction of the π spin density located at the carbenic center can be estimated from the D value of the carbene. In spite of the predominance of this one-center interaction the spin density at atoms several bonds removed from the divalent carbon atom can also have a significant effect on the zfs parameters as indicated by the observation of geometric isomerism for some carbenes.

This phenomenon was first observed in 1965 for the pairs of 1- and 2-naphthylmethylenes.[1] It took 9 years for another example, vinylmethylene,[2,3] to emerge and another 4 years before the third case, that of the carbalkoxycarbenes,[4] was reported. More recently, however, reports of geometric isomerism in triplet carbenes have appeared with increasing frequency. These studies include *N*-phenyliminocyclohexadienylidene,[5] dibenzoylmethylene,[6] phenylbenzoylmethylene,[7] and, most recently, several quinolylmethylenes.[8] In all these cases, the presence of isomers of these carbenes was deduced from EPR spectra in which two sets of triplet signals having similar but non-identical zfs parameters were observed. The spectra were assigned to the two conformations of the carbene in which the σ orbital at the divalent carbon and the aromatic moiety are coplanar.[1] When the distribution of the spin in the π orbital is unsymmetric, the dipolar spin–spin interaction of the π electron with the electron localized in the σ orbital is different for the two conformations. Consequently, the zfs parameters will be different and in cases where the differences are sufficiently large it is possible to observe the spectra of the two isomers. It should be emphasized that the observation of only one set of triplet lines in cases where geometric isomers are possible does not preclude the presence of both isomers. The spectra depend on the difference in the π spin distribution for the two orientations. It is possible that both isomers would be present but because their spin distributions are only slightly different the two sets of triplet signals cannot be resolved (vide infra).

The assignment of the zfs parameters to specific conformations of the carbenes is of particular interest and is facilitated by theoretical calculations of the parameters. Although the theory for the evaluation of zfs parameters appears to be well understood,[9] little work has been done on carbenes. Rigorous calculations have been carried out only for the zfs parameters of methylene,[10] and approximate calculations have been reported for several substituted methylenes.[11] For molecules of the size discussed here calculations

---

(1) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129.

(2) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wasserman, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680.

(3) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511.

(4) Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4324.

(5) Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1980**, *102*, 1421.

(6) Murai, H.; Torres, M.; Strausz, O. P. *Chem. Phys. Lett.* **1980**, *70*, 358.

(7) Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1980**, *102*, 7390.

(8) Hutton, R. S.; Roth, H. D.; Manion Schilling, M. L.; Suggs, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5147.

(9) Langhoff, S. R.; Kern, C. W. In "Applications of Electronic Structure Theory"; Schaeffer, H. F., III, Ed.; Plenum: New York, 1977; Chapter 10.

(10) (a) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1973**, *7*, 759. (b) Langhoff, S. R.; Elbert, S. T.; Davidson, E. R. *Ibid.* **1973**, *7*, 999.

(11) (a) Higuchi, J. *J. Chem. Phys.* **1963**, *38*, 1237. (b) Serre, J.; Schneider, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 1655.

0002-7863/82/1504-7395$01.25/0

using ab initio wave functions are impractical and alternative methods of evaluating the parameters must be considered. One semiempircal approach that has been employed for several phosphorescent triplets[12] and for some biradicals[13] approximates the electrons in the π orbitals by point dipoles. Since the purpose of our calculations is to facilitate the assignment of the zfs parameters to the geometric isomers rather than to determine rigorous theoretical values, such a point-spin model was chosen since it permits easy (and inexpensive) computation.

Calculations

1. Zero-Field Splitting Parameters. The experimentally determined zfs parameters of carbenes include contributions from both the dipolar spin–spin interaction and the spin–orbit coupling of the two electrons.[14] However, for carbenes containing only first-row atoms, the spin–orbit coupling contribution is small and has not been included in our calculations. The spin–spin interaction is described by the hamiltonian

$$\mathcal{H}_{\mathrm{ss}} = \hat{\mathbf{S}}\cdot\mathbf{D}\cdot\hat{\mathbf{S}} \tag{1}$$

where $\hat{\mathbf{S}}$ is the total spin operator and $\mathbf{D}$ is the dipolar coupling tensor

$$\mathrm{D} = \frac{g^2\beta^2}{2}\begin{bmatrix} \frac{(r^2 - 3x^2)}{r^5} & \frac{-3xy}{r^5} & \frac{-3xz}{r^5} \\ \frac{-3xy}{r^5} & \frac{(r^2 - 3y^2)}{r^5} & \frac{-3yz}{r^5} \\ \frac{-3xz}{r^5} & \frac{-3yz}{r^5} & \frac{(r^2 - 3z^2)}{r^5} \end{bmatrix} \tag{2}$$

When the elements of $\mathbf{D}$ are averaged over the spatial part of the wave function, i.e., $\mathrm{D}_{xy} = (g^2\beta^2/2)\langle\varphi|-3xy/r^5|\varphi\rangle$, etc., and the matrix is diagonalized, the spin–spin hamiltonian may be reduced to

$$\mathcal{H}_{\mathrm{ss}} = -X\hat{S}_x^{\,2} - Y\hat{S}_y^{\,2} - Z\hat{S}_z^{\,2} \tag{3}$$

where $-X$, $-Y$, and $-Z$ are set equal to D_{XX}, D_{YY}, and D_{ZZ}, the elements of the diagonal matrix. The energy levels of the triplet may be calculated by evaluating the full hamiltonian matrix with use of the spin functions of the triplet as a basis set.[14] In zero magnetic field the three energy levels equal X, Y, and Z. Since $X + Y + Z = 0$, the zero-field splitting may be described in terms of two parameters called D and E where

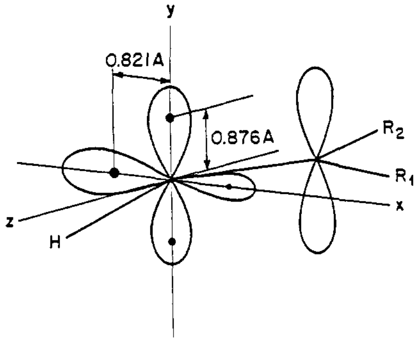
$$D = -\tfrac{3}{2}Z \tag{4}$$

and

$$E = -\tfrac{1}{2}(X - Y) \tag{5}$$

The accuracy of the calculated zfs parameters depends on the approximations made in the evaluation of the integrals in the tensor, $\mathbf{D}$. In our calculations, as in other calculations for large molecules,[12,15] multicenter and exchange integrals have been neglected. This simplification causes large deviations in the calculated values of the parameter E, whereas the values of D are only slightly affected.[16] The calculations are also restricted to a single determinant wave function in which the orbitals are paired. This eliminates any contributions to D from other electron configurations or from polariztion of the σ electrons. Although the magnitude of these contributions is uncertain for the carbenes discussed here, we note that for methylene such effects are relatively small near the actual geometry (∠HCH ~ 135–140°) of the triplet state.[10] The greatest simplification is the evaluation of the Coulomb integrals for point spins. Pullman and Kochanski have shown that this approach yields good estimates of D when the separation of the two points was adjusted to optimize the Coulomb integrals for close interactions.[12] In view of these considerations the point-spin model appears to be sufficiently accurate for our purpose.

The model is similar to the one used by Hutchinson and coworkers to interpret their ENDOR studies of fluorenylidene[17a] and diphenylmethylene.[17b] The electron in the π orbital is simulated by two point spins above and below each atom having a density $\rho_i/2$, where ρ_i is the spin density at atom i. The electron in the σ orbital is simulated by two point spins on the x axis corresponding to the positive and negative lobes of the orbital.



The ratio of the spin density in each of these lobes $\rho_+/\rho_- \sim 0.3/0.7$ was derived by Hutchinson and Pearson.[17a] The values of the coordinates, ±0.876 Å for the π spin and ±0.821 Å for the σ spin, were determined by fitting the model to the zfs parameters of methylene.[18] The bond angle at the divalent carbon[19] was assumed to be 140° for all carbenes studied and bond angles of 120° and bond lengths of 1.40 Å were used in all cases to determine the x and z coordinates of the atoms in the aromatic moieties.

When this model is used, computation of the elements of $\mathbf{D}$ is straightforward because the values of x, y, z, and r are simply the values of the components of the vectors between the fixed point spins. The dipolar interaction matrix, $\mathbf{D}$, for the triplet is evaluated by summing the matrices calculated for the interactions of each point-spin representing the σ electron with each of the point-spins representing the π electron. Diagonalization of this matrix yields the principal values that are used to calculate the zfs parameters according to eq 4 and 5.

2. Spin Densities. It is assumed that the spin density distribution of the π electron is very similar to the distribution in the analgous radicals. Evidence of this similarity is provided by the nearly identical absorption and emission spectra that have been reported for several arylmethylenes and the corresponding radicals.[20] In cases where the hfc's of the appropriate radicals have been determined, the π spin density distribution could be derived from these experimental results. However, in view of the uncertainties in the conversion of hfc data to spin densities and in order to have a consistant set of values, all the spin densities have been calculated by using the method of McLachlan.[21] Although more rigorous methods of spin density calculations are available, the McLachlan method is still widely used because of its simplicity and ease of computation. For the calculations reported here, we have employed a modification of the McLachlan (MML)

---

[12] Pullman, A.; Kochanski, E. *Int. J. Quantum Chem., Symp.* **1967**, *1*, 251.

[13] Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.

[14] Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance: Elementary Theory and Practical Applications"; McGraw-Hill: New York, 1972; pp 226–227.

[15] Motten, A. G.; Davidson, E. R.; Kwiram, A. L. *J. Chem. Phys.* **1981**, *75*, 2603.

[16] Godfrey, M.; Kern, C. W.; Karplus, M. *J. Chem. Phys.* **1966**, *44*, 4459.

[17] (a) Hutchinson, C. A., Jr.; Pearson, G. A. *J. Chem. Phys.* **1967**, *47*, 520. (b) Hutchinson, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327.

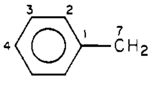
[18] Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Yager, W. A. *J. Chem. Phys.* **1971**, *55*, 2593.

[19] Trozzolo, A. M.; Wasserman, E. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1976; Vol. II, Chapter 5.

[20] Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

[21] McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.

Table I. Calculated Spin Densities and Proton Hyperfine Coupling Constants for the Benzyl Radical



		a^H (G)	
	ρ	calcd	exptl[26]
1	−0.101		
2,6	0.168	−4.5	−5.14
3,5	−0.052	1.4	1.75
4	0.175	−4.7	−6.14
7	0.693	−16.6	−16.35

treatment that excludes the orbital containing the unpaired electron from the calculation of the atom–atom polarizabilities.[22] For many π radicals the spin densities obtained by using this modification are in better agreement with the values calculated from experimental hfc's than those calculated by using the original McLachlan method and compare favorably with the results of more sophisticated calculations.

The McLachlan calculation of the spin densities is a perturbation treatment in which the orbital coefficients derived from simple HMO theory are used to determine the "zero-order" spin densities. The usual definitions of HMO theory, $\alpha_X = \alpha_0 + h_X\beta_0$ and $\beta_{XY} = k_{XY}\beta_0$, were employed and the values of h and k were taken from the parameter set recently calculated by Van-Catledge:[23] $h_C = 0.0$, $h_N = 0.52$, $k_{CC} = 1.00$, and $k_{CN} = 1.02$. The McLachlan correction factor, λ, was set equal to 1.00. The value of k for the C–CH_2 bond was changed slightly from k_{CC} in consideration of the difference between the C–CH_2 bond and the C–C bonds in aromatic rings. Theoretical calculations of β indicate that k should decrease as the bond distance increases.[24] Analysis of the vibrational spectrum of the benzyl radical indicates that the C–CH_2 bond length is 1.43 Å,[25] slightly longer than the value assigned to an aromatic C–C bond. Accordingly, the parameter k_{CCH_2} was adjusted so that the value of D derived from the calculated spin densities for phenylmethylene was in agreement with the experimental result (0.510 cm^{-1}).[19] The value obtained in this way, $k_{CCH_2} = 0.84$, is in good agreement with the results of theoretical calculations.[24] The spin densities calculated for the benzyl radical with use of these parameters are given in Table I along with the experimental[26] and theoretical values of the proton hyperfine coupling constants. These hfc's were calculated by using the McConnell relationship[27] $a_i = Q\rho_i$ with $Q_{ring}{}^H = 27$ G and $Q_{benzyl}{}^H = 24$ G.[28] The agreement for the hfc values is quite satisfactory and is as good as other more sophisticated calculations.[29]

Results and Discussion

We have applied this method of calculating zfs parameters to a series of triplet carbenes. In order to establish the usefulness of the method we first applied it to carbenes for which spin densities had been calculated by other methods: the naphthylmethylenes and the pyridylmethylenes. The pairs of 1- and 2-naphthylmethylenes allowed us to evaluate the method on the carbenes for which geometric isomers were first observed and the 2-, 3-, and 4-pyridylmethylenes provided simple representatives of carbenes containing a nitrogen atom in the aromatic ring. Calculations were also carried out for several quinolylmethylenes whose EPR spectra were reported recently in order to further determine the effect of the presence of a nitrogen atom on the spin density distribution and on the zero-field splittings of the geometric isomers. The following discussion is limited to the parameter D because several of the approximations made in the calculations, i.e., neglecting the multicenter and exchange integrals and assuming the same divalent carbon angle for all the carbenes, make the calculated values of E much less reliable than the values of D.

Table II. Calculated Spin Densities for 1- and 2-Naphthylmethyl Radicals

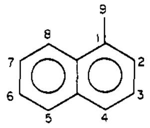
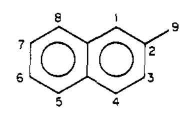
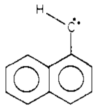
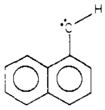
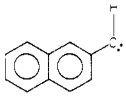
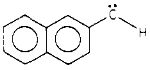
				
	MML	UHF	MML	UHF
1	−0.113	−0.085	0.271	0.262
2	0.228	0.252	−0.104	−0.071
3	−0.069	−0.070	0.078	0.098
4	0.242	0.209	−0.051	−0.065
4a	−0.031	−0.038	0.072	0.069
5	0.074	0.062	−0.033	−0.042
6	−0.028	−0.036	0.080	0.053
7	0.067	0.056	−0.025	−0.034
8	−0.041	−0.043	0.083	0.063
8a	0.061	0.073	−0.035	−0.036
9	0.608	0.620	0.665	0.703

Table III. Calculated and Experimental Values of the Zero-Field Splitting Parameter, D(cm^{-1}), for 1- and 2-Naphthylmethylenes

			
calcd	MML	0.4416	0.4558
	UHF	0.4436	0.4614
exptl		0.4426	0.4629
			
calcd	MML	0.4975	0.4787
	UHF	0.5218	0.5057
exptl		0.4926	0.4711

1. Naphthylmethylenes. The 1- and 2-naphthylmethylenes were the first carbenes for which the EPR spectra of geometric isomers were observed and for which the zfs parameters were assigned to particular structures.[1] These assignments were made by using calculations of the differences in D based on the differences in the spin densities at the carbon atoms β to the carbenic center. The naphthylmethylenes thus provide good examples of carbenes on which both the MML calculation of spin density and the point-spin model used to calculate D may be evaluated.

In their assignment of the isomers of the naphthylmethylenes, Trozzolo, Wasserman, and Yager assumed that the π spin density distribution of the carbenes could be represented by that of the radicals. They used spin densities calculated from unrestricted Hartree–Fock (UHF) wave functions with spin annihilation.[30] Comparison of the UHF results for the 1- and 2-naphthylmethyl radicals[31] with the spin densities calculated by using the mML method (Table II) shows quite satisfactory agreement between the two calculations. The values of the zfs parameter, D, calculated from both sets of spin densities are compared in Table III. For 1-naphthylmethylene, the D values calculated from the UHF spin densities are in especially good agreement with the experimental results whereas the results of the MML calculation give good values for the magnitude of D but underestimate

---

(22) Devolder, P. *Tetrahedron* **1979**, *35*, 1307.

(23) Van-Catledge, F. A. *J. Org. Chem.* **1980**, *45*, 4801.

(24) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; pp 103–104.

(25) Lutoshkin, V. I.; Kotorlenko, L. A.; Kaugliak, Yu. A. *Teor. Eksp. Khim.* **1972**, *8*, 542.

(26) Carrington, A.; Smith, I. C. P. *Mol. Phys.* **1965**, *9*, 138.

(27) McConnell, H. M. *J. Chem. Phys.* **1958**, *28*, 1188.

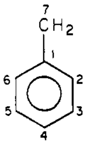
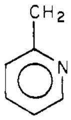
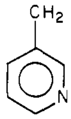
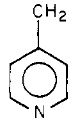
(28) Reference 14, p 122.

(29) Raimondi, M.; Simonetta, M.; Tantardini, G. F. *J. Chem. Phys.* **1972**, *56*, 5091 and references therein.

(30) Snyder, L. C.; Amos, T. *J. Chem. Phys.* **1965**, *42*, 3670.

(31) Snyder, L. C., private communication.

Table IV. Calculated Spin Densities for the Benzyl and Pyridylmethyl Radicals and D Values (cm^{-1}) for Phenyl- and Pyridylmethylenes

ρ					
1	−0.101		−0.095	−0.100	−0.094
2	0.168		0.148 (N)	0.166	0.164
3	−0.052		−0.034	−0.048 (N)	−0.040
4	0.175		0.170	0.173	0.157 (N)
5	0.052		−0.041	−0.051	−0.040
6	0.168		0.166	0.167	0.164
7	0.693		0.686	0.693	0.689
D					
calcd	0.510	cis	0.505	0.510	0.506
		trans	0.504	0.510	
exptl	0.510		0.537	0.513	0.533

somewhat the differences in the D values of the two isomers. For 2-naphthylmethylene, the results of the MML calculation yield D values in agreement with the observed values whereas the UHF values are somewhat larger. In this case both sets of spin densities yield differences in D that are lower than the experimentally observed differences.

It is instructive to examine the manner in which the spin density on the various atoms contributes to the magnitude of D. Considering only the spin on the divalent carbon (ρ_9), we calculate D values of 0.456 and 0.499 cm^{-1} for 1- and 2-naphthylmethylene. A comparison of these values with the averages of the experimental values of the cis and trans isomers of these two carbenes, 0.453 and 0.482 cm^{-1}, illustrates the predominance of the one-center interaction in determining the zero-field splitting. These averages can also be used to estimate the spin density at the divalent carbon by comparing them to the D value of methylene (0.75 cm^{-1}).[18] This comparison yields spin densities of 0.60 and 0.64 cm^{-1}, respectively, for the 1- and 2-naphthylmethylenes in good agreement with the calculated values.

Although the contributions of the spin densities on the other atoms to the zero-field splitting are small, they are the determining factor for the observation of the geometric isomers. For the naphthylmethylenes the calculations indicate that the difference in spin density at the atoms β to the divalent carbon accounts for the largest part of the differences in the D values of the two isomers. For example, the differences in D for the isomers of 1- and 2-naphthylmethylene are 0.013 and 0.015 cm^{-1}, respectively, when only the spin density at the β carbons is used in the calculation compared with differences of 0.014 and 0.019 cm^{-1} when the spin density on all the atoms of the aromatic moiety are included. On the basis of the results obtained for 1- and 2-naphthylmethylene we conclude that although the D value difference between the geometric isomers may be slightly underestimated, this empirical technique provides a useful method of calculating D.

2. Pyridylmethylenes. The recent observation of the triplet EPR spectra of the 2-, 3-, and 4-pyridylmethylenes in an argon matrix[32] suggests a test of our model on a system in which a heteroatom is included and for which spin densities have been calculated by INDO[33] and UHF[31,34] methods. The MML spin densities for the three pyridylmethyl radicals and the benzyl radical are listed in Table IV. As with the naphthylmethyl radicals, there is good agreement almong the results of the MML, UHF, and INDO calculations. All of the calculations indicate only small differences between the spin density distributions for the pyridylmethyl radicals and the benzyl radical. This strong similarity in the spin density distributions is reflected in the values of the zfs parameters of the phenyl- and pyridylmethylenes (Table IV). The calculated D values for all three pyridylmethylenes are nearly identical with the value for phenylmethylene. The experimental values, on the other hand, show some differences. The value for 3-pyridylmethylene is very close to that of phenylmethylene whereas the values for 2- and 4-pyridylmethylene are ~0.02 cm^{-1} larger. In explaining this differnce, we note that in contrast to 3-pyridylmethylene, both 2- and 4-pyridylmethylene, have significant spin density on the nitrogen atom. Accordingly, this small increase in D is attributed to a spin–orbit contribution due to the larger nuclear mass of the nitrogen, an effect that is not included in this model.

Another aspect of the spin density distribution of the 2- and 3-pyridylmethylene that deserves comment is the small difference in the amount of spin at the positions β to the divalent carbon atom. For 3-pyridylmethylene the difference in spin density is so small that the calculated values of D for both isomers are identical to three significant figures, whereas for 2-pyridylmethylene the calculated difference in D is slightly larger. However, for a difference of this magnitude even the z lines of the two isomers would only be separated by ~10 G, a fraction of the typical line width (90–100 G) of triplet EPR spectra.[35] In view of the fact that the presence of two isomers would not even manifest itself in any significant broadening of the z lines, it is not surprising that only one set of triplet lines is observed in the EPR spectra of these carbenes.

It is interesting to note that the results of our calculations as well as earlier ones for the 2- and 3-pyridylmethyl radicals are at odds with the spin densities calculated from the proton hfc assigned on the basis of the spectra of these radicals in an adamantane matrix.[33] These experimental splittings suggest spin density differences for both 2- and 3-pyridylmethylenes that are comparable to the differences in the naphthylmethylenes, $\Delta\rho \sim 0.15$. For spin density differences of this magnitude the EPR spectra of the geometric isomers should be sufficiently different to be observed separately. The z lines, for example, would be separated by 130 G, well outside the experimental line width.

The observation of only one set of EPR signals for 2- or 3-pyridylmethylene in an argon matrix tends to support the calculations. However, it has been noted that sample preparation may affect the relative concentration of the two isomers. Indeed, only one isomer of vinylmethylene was observed in a pentane matrix deposited from the vapor phase at 8 K whereas two isomers were observed in frozen solution under otherwise identical conditions.[2] To eliminate this potential source of error, we obtained EPR spectra of 2- and 3-pyridylmethylene in frozen solutions at 5 K. In none of the solvents used was there any evidence for more than one set of triplet lines in the spectrum. The zfs parameters for both pyridylmethylenes were in good agreement with those reported by Chapman, Sheridan, and LeRoux[32] (Table III). These results support the conclusion that the presence of the nitrogen atom in an aromatic ring does not substantially alter the spin density distribution. In the light of this conclusion, we suggest that it may be necessary to reexamine the assignments of the proton hfc in the 2- and 3-pyridylmethyl radicals.

3. Quinolylmethylenes. Having verified the value of the above method of calculating D, we turn to its application to several quinolylmethylenes. Of the four quinolylmethylenes that have been studied,[8] 4- and 8-quinolylmethylene are the structural analoga of 1-naphthylmethylene whereas 2- and 3-quinolylmethylene are the structural analoga of 2-naphthylmethylene. This similarity in structure is reflected in the nearly identical spin density distributions calculated for the quinolylmethylenes and the corresponding naphthylmethylenes. The only significant difference between the two types of carbenes lies in the somewhat reduced spin density on the nitrogen atom. Compared to the the corresponding carbon atom in the naphthylmethylenes the spin

---

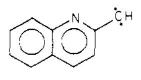
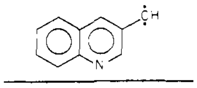
(32) Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 6245.

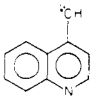
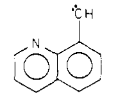
(33) Lloyd, R. V.; Wood, D. E. *Mol. Phys.* **1971**, *20*, 735.

(34) Hirst, D. M.; Treeweek, R. F.; Vilain, C. A. *Chem. Phys.* **1973**, *1*, 149.

(35) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 1663.

Table V. Calculated and Experimental Values of the Zero-Field Splitting Parameter, $D(\text{cm}^{-1})$, for the Quinolylmethylenes

				
	cis	trans	cis	trans
calcd	0.4880	0.4729	0.4974	0.4785
exptl	0.5313	0.5038	0.4975	0.4702

				
	cis	trans	cis	trans
calcd	0.4376	0.4515	0.4414	0.4556
exptl	0.4666	0.4865	0.4434	0.4641

density is 10–12% lower. The largest part of this decrease is compensated by changes in the spin density at the adjacent carbon atoms. Once again, the substitution of nitrogen in the aromatic ring does not result in a major redistribution of the spin density.

The *D* values calculated for the quinolylmethylenes (Table V) are in agreement with the structures assigned previously[8] and reflect many of the same effects that have been discussed for the naphthylmethylenes and the pyridylmethylenes. For 3- and 8-quinolylmethylene, both the calculated and experimental *D* values are nearly identical with those of their naphthylmethylene analoga. This is not unexpected because the nitrogen atoms are in positions of low spin density where the already small effect of the nitrogen would be minimized. For 2- and 4-quinolylmethylene, the calculated *D* values are lower than the values calculated for the corresponding naphthylmethylenes, reflecting the smaller spin density on the nitrogen. However, the experimental *D* values of these quinolylmethylenes are larger than the values of the naphthylmethylenes. As with 2- with 4-pyridylmethylene, this increase is attributed to a spin–orbit interaction with the nitrogen. Once again, we note that this is an effect that is not included in our model. The differences in the *D* values of the isomers of 2-quinolylmethylene compared with those of 2-naphthylmethylene are greater than for the other carbenes and it is tempting to assign this to a steric or electronic interaction between the carbenic center and the lone pair of the nitrogen atom. However, this effect is subtle and not of overriding significance.

4. Vinylmethylene. In view of the success of this model in reproducing not only the magnitude of *D* for several aryl methylenes but also the difference between pairs of geometric isomers, it is of interest to discuss briefly its application to vinylmethylene, the simplest system for which geometric isomerism has been observed.[2,3] An MML calculation for the allyl radical produces spin densities $\rho_{1,3} = 0.588$ for the terminal carbon atoms and $\rho_2 = -0.176$ for the internal carbon. These values are in excellent agreement with the spin densities derived from the proton hyperfine coupling constants,[28] $\rho_{1,3} = 0.589$ and $\rho_2 = -0.155$, respectively. When the calculated spin densities and C–C bond lengths of 1.41 Å and an internal bond angle of 120° are used, the point-spin model yields zfs parameters that are in superb

Table VI. Spin Densities and Zero-Field Splitting Parameters for Vinylmethylene

	calculated (π system)		
	delocalized[b]	localized[c]	exptl[a]
ρ_1	0.588	0.96	
ρ_2	−0.176	0.00	
ρ_3	0.588	0.04	
D_c	0.4498	0.7188	0.4578
D_t	0.4009	0.7156	0.4093
ΔD	0.0489	0.0032	0.0485

[a] Reference 2. [b] Modified McLachlan calculation for the allyl radical. [c] Generalized valence bond calculation for vinylmethylene.[36]

agreement with the EPR results (Table VI). In contrast, models assuming a substantially unsymmetrical distribution for the π spin density of vinlmethylene[36] fail to reproduce either the absolute magnitude of *D* or the difference between the isomers (Table VI).

Conclusion

The results presented in this paper demonstrate that the zero-field splitting parameter, *D*, of triplet carbenes can be calculated on the basis of a relatively simple point-spin model. For carbenes in which the dipolar spin–spin interaction dominates the zero-field splitting, this method not only reproduces *D* but, in addition, accounts satisfactorily for the differences between geometric isomers. For systems without heteroatoms, i.e., naphthylmethylene, and for systems with a nitrogen atom in a position of low spin density, i.e., 3-pyridylmethylene or 3- or 8-quinolylmethylene, the agreement is excellent. Systems with nitrogen atoms in positions of high spin density, i.e., 2- and 4-pyridylmethylene or 2- and 4-quinolylmethylene, show small but systematic deviations that can be assigned to the effects of spin–orbit coupling. Larger deviations must be expected in systems with larger heteroatoms in which contributions due to spin–orbit coupling may be more significant. Accordingly, application of this method to new classes of divalent-carbon species such as the carbonylcarbenes[4,6,7] must be carefully evaluated.

Acknowledgment. The authors express their appreciation to Marcia L. M. Schilling for synthesizing the 2- and 3-pyridylmethylene precursors and to Professor Lawrence C. Snyder for providing the UHF calculations of the spin densities of the naphthylmethyl and pyridylmethyl radicals.

Registry No. Benzyl radical, 2154-56-5; 1-naphthylmethyl radical, 7419-60-5; 2-naphthylmethyl radical, 7419-61-6; 1-naphthylmethylene, 4399-95-5; 2-naphthylmethylene, 4399-96-6; 2-pyridylmethyl radical, 52962-96-6; 3-pyridylmethyl radical, 61204-14-6; 4-pyridylmethyl radical, 51010-00-5; phenylmethylene, 3101-08-4; 2-pyridylmethylene, 21963-51-9; 3-pyridylmethylene, 37998-86-0; 4-pyridylmethylene, 37998-87-1; 2-quinolylmethylene, 78759-52-1; 3-quinolylmethylene, 78759-51-0; 4-quinolylmethylene, 78759-49-6; 8-quinolylmethylene, 78759-50-9; vinylmethylene, 19527-08-3.

---

(36) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427.