

## Substituent Effect on Singlet-Triplet Splitting: Diarylcarbene-Diarylmethylene; Electron Spin Resonance Study. Merostabilization in Diarylmethylenes

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**Summary** An analysis of the e.s.r. spectra of unsymmetrically substituted diphenylmethylenes (*e.g.* *p,p'*-methoxy, cyano, dimethylamino, or nitro) indicate these species have a triplet ground state which is delocalized by merostabilization.

studied. Therefore, these molecules have triplet ground states, or singlet ground states separated by somewhat less than 5 cal mol<sup>-1</sup> from the upper triplet state. We consider the latter to be highly unlikely for the diphenylmethylenes reported here.

It is generally accepted that the ground state of the diphenyl divalent carbon species is the triplet, *e.g.* diphenylmethylene.<sup>1</sup> More recent evidence indicates that the energy separation between the ground triplet state and the singlet state of diphenylmethylene may be as small as 3 kcal mol<sup>-1</sup> or less.<sup>2</sup> In an attempt to invert the lowest two states of diphenylmethylene, we have prepared a series of *para*-substituted and *para,para'*-disubstituted diphenylmethylenes and have studied the temperature dependence of the triplet e.s.r. signal intensity to determine the ground-state multiplicity of each species. The results for some cyano- and methoxy-substituted derivatives have been reported previously.<sup>3</sup> The series has been extended to include *p*-nitro and *p*-dimethylamino substituents as the best, conveniently synthesized electron-withdrawing and donating groups, respectively.

The diphenylmethylenes were generated at low temperature in the e.s.r. cavity by irradiation ( $\geq 280$  nm) of either the corresponding diazo compounds in a rigid glass or the corresponding tosylhydrazone potassium salts.

The temperature dependence experiments were carried out over the range *ca.* 5–30 K using the intensity of the H<sub>x2</sub> line of the methylene in every case. The detailed experimental procedure has been described previously.<sup>4</sup>

The temperature-dependence studies indicate that the intensity of the triplet signal for all diphenylmethylenes in the series follows the Curie law over the temperature range

TABLE. Zero field splitting parameters for some diarylmethylenes.

<i>para</i>	<i>para'</i>	( <i>D</i> / <i>hc</i> )/cm <sup>-1</sup>	( <i>E</i> / <i>hc</i> )/cm <sup>-1</sup>	Glass or matrix
H	H	0.4088	0.0170	b
"	"	0.4050 <sup>a</sup>	0.0194 <sup>a</sup>	
H	NO <sub>2</sub>	0.3778	0.0168	c
"	"	0.3765 <sup>a</sup>	0.0175 <sup>a</sup>	
H	NMe <sub>2</sub>	0.3876	0.0168	d
NO <sub>2</sub>	NO <sub>2</sub>	0.3773	0.0177	d
NMe <sub>2</sub>	NMe <sub>2</sub>	0.3748	0.0180	e
NO <sub>2</sub>	NMe <sub>2</sub>	0.3351	0.0164	d
NO <sub>2</sub>	Me	0.3711	0.0176	c
NO <sub>2</sub>	MeO	0.3599	0.0159	c
CN	NMe <sub>2</sub>	0.3518	0.0163	c

<sup>a</sup> Previously reported values; A. M. Trozzolo and E. Wasserman, 'Carbenes,' Vol. 2, eds. M. Jonez, Jr. and R. A. Moss, Wiley, New York, 1975. <sup>b</sup> Diazo-compound in methylcyclohexane-isopentane (4:1). <sup>c</sup> Tosylhydrazone salt. <sup>d</sup> Diazo compound in tetrahydrofuran. <sup>e</sup> Diazo compound in methylcyclohexane-tetrahydrofuran (4:1).

At first glance, there seems to be no obvious correlation between substituents and the values of *D* and *E* for the various diphenylmethylenes (*e.g.* there is no correlation with Hammett substituent parameters  $\sigma$ ,  $\sigma^+$ , *etc.*). In fact, the variation in the zero field splitting parameters is rather small. However, the largest decreases in *D* from the value for the parent diphenylmethylene occur for disubstituted derivatives in which one *para*-substituent is a strong

electron-withdrawing group and the other *para*-substituent is a strong electron-donating group. Furthermore, the effect of this unsymmetrical substitution is considerably larger than can be accounted for by taking the sum of the effects in the mono-substituted derivatives (*e.g.* compare *p*-nitro, *p*-dimethylamino, and *p*-nitro-*p'*-dimethylamino; Table).

We attribute the effect of unsymmetrical disubstitution with strong resonance electron-withdrawing and donating groups to merostabilization, a term first suggested by Katritzky<sup>5</sup> to describe increased delocalization in radicals for which reasonable charge-separated resonance structures can be drawn. The merostabilization of one diphenylmethylene derivative is shown in the Figure. These charge-separated resonance structures contribute only in unsymmetrically disubstituted diphenylmethylenes containing strong electron-withdrawing and -donating groups. The charge-separated resonance structures allow the unpaired electron in the  $\pi$ -orbital of the diphenylmethylenes to be delocalized into positions *ortho* to the substituents (Figure), which is not possible in mono- or symmetrically di-substituted cases unless high-energy valence-bond canonical forms are drawn. This increased delocalization into the *ortho* positions should lead to a decrease in the net spin density at the benzyl carbon atom. The experimental result is a

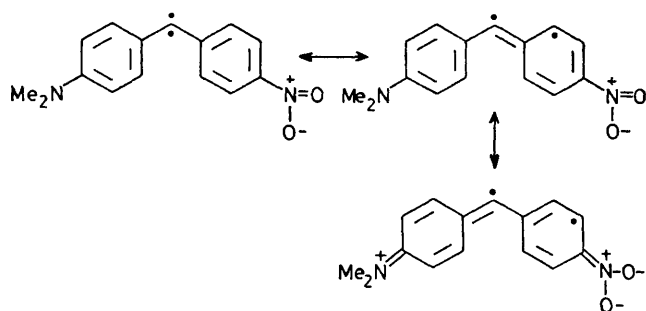


FIGURE. Merostabilization in a diphenylmethylene.

significant decrease in *D*. The direct determination of the spin density change at the *ortho* positions by measurement of the proton hyperfine coupling constants at these positions and comparison with the parent diphenylmethylene is not possible with these randomly oriented triplets. This spin density change has been observed in merostabilized radicals.<sup>5a</sup>

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<sup>4</sup> D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, *J. Amer. Chem. Soc.*, 1976, **98**, 6225.

<sup>5</sup> (a) R. W. Baldock, P. Hudson, and A. R. Katritzky, *J.C.S. Perkin I*, 1974, 1422; (b) A. R. Katritzky, *ibid.*, p. 1427.