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DIRECT PHOTOCHEMICAL POPULATION OF TRIPLET DIAZIRINES: COMPARISON OF TRIPLET ENERGIES BY DIRECT EXCITATION AND BY ENERGY TRANSFER

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Summary

The $S_0 \rightarrow T_1$ absorption spectra of diazirine, 3-phenyl-3-chlorodiazirine and two 4-substituted 3-aryl-3-chlorodiazirines have been observed in fluid solution at ambient temperatures. These measurements, which allow direct determination of the triplet energy E_T of the diazirines, are compared with those obtained by plots of sensitizer triplet quenching by diazirine and 3-phenyl-3-chlorodiazirine as a function of triplet sensitizer energy. The corresponding triplet energies are determined to be 73 ± 3 kcal mol^{-1} and 63 ± 0.5 kcal mol^{-1} respectively.

1. Introduction

Diazirines have served as an important source of carbenes via thermolysis or photolysis [1]. Although there have been extensive investigations of the photochemical production of carbenes from diazirines [2], there has been relatively little published concerning the nature of the electronically excited states of these interesting small ring heterocycles. Some preliminary investigations have provided evidence that polycyclic azoalkanes [3] and diazirines [4] possess measurable $S_0 \rightarrow T_1$ absorption spectra.

2. Results and discussion

The UV–visible absorption spectra of diazirine (1), 3-phenyl-3-chlorodiazirine (2), 3-(4-methylphenyl)-3-chlorodiazirine (3) and 3-(4-methoxy-

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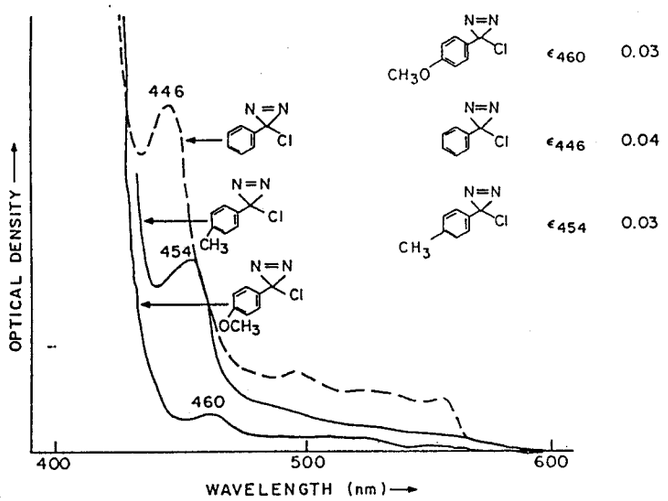
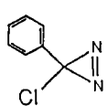
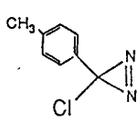
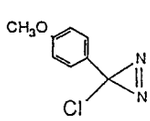


Fig. 2. $S_0 \rightarrow T_1$ absorption spectra of 2 (about 1.6 M), 3 (about 0.6 M) and 4 (about 0.1 M) in *n*-pentane (cell path length, 10 cm).

TABLE 1

Triplet energies of diazirines studied

Compound	*Structure*	E_T (kcal mol^{-1})	
		$S_0 \rightarrow T_1$ transition (nm)	*Triplet quenching*
1		77 ± 1 (~ 370)	73 ± 3
2		64 ± 1 (446)	63 ± 0.5
3		62 ± 1 (454)	—
4		62 ± 1 (460)	—

3. Conclusion

The very weak absorption bands of the diazirines 1, 2, 3 and 4 in the region 360 - 460 nm are assigned to $S_0 \rightarrow T_1$ transitions. This assignment is consistent with a kinetic analysis of quenching of triplet energy donors by diazirines. The finding that diazirines possess observable $S_0 \rightarrow T_1$ absorption bands potentially provides a method to populate the triplet states of diazirines directly.

4. Experimental details

1 [8], and 2, 3 and 4 (for prior preparations of arylchlorodiazirines, see ref. 9) were prepared as in the literature. Acetonitrile (MCB, OmniSolv), *n*-pentane (MCB, OmniSolv) and triplet sensitizers (*i.e.* 1-indanone, xanthone, acetophenone, 4-methoxyacetophenone, 4,4′-dimethoxybenzophenone, benzophenone, 4-phenylbenzophenone, thioxanthone, phenanthrene, 4-phenylacetophenone and 2-naphthyl methyl ketone) were used as supplied. 2-Naphthyl methyl ketone was obtained from Fluka AG and Buchs SG, and the others were obtained from Aldrich.

The UV–visible absorption spectra were obtained on a Perkin–Elmer 559A UV–visible spectrophotometer. The concentrations of the diazirine 1 were determined from UV–visible absorption spectra [5] and the others were determined by weight. The laser flash photolysis system is the same as previously described [10]. The triplet sensitizers were excited at 266 nm (YAG, 8 ns pulse) for 1 as acceptor and at 308 nm (XeCl, 20 ns pulse) for 2 as quencher. Bimolecular quenching rate constants k_q were obtained from the slope of the plots of the observed first-order rate for decay of sensitizer triplet *vs.* diazirine concentration. The observed quenching rate constants k_q were fitted to eqn. (1) by choosing a suitable triplet energy of acceptor. The triplet energies of sensitizers were obtained from the literature [11]. The diffusion rate k_{dif} in acetonitrile was assumed to be $1.2 \times 10^{10}\ M^{-1}\ s^{-1}$, which is the largest bimolecular rate constant observed in this experiment.

Acknowledgments

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References

1 M. T. H. Liu, *Chem. Soc. Rev.*, *11* (1981) 127.
H. M. Frey, *Adv. Photochem.*, *4* (1966) 225.
2 D. P. Cox, I. R. Gould, N. P. Hacker, R. A. Moss and N. J. Turro, *Tetrahedron Lett.*, *24* (1983) 5313.
I. R. Gould, N. J. Turro, J. Butcher, Jr., C. Doubleday, Jr., N. P. Hacker, G. F. Lehr,