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GEOMETRICAL ISOMERISM IN DIVALENT-CARBON INTERMEDIATES

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Abstract—Three classes of monosubstituted carbenes (aryl-, vinyl-, carbonyl-) and one class of disubstituted carbenes (dicarbonyl-), all of them ground state triplets, can exist in more than one rotameric form with distinct zero field splitting parameters. Representative examples of these carbenes are discussed and selected aspects of triplet carbenes are evaluated, including their π spin density distribution, intramolecular H-abstraction, and *cis–trans* isomerization. Lastly, the structures assigned to two triplets generated by photolysis of dibenzoyldiazomethane are re-evaluated.

The field of carbene chemistry as it is known today received its decisive stimulus in the early 1950s from the work of Hine, who postulated dichlorocarbene as an intermediate in the basic hydrolysis of chloroform,[1] and by the discovery of Doering and Hoffmann that this species could be trapped in good yield with cyclohexene.[2] Before these milestones, intermediates with divalent carbon had been the subject of only occasional interest. The first recorded attempt to obtain such a species was that of Dumas,[3] who tried to dehydrate methanol. Of course, the quadrivalence of carbon was not recognized at his time. In 1862, Geuther[4] carried out the experiment which was repeated by Hine. Almost a century ago, Buchner and Curtius[5] introduced the thermolysis of diazo compounds as a source of carbenes, and 25 years later Staudinger and Kupfer pioneered the photolysis of ketenes.[6] Both types of precursors were used in Herzberg's search for methylene.[7]

The development of divalent-carbon chemistry since the early 1950s has involved: the introduction of the concept of spin multiplicity;[8] chemical studies which established the reactivity of the postulated intermediates and the stereochemistry of their principal reactions;[8–10] the formulation of several concepts which linked the reactivity to the spin multiplicity;[8,11,12] the application of new physical methods which provided more direct information about the spin multiplicity[13] and allowed the direct observation of the intermediates.[14–21] Among these techniques we mention electron paramagnetic resonance (EPR)[14,15] and electron nuclear double resonance (ENDOR),[16] chemically induced dynamic nuclear polarization (CIDNP),[13,22] and optical spectroscopy, either in low temperature glasses[17] or in the liquid phase with increasing time resolution.[18–21]

The observation of geometrical isomerism for the naphthylmethylenes has to be considered as one of the milestones in the history of carbene chemistry.[23] This result established beyond any doubt that these triplet methylenes are bent. In contrast, the optical spectra of the parent triplet methylene were at that time interpreted in terms of a linear structure.[24] After the original single observation, the second and third examples of geometrical isomerism, vinylmethylene[25,26] and carbomethoxycarbene,[27] were slow to follow. However, in recent years reports concerning this phenomenon have become more frequent.[28–32] Today, the field has developed to a state where the application of a simple model allows the reliable prediction of the magnitude of the zero-field splitting parameters, D, for aromatic and polyolefinic triplet methylenes. More importantly, this method even accounts for the difference in the Ds of pairs of geometric isomers.[33]

For the discussion of geometric isomerism in carbenes it is useful to consider the principal features which allow this type of isomerism in trivalent carbon species. In these intermediates the unpaired spin may be contained in a π or in a σ orbital. In the former case, geometrical isomerism may be observed if this spin is part of an extended π system such as an allyl radical,[34,35] and the substituents are held in different positions relative to the π system and to each other. In the second case isomerism may be observed if the σ orbital containing the unpaired spin is held within a rigid framework. The rigidity may be imposed by a π system, as in the vinyl radical,[34] by a small ring, as in the oxiranyl radical,[36] or by the interaction of a small ring Walsh π orbital with a second π orbital, as in the cyclopropylacetyl radical (cf. Table 1).[37,38]

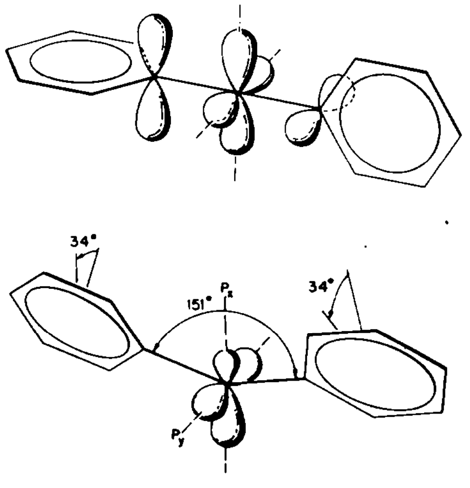
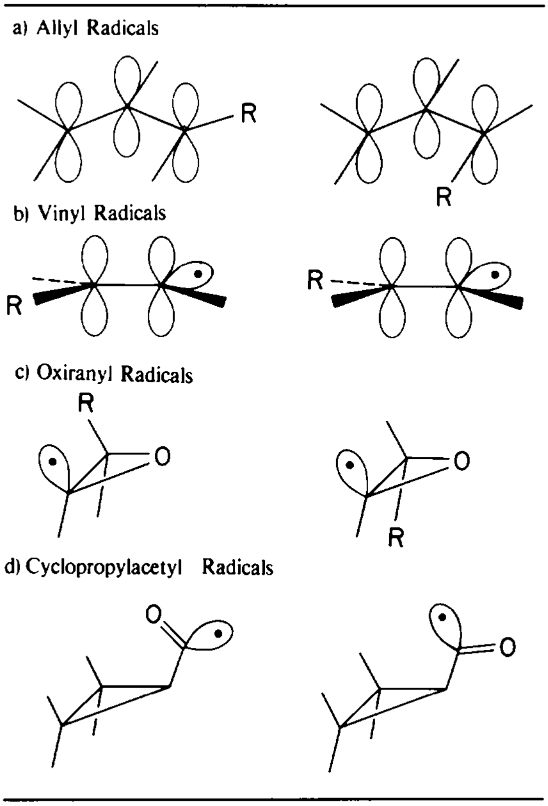


Fig. 1. Diphenylmethylene structures; top: linear structure suggested by R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.* **81**, 1008 (1959); bottom: bent structure derived on the basis of ENDOR experiments (Doetschman and Hutchison).[16]

Table 1. Geometric isomerism in radicals



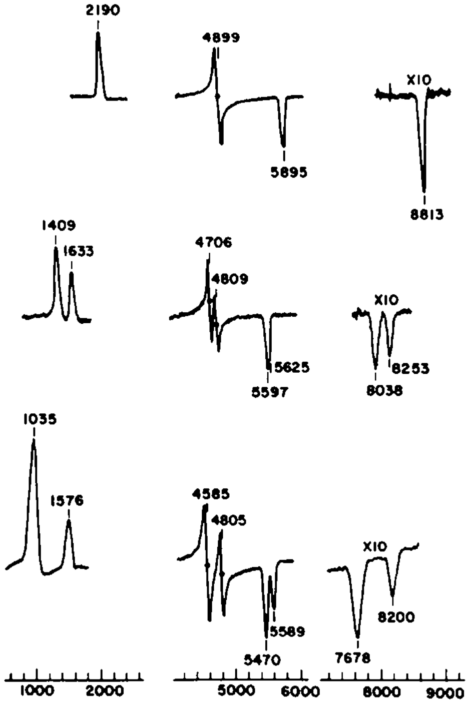


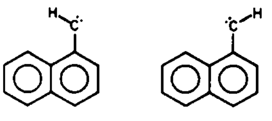
Fig. 2. EPR spectra of phenylmethylene (top), 1-naphthylmethylene (center) and vinylmethylene (bottom) in frozen solutions (MTHF) at 6 K. Fields are given in gauss: $h\nu/g\beta = 3304.4$ G.

Triplet carbenes contain two unpaired electrons, one each in a σ and in a π orbital, at the same carbon atom. For such an intermediate, geometrical isomerism appears feasible if the divalent carbon can be held rigidly in two different orientations of an asymmetric environment. There are two approaches to inhibit free rotation in such an intermediate: steric crowding of the divalent carbon, or conjugation of its partially filled π orbital with an adjacent π system. The first approach has the disadvantage that the reactive divalent carbon is in close propinquity to groups with which it may react. In fact, no pair of carbene isomers has been reported to date which owes its existence to steric crowding. The second approach, on the other hand, is successful, even though the mere conjugation with a π system is not sufficient to observe geometric isomerism. In addition, the distribution of the π electron spin must be sufficiently asymmetric to render the dipolar spin–spin interaction of σ and π electrons in the two isomers appreciably different. This condition is met for several pairs of carbenes, in which the divalent carbon is conjugated with aryl,[23,31] vinyl[25,26] or carbonyl[27,32] moieties, and geometric isomers have been observed in these systems. EPR spectra of a carbene with only one possible isomer (phenylmethylene) and of two carbenes with pairs of geometric isomers (1-naphthylmethylene and vinylmethylene) are compared in Fig. 2.

In this paper, we will discuss several examples of geometrical isomerism in the three families of divalent-carbon triplets, for which this phenomenon has been observed: arylmethylenes, vinylmethylenes and carbonylmethylenes. In addition, we will consider the extension of this type of isomerism to divalent-carbon species substituted with two simple π systems. In appropriate systems of this type, three isomers can be expected. 1,4-Disubstituted butadienes are the prototype of this kind of isomerism, and the pentadienyl radical is the simplest trivalent-carbon analog. Divinyl- and dicarbonylmethylenes are potential examples of divalent-carbon species with three isomers.

Arylmethylenes

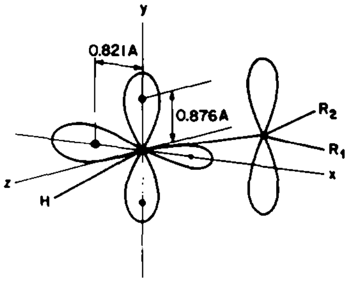
Two naphthylmethylenes (NMs), 1-NM and 2-NM, were the first carbenes for which geometrical isomerism was observed. Average zero-field splitting parameters (D) of 0.45 cm^{-1} and 0.48 cm^{-1} for the 1-NMs and for the 2-NMs indicate spin densities of 0.60 and 0.64, respectively, on the divalent-carbon centers. The difference between the zero-field splitting parameters of the geometrical isomers, 0.020 cm^{-1} for the 1-NM isomers, 0.022 cm^{-1} for the 2-NM isomers, can be ascribed to the unsymmetrical distribution of the π spin density relative to the naphthyl-divalent carbon bond. In both cases the ΔDs amount to 4.4% of the larger D value.[23]



Scheme 1.

Similar cases of geometrical isomerism have been observed for four quinolylmethylenes, 2-, 3-, 4- and 8-QM.[31] The magnitude of their zero-field splitting parameters and the ΔDs for each pair of geometrical isomers are similar to those observed for the analogous NMs. The zero-field splitting parameters of the 2-QMs and the 4-QMs show noticeable increases relative to the analogous NMs. This effect has been ascribed to moderate spin orbit coupling, since in both QMs the nitrogen atoms are located in positions of relatively high spin density. The largest ΔD was found for the 3-QMs, 0.0275 cm^{-1} or 5.5% of the larger D.[31]

The magnitude of the zero-field splitting parameter of every one of these carbenes and, more importantly, the difference in D for every pair of geometrical isomers can be reproduced remarkably well (Table 2) by a point spin model[33] similar to one introduced by Doetschman and Hutchison.[16] The electron in the σ orbital is simulated by point spins on the x axis corresponding to the positive and negative lobes of the orbital. 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. It is assumed that the π spin density distribution in the carbenes is very similar to the distribution in the analogous radicals. These spin densities are calculated by a modified McLachlan treatment.



Scheme 2.

Obviously, the spin density calculations are not state of the art *ab initio* calculations and the point spin model is an approximation which considers only the dipolar interaction between π and σ spins and neglects all other interactions. Nevertheless, we consider this approximation satisfactory. First, it has been established that the dipolar interaction dominates the D splitting of simple methylenes.[39] Secondly, the aryl substituents of the carbenes discussed here are sufficiently large to render *ab initio* calculations prohibitively expensive. Furthermore, we note that the *ab initio* approach, despite impressive successes in predicting the geometry of carbenes,[40–42] has not been very successful in calculating D values for phosphorescent triplets or simple carbenes (*vide infra*).

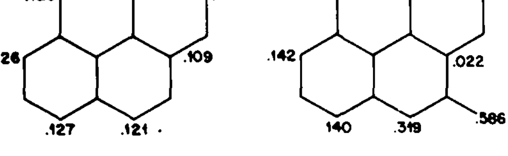
In view of the success of this model in reproducing the zero field splittings of known arylmethylenes, it appeared worthwhile to test its application to carbenes substituted with even larger aryl groups. Accordingly, we calculated the π spin densities of several anthryl-, phenanthryl- and pyrenylmethyl radicals and from these the zero-field splittings of the corresponding methylenes. The following features deserve comment.

The 1- and 2-anthrylmethylenes were calculated to have slightly lower zero-field splitting parameters, $\sim 0.41\ \mathrm{cm}^{-1}$ and $\sim 0.46\ \mathrm{cm}^{-1}$, respectively, than the corresponding naphthylmethylenes and comparable differences in D between the geometrical isomers. For 9-anthrylmethylene, a noticeably lower D value was calculated (0.352), suggesting a more efficient delocalization of π spin density. The experimental value (0.301 cm^{-1})[23] is even lower, indicating that the actual delocalization is even greater than suggested by the McLachlan calculations. This species shows the largest discrepancy between experiment and calculation for any of the arylmethylenes.

Of the phenanthrylmethylenes, two isomers were chosen for investigation. The 4-isomer contains a hydrogen atom quite close to the functional group, which may react readily either with the divalent carbon or with the diazo group. It appeared to be of interest to compare the reactivity of this species with that of 1-(8-methylnaphthyl)-diazomethane, which had been found to give rise to naphthalene-1,8-diyl.[43] The photolysis of 4-phenanthryldiazomethane in the cavity of an EPR spectrometer failed to produce any evidence for either an arylmethylene or a biradical. The only EPR signal generated in this reaction is a $\Delta m = 2$ line of a phosphorescent triplet, presumably cyclopenta[d,e,f]-phenanthrene.

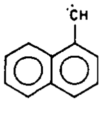
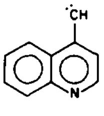
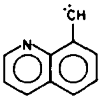
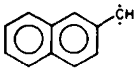
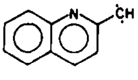
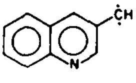
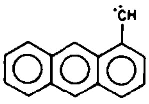
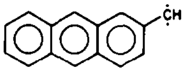
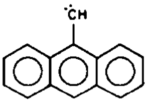
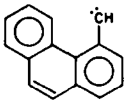
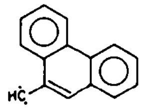
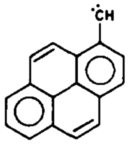
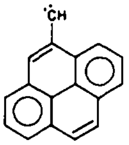
For the 9-phenanthrylmethylenes the calculations indicated a D parameter difference, $\Delta D = 0.027\ \mathrm{cm}^{-1}$, larger than that of any other pair of arylmethylenes. This prediction was verified experimentally. The EPR spectra observed for the 9-phenanthrylmethylenes show clearly separated signals for the z and x lines. As expected from the analogy with other arylmethylenes, the experimentally determined ΔD is somewhat larger (0.035 cm^{-1})[44] than the calculated value. We consider the good agreement between experiment and calculation an additional argument for the validity of these point spin calculations.

The final systems to be discussed in this section are two pairs of carbene isomers having quadrinuclear aromatic substituents, 1- and 4-pyrenylmethylene. Since these methylenes resemble the naphthylmethylenes, one may be led to expect substantial π delocalization and consequently, substantial differences between the D values of these pairs of isomers. This is indeed the case for 4-pyrenylmethylene; the D values of the *cis* and *trans* isomers are calculated to differ by 0.028 cm^{-1}, an even larger ΔD than that calculated for the 9-phenanthrylmethylenes. However, the corresponding isomers of 1-pyrenylmethylene have nearly identical D values; they differ by only 0.001 cm^{-1}. As in the case of other arylmethylenes, the differences in the D values is caused largely by the difference, $\Delta\rho$, in the spin densities at the carbon atoms β to the divalent carbon. For the isomers of 1-pyrenylmethylene $\Delta\rho$ is only 0.007 whereas for 4-pyrenylmethylene $\Delta\rho$ is 0.297, the largest difference of any of the carbenes discussed here.



Scheme 3.

Table 2. Geometric isomerism in arylmethylenes

										Reference		
	cis	trans	ΔD[a]	cis	trans	ΔD	cis	trans	ΔD			
calc.	0.442	0.456	0.015	0.438	0.452	0.014	0.441	0.455	0.014	33,	33,	33,
exp.	0.443	0.463	0.020	0.467	0.487	0.020	0.433	0.464	0.021	23,	31,	31,
												
	cis	trans	ΔD	cis	trans	ΔD	cis	trans	ΔD			
calc.	0.498	0.479	0.019	0.488	0.473	0.015	0.497	0.478	0.019	33,	33,	33,
exp.	0.493	0.471	0.022	0.531	0.504	0.027	0.497	0.470	0.027	23,	31,	31,
												
	cis	trans	ΔD	cis	trans	ΔD						
calc.	0.404	0.424	0.020	0.475	0.452	0.023		0.352		b,	b,	b,
exp.	0.390	0.420	0.030					0.301		c,		23,
												
	cis	trans	ΔD	cis	trans	ΔD						
calc.	0.477	0.491	0.014	0.432	0.459	0.027				b,	b,	
exp.		d,		0.436	0.470	0.034				b,	b,	
												
	cis	trans	ΔD	cis	trans	ΔD						
calc.	0.400	0.401	0.001	0.417	0.445	0.028				b,	b,	
exp.	0.40									45,		

a) $\Delta D = |D_{cis} - D_{trans}|$

b) this paper

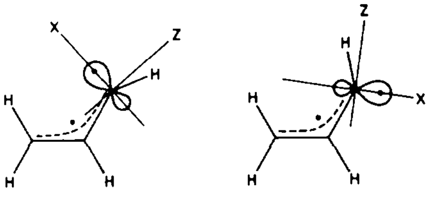
c) M. Platz, private communication

d) no ground-state triplet spectra observed

These calculations are in excellent agreement with the recent report of the triplet EPR spectrum of 1-pyrenylmethylene, which showed one triplet spectrum with $D = 0.40\,\text{cm}^{-1}$.[45] Since only minor differences are predicted for the two isomers, the fact that only one set of signals is observed cannot be interpreted as evidence for the existence of a single isomer.

Vinylmethylenes

The second family of ground state triplet methylenes for which geometric isomerism was observed are the vinylmethylenes. Suitable representatives of this system show more pronounced differences between the D values of the two isomers ($D_c = 0.4578$, $D_t = 0.4093$) than do the arylmethylenes. Accordingly, the x-lines are completely separated whereas the y-lines still show some overlap (Fig. 2).[25]



Scheme 4.

One of the most interesting aspects of the vinylmethylenes, and certainly the most controversial one, is the π spin density distribution in these species. Two features of the EPR spectra have a bearing on this problem. First a comparison of the average zero-field splitting ($D_{\text{avg}} = 0.434\ \text{cm}^{-1}$) with that of CH_2 ($D = 0.75\ \text{cm}^{-1}$)[46] suggests a spin density of $\rho = D_{\text{avg}}/D_{\text{CH}_2} = 0.58$ at the divalent carbon center. Independently, the large difference between the zero-field splitting parameters of the two isomers ($\Delta D = 0.0485\,\text{cm}^{-1}$, 10.6% of D_c) requires high spin density on C-3. The value derived for ρ_1 corresponds to the spin densities at the terminal carbon atoms of the allyl radical.[34,35] A modified McLachlan calculation of the π spin density distribution gave $\rho_1 = \rho_3 = 0.588$ and $\rho_2 = -0.176$. With this approximation, the point spin model discussed earlier yields zero-field splitting parameters, $D_c = 0.450\,\text{cm}^{-1}$ and $D_t = 0.401\,\text{cm}^{-1}$ in good agreement with the experimentally determined values.[33]

The assignment of identical spin densities at C-1 and C-3 and the implicit assumption of identical bond length for C-1—C-2 and C-2—C-3 was challenged on the basis of general valence bond (GVB) calculations by Davis *et al.* These calculations indicated that the unpaired σ spin on C-1 has a pronounced effect on the π spin density causing considerable localization ($\rho_1 = 0.96, \rho_3 = 0.04$).[47] However, this result is seriously at odds with the experimental results. The calculated spin density distribution cannot explain the observation of two isomers with different Ds and can produce a D of somewhat acceptable magnitude only when an artificially low D_{CH_2} ($0.627\ \text{cm}^{-1}$) is used instead of the actual value ($0.75\ \text{cm}^{-1}$).

In order to reconcile the comparatively low D values of the vinylmethylenes with the high spin density calculated by Davis *et al.* for C-1, one might consider that the zero-field splitting parameters are lowered by rapid rotation of the carbenes in the matrix. A similar argument was used to account for the relatively low D-values observed for CH_2 in matrices ($D = 0.62\,\text{cm}^{-1}$)[48] compared to the gas phase ($0.778\ \text{cm}^{-1}$)[49] and to the best available calculation ($0.75\ \text{cm}^{-1}$).[48,50] For CH_2, the assignment of rotation is born out by experimental results, e.g. by characteristic changes in D and E upon isotopic substitution.[48]

In contrast, the experimental evidence available for vinylmethylene, specifically the temperature dependence of D between 4 and 50 K, does not support rotation in the matrix. The D values of *cis*- and *trans*-1-methylvinylmethylene increase linearly with decreasing temperature (Fig. 3). This linear dependence suggests a classical type of motion in a harmonic oscillator well.

It is interesting to note that the adjusted slope, $(\Delta D/D)/\Delta T$, of the temperature dependence, $2.6 \times 10^{-4}\ \text{K}^{-1}$ for the *cis* isomer, $2.1 \times 10^{-4}\ \text{K}^{-1}$ for the *trans* isomer, is of the same magnitude as that measured for dianthrylmethylene,[51] $(\Delta D/D)/\Delta T = 2.5 \times 10^{-4}\ \text{K}^{-1}$. However, in view of the large difference in mass, dianthrylmethylene ($m = 366$) has nearly seven times the mass of methylvinylmethylene ($m = 54$), this similarity does not necessarily imply a similar type of motion. Nevertheless, the results clearly rule out rotation of the vinylmethylenes in the matrix.

In a different theoretical approach, Feller *et al.* carried out multiconfiguration self consistent field (MCSCF) and multireference configuration interaction (MRCI) *ab initio* calculations on the lowest lying $^3A''$ state of vinylmethylene.[52] They arrived at a considerably different optimized geometry with bond lengths of 1.413 Å and 1.400 Å and π spin densities of $\rho_1 = 0.65$ and $\rho_3 = 0.47$. Based on these parameters, zero-field splittings of $D_c = 0.587\ \text{cm}^{-1}$ and $D_t = 0.563\ \text{cm}^{-1}$ were calculated, both considerably larger than the experimental values. Even more importantly, the theoretical difference is only half as large as the difference between the experimental values. To put

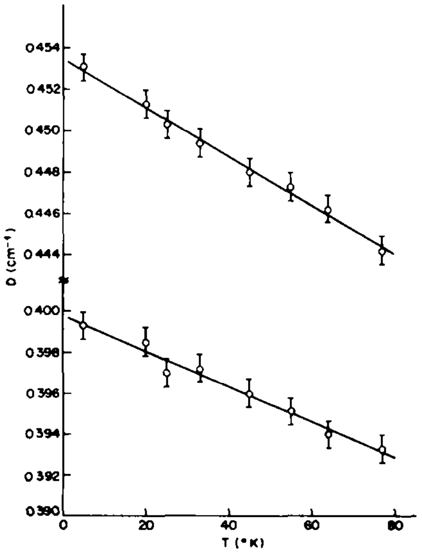
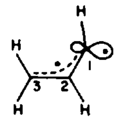
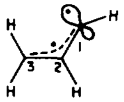
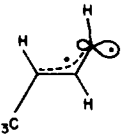
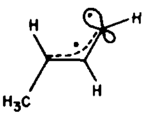
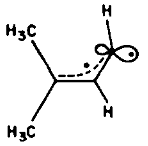
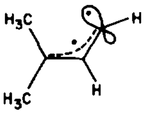
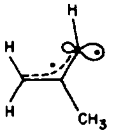
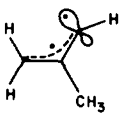
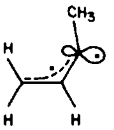
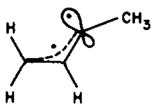
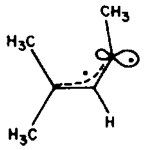
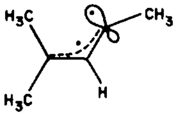
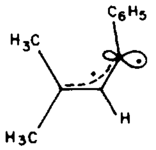


Fig. 3. Temperature dependence of the zero-field splitting parameter, D, for *cis*-1-methylvinylmethylene (bottom) and for the *trans* isomer (top). Except for irreversible decreases in intensity at temperatures above 50 K, the spectra are independent of the previous thermal history of the sample.

Table 3. Geometric isomerism in vinylmethylenes

	D' (cm^{-1})	E' (cm^{-1})		D' (cm^{-1})	E' (cm^{-1})
	0.4582	0.0197		0.4078	0.0233
	0.4574	0.0208		0.4094	0.0236
	0.4538	0.0202		0.4124	0.0237
	0.4310	0.0249		0.4009	0.0249
	0.4531	0.0200		0.3990	0.0220
	0.4421	0.0234		0.4002	0.0220
	0.357	0.0194			

these results into perspective, the authors noted that the calculated energy surface is very shallow and that the spin density distribution (and the magnitude of *D*) is very sensitive to the difference in bond lengths.

Most recently, MCSCF wave functions with a 4-31g basis were employed in a rigorous *ab initio* calculation of the entire C_3H_4 potential energy surface. These calculations resulted in bond lengths of 1.385 and 1.391 Å.[53] Spin densities or *D* values were not reported. In summary, none of these calculations provides compelling evidence for a structure with a pronounced unsymmetrical π spin density. Indeed, the more sophisticated calculations tend to move toward a symmetrical π spin distribution. Accordingly, there does not appear to be any reason to revise the originally proposed structure.

Since the vinylmethylene structure allows functional groups to be introduced at the divalent carbon as well as at C-2 and C-3, it appeared suitable to probe the propensity for intramolecular hydrogen abstraction in this system. Thus, the 1- and 2-methyl- and 3,3-dimethyl derivatives were scrutinized, respectively, for 1,2-, 1,3- and 1,4-hydrogen abstraction. Of these, the 2-methyl derivative seemed particularly attractive, since it held the promise of an alternative entry into the trimethylenemethane system.[54,55]

A series of appropriate methyl substituted diazopropenes, when photolyzed in frozen solution, gave rise to triplet EPR spectra which in each case indicated the presence of two similar triplets. The *D*s and Δ*D*s were quite close to the respective data of the parent species (Table 3). Interestingly, additional triplet spectra were observed upon photolysis of diazo-1-methylpropene ($D = 0.029$ cm^{-1}, $E = 0$), diazo-2-methylpropene ($D = 0.031$ cm^{-1}, $E = 0$), diazo-3,3-dimethylpropene ($D = 0.026$ cm^{-1}, $E = 0$; Fig. 4) and diazo-*trans*-3-methylpropene ($D = 0.028$ cm^{-1}, $E = 0$). On cursory inspection, these triplet spectra may appear compat-

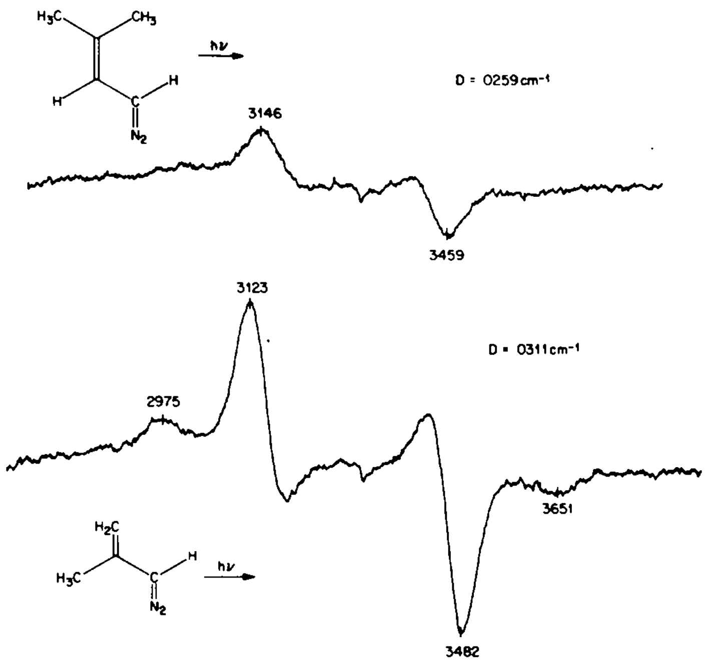
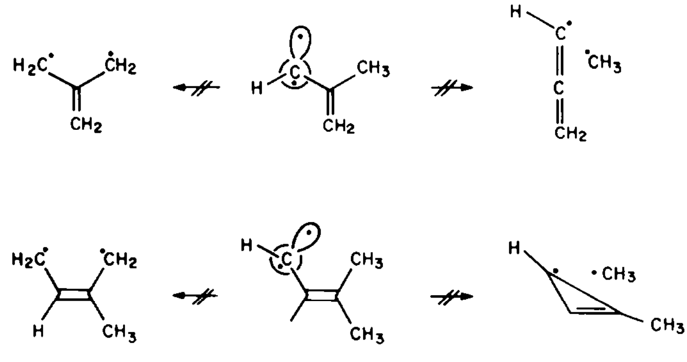


Fig. 4. EPR spectra (g of 2 region) observed during the photolysis of diazo-2-methylpropene (bottom) and of diazo-3,3-dimethylpropene (top) in frozen solutions at 6 K.

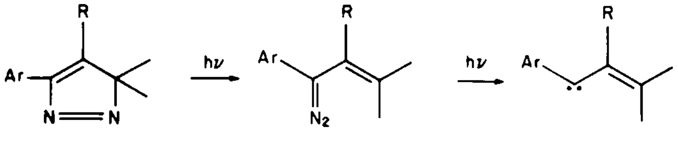
ible with intramolecular hydrogen abstraction. Particularly, the triplet generated from diazo-2-methylpropene has zero-field splitting parameters essentially identical to those of trimethylenemethane. However, the very similar D values observed for three systems, which should give rise to substantially different biradicals, argues against this explanation.

Consequently, we propose that the triplet spectra are due to radical pairs generated by either intramolecular or intermolecular reactions of the vinylmethylenes. The observed zero-field splittings correspond to pairs separated by 4.4–4.6 Å. We have considered fragmentation of the substituted vinylmethylenes, for example, loss of a β Me group from 2-methylvinylmethylene. However, we have eliminated this possibility, because the fragmentation of a triplet to a radical pair is without precedent in carbene chemistry and because the formation of these triplets appears to be matrix related. The low D triplets were observed only in methylcyclohexane and in methyltetrahydrofuran, but not in inert matrices. These results strongly suggest the formation of radical pairs by intermolecular hydrogen abstraction from an appropriate matrix. As for intramolecular hydrogen abstraction in carbenes, only 1,5-transfer remains as a possibility, if indeed a triplet carbene is an intermediate in the formation of naphthalene-1,8-diyl upon photolysis of 1-(8-methylnaphthyl)-diazomethane.[43]

It should be mentioned in this context that the EPR spectra of several derivatives of vinylmethylene had been measured prior to that of the parent.[56–58] None of these species showed any evidence for the presence of geometric isomers and we propose that a single isomer is present in each of these systems. All these vinylmethylenes were generated from pyrazolines in which the position of the substituents is fixed. This stereochemistry is likely to be preserved upon photochemical ring opening and the rotation of either



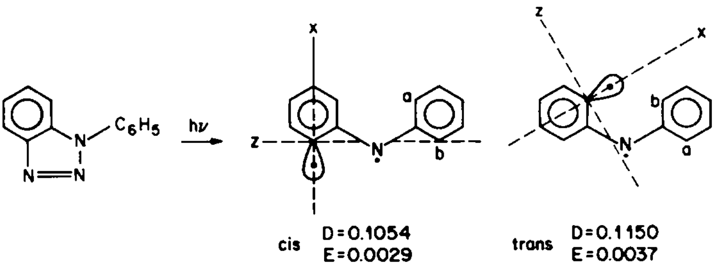
Scheme 5.



Scheme 6.

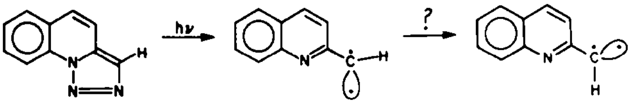
the resulting diazo compound or of the subsequent carbene should not be trivial in view of the bulky substituent.

In this context it is useful to examine the incidents of geometrical isomerization in triplet carbenes. This process has been invoked in three systems. Murai *et al.* presented evidence for the light-induced conversion of *cis*-phenyliminocyclohexadienylidene ($D = 0.1054$ cm^{-1}) to the *trans* isomer ($D = 0.1150$ cm^{-1}).[28] The mechanism was not discussed, but in-plane N-inversion or rotation of the cyclohexadienylidene moiety appears to be possible.



Scheme 7.

A second, less clear-cut example involves the photolysis of 5,6-benzopyridotriazole. Depending on the matrix, this reaction generates only the *trans* isomer or both *cis* and *trans* isomers. Since the precursor clearly has a pre-*trans* geometry the *cis*-isomer must be an isomerization product.[31] However it remains to be established whether the triplet carbene is indeed involved in the reorganization.



Scheme 8.

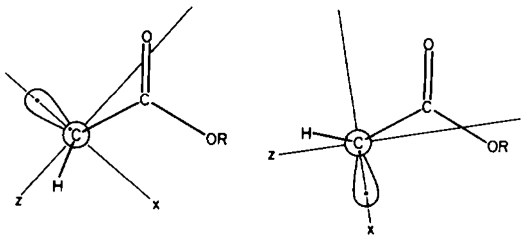
Finally, Senthilnathan and Platz discussed the interconversion of *cis*- and *trans*-naphthylmethylene.[45] Based on a subtle kinetic argument, they identified the activation barrier as greater than 5–6 kcal/mol. The interconversion in question could proceed via inversion of the divalent carbon or by rotation around the C—C bond. Theoretical studies have indicated an inversion barrier of ~9 kcal/mol for vinylmethylene[47] and a rotational barrier of ~5 kcal/mol for carbohydroxymethylene.[59] Although the rotational barriers depend on the bond order at the C—C junction—they should be higher for carbenes with delocalized π spin—the agreement between experimental and calculated value may indicate that the naphthylmethylenes may indeed interconvert. On the other hand, if these barriers are at all representative, the *cis–trans* isomerization of most triplet carbenes would be quite unlikely considering their low barriers to decay.

Carbonylmethylenes

The carbonylcarbenes are the latest family for which geometrical isomerism was established. The paradigm of this family can be obtained by direct irradiation, or better by sensitized photolysis of methyldiazoacetate.[27] The resulting EPR spectra once again indicate the presence of two similar triplets with zero-field splitting parameters, $D_c = 0.663$, $E_c = 0.030$ cm^{-1} and $D_t = 0.617$, $E_t = 0.053$ cm^{-1}. The average D value (0.64 cm^{-1}) lies between those of methylene ($D_{\mathrm{CH}_2} = 0.75$ cm^{-1}) and vinylmethylene ($D_{\mathrm{avg}} = 0.434$ cm^{-1}) suggesting a π spin density, $\rho = 0.85$ for the divalent carbon center.[27] This value is in good agreement with the π spin densities of the carboxymethyl[60] and alkanonyl radicals.[61]

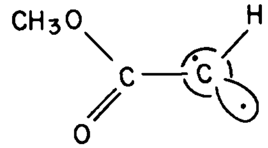
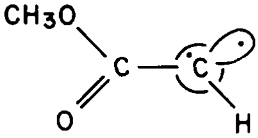
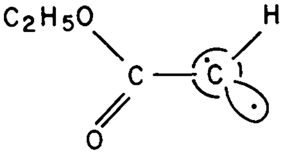
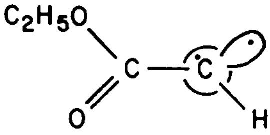
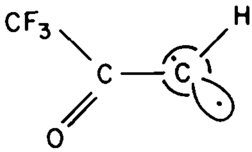
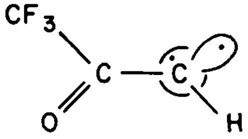
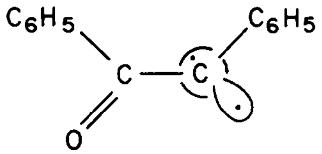
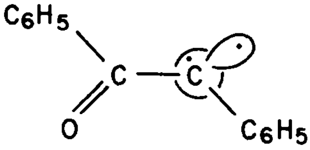
The assignment of the two EPR spectra to the two isomers was based on essentially the same arguments as in the case of naphthyl- and vinylmethylene. The key to these assignments are the spin densities in the γ-positions, in this case on the carboxyl oxygen. Since the vector r is approximately parallel to the z axis, a sizeable negative contribution to D is expected for the *trans* isomers, whereas the contribution of ρ_y to the *cis* isomer is negligible. Hence, the *trans* isomer is assigned the lower value of D (cf. Table 4).

However, these arguments are only qualitative. In contrast to vinyl- and arylmethylenes, the zero-field



Scheme 9.

Table 4. Geometric isomerism in carbonylmethylenes

	D (cm^{-1})	E (cm^{-1})		D (cm^{-1})	E (cm^{-1})
	0.617	0.053		0.663	0.030
	0.616	0.053		0.661	0.031
	0.572	0.079		0.605	0.034
	0.312	0.052		0.392	0.052

splitting parameters of carbalkoxycarbenes cannot be reproduced by the simple point spin model discussed above. Indeed, if ρ_1 is as high, and ρ_3 as low as the analogy with carboxymethyl and alkanonyl radicals suggest, it is difficult to rationalize a ΔD of the magnitude observed. Clearly, additional contributions to D, due to spin orbit coupling, σ delocalization, or other effects will have to be considered for an exact analysis.

Whereas the factors determining the zero-field splittings of the carbalkoxycarbenes may be an open question, there is little doubt that these carbenes are ground state triplets. The relative ordering of carbene singlet and triplet states may be revealed by the temperature dependence of the EPR intensity. Ground state triplets follow the Curie law

$$\chi = c/T \tag{5}$$

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[62]

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

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

For the carbalkoxycarbenes the x and y lines of the spectra assigned to the *trans* isomers are sufficiently strong to allow a meaningful study of their temperature dependence. These signals show the linear relation (Fig. 5) expected for a ground-state triplet or for a triplet state that lies a maximum of 10 cal above the singlet state.[58] The observed changes are reversible in the temperature range of 10–40 K. At higher temperatures, the signals vanish irreversibly, presumably by reaction of the triplet with the matrix or by conversion of the triplet state to a more reactive state capable of undergoing intra- or intermolecular reactions. An interconversion of the geometric isomers is not observed under these

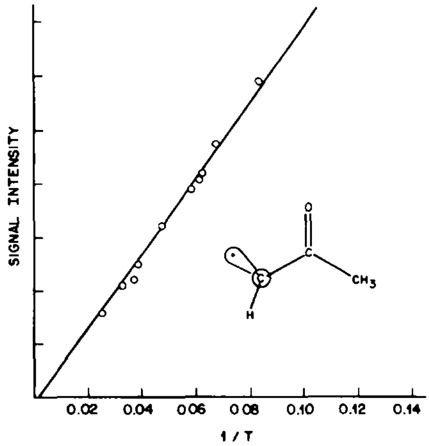
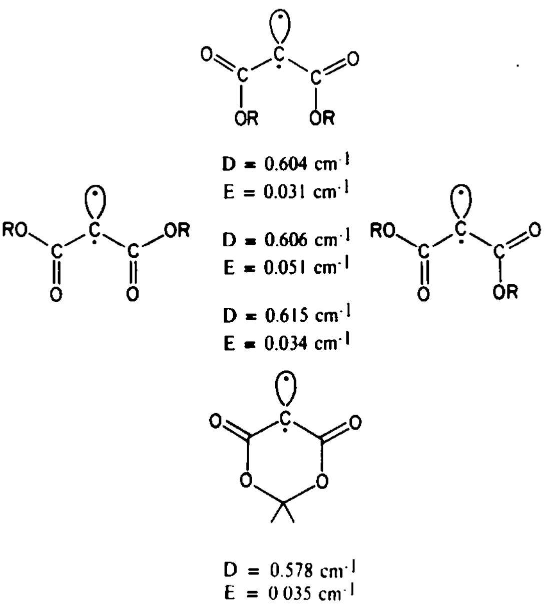


Fig. 5. Signal intensity of the x line of *trans*-carbomethoxycarbene *vs* $1/T$. Experimental results are shown as circles; the line represents the best linear least-squares fit of the data.

Table 5. Geometric isomerism in dicarbonylmethylenes



conditions; apparently, the energy of activation for the reaction is lower than that for isomerization.

Two additional examples of geometrical isomerism in carbonylcarbenes were observed in the laboratory of Strausz. The photolysis of azibenzil was reported to produce not only the strong signals of the previously known *trans*-benzoylphenylmethylene[18,63] ($D = 0.3916\,\mathrm{cm}^{-1}$) but also several weaker transitions, which were assigned to the *cis* isomer ($D = 0.3123\ \mathrm{cm}^{-1}$).[32] The difference in D ($0.079\ \mathrm{cm}^{-1}$; 20% of D_{trans}) is by far the largest observed for any pair of carbene isomers. The explanation of this difference presents quite a challenge. The other example, a pair of perfluoroacetylmethylenes ($D_{trans} = 0.605\ \mathrm{cm}^{-1}$; $D_{cis} = 0.572\ \mathrm{cm}^{-1}$; $\Delta D = 0.033\ \mathrm{cm}^{-1}$; 5.4% of D_{trans})[32] shows values of D and ΔD similar to those of the carbalkoxy carbenes.

Carbenes with two unsaturated substituents

The concept of geometric isomerism in three-center radicals can be logically extended to five-center homologs. Appropriate representatives of this class can have as many as three isomers. For example, the EPR spectra of the pentadienyl radical suggest the existence of two isomers, with *E*,*E* and *E*,*Z* configuration.[64–67] Although no evidence was found for the *Z*,*Z* form, many derivatives of this isomer are known, specifically cyclohexadienyl radicals,[34] in which the *Z*,*Z* configuration is fixed by a bridging methylene group.

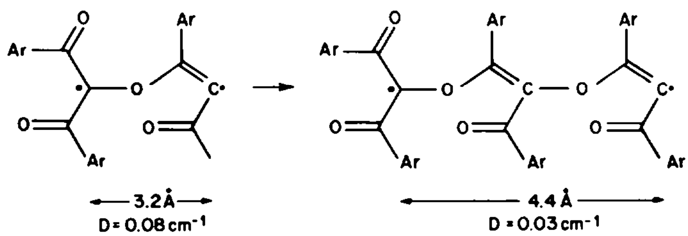
Scheme 10.

Analogously, divinylmethylene also might have as many as three isomers. The 1,1,5,5-tetramethyl derivative of this carbene may be readily accessible by an unexceptional reaction sequence from phorone, but it has not been studied as yet. On the other hand, a 1,5-dioxa analog was studied in our laboratory. Photolysis of dimethyl diazomalonate in frozen MTHF solution gave rise to three distinct EPR spectra compatible with the presence of biscarbomethoxycarbenes (BCMC). The zero-field splitting parameters of the three triplets ($D \sim 0.6\,\mathrm{cm}^{-1}$) reflect a limited delocalization of π spin density, but are too close to permit an assignment of individual isomers. Some evidence for the assignment of the BCMC isomers is provided by the observation of a triplet EPR spectrum with a slightly lower D ($\sim 0.58\ \mathrm{cm}^{-1}$) for a cyclic derivative of the *Z*,*Z* form (Table 5). Since the *Z*,*Z* isomer is expected to have the lowest D value, the absence of a comparable BCMC spectrum may well indicate that this isomer is not present. Given the absence of one isomer, two of the three triplets may represent the same isomer in two different environments (sites).

In the light of the relatively high D values observed for BCMC, the identification of two triplets with relatively low D values as dibenzoylmethylene isomers[29] must be questioned. Murai *et al.* photolyzed dibenzoyldiazomethane powder and observed two triplets with $D = 0.08$ and $D = 0.03\ \mathrm{cm}^{-1}$, respectively.[29] All available analogs, including phenylbenzoyl carbene,[17,32,63] suggest that these D values are rather low for a dicarbonylcarbene. A more likely assignment is that of extended triplets, generated by attack of the primary photo-product, dibenzoylmethylene, on the diazo compound. This type of reaction is observed occasionally in frozen solutions and can be prevented by high dilution (matrix isolation).[68,69] It presents an especially serious hazard in a powder of pure reactant and cannot be eliminated under these reaction conditions.

The D values of the triplets observed by Murai *et al.*[29] suggest biradicals in which the two electrons are separated by 3.2 and 4.4 Å, respectively. These distances are readily accommodated by a "dimer" and "trimer" of the postulated carbene.

As for dibenzoylmethylene, we see no reason why this species should not be a detectable ground state triplet, and why its zero-field splitting parameters, D, should be substantially lower than $0.6\ \mathrm{cm}^{-1}$, the value observed for the dicarbomethoxycarbenes. Photolysis of dibenzoyldiazomethane in an appropriate matrix at



Scheme 11.

sufficient dilution should produce the carbene, possibly several distinct isomers, unencumbered by secondary reactions.

Perspective

The various aspects of divalent-carbon structure and reactivity discussed in the foregoing sections cannot be considered fully elucidated. In many aspects, our understanding is still sketchy. Specifically, the detailed pathways of product formation are not always understood. Are carbenes necessary intermediates, or are excited states of diazo compounds capable of intermolecular as well as intramolecular reactions? Absorption and phosphoresence spectra have been observed for a limited number of triplet carbenes. Do excited carbene states undergo intersystem crossing, fragmentation, hydrogen abstraction or rearrangements, as an analogy with carbonyl excited states may suggest? Furthermore, can the reactivities of excited state carbenes be modified by incorporation in matrices or crystals?

In the realm of *ab initio* theory, the calculation of zero-field splitting parameters for aryl- and vinylmethylenes needs to be refined, and an entirely new approach may have to be devised to account for the *D* values of carbonylmethylenes. We are confident that elegant solutions to some of these questions will emerge within the current decade.

Acknowledgements—The authors are indebted to Dr. E. Wasserman, a pioneer in the EPR of triplet states, who collaborated in the investigation of the vinylmethylene derivatives; to M. L. M. Schilling, who synthesized several substituted diazopropenes; to Professor M. Jones, Jr., who provided samples of the dicarbonyldiazo compounds; and to Professor W. T. Borden and Dr. J. J. Pacansky, who made available manuscripts prior to publication. This paper is dedicated to Professor William v. E. Doering, in whose laboratory one of us received much inspiration.

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