

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

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(Received August 12, 1986)

### 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  $73 \pm 3$  kcal mol<sup>-1</sup> and  $63 \pm 0.5$  kcal mol<sup>-1</sup> 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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phenyl)-3-chlorodiazirine (4) all show a finely structured absorption band of relatively low extinction coefficient ( $\epsilon_{\max} \approx 200$ ) in the region 280 - 350 nm which has been assigned to an  $n, \pi^*$  ( $S_0 \rightarrow S_1$ ) transition [4]. Very weak bands ( $\epsilon_{\max} \approx 0.01$ ) in the region 360 - 420 nm are tentatively assigned to the  $S_0 \rightarrow T_1$  transition (Figs. 1 and 2; Table 1). For example, 1 shows a finely structured band with a maximum at about 320 nm ( $\epsilon_{\max} \approx 200$ ) [5] and a very weak band at about 370 nm ( $\epsilon_{\max} \approx 0.01$ ) in *n*-pentane solvent. For diazirines 2, 3 and 4 the corresponding bands for  $S_0 \rightarrow T_1$  absorption appear at about 445 - 460 nm.

In order to obtain confirmatory evidence for the assignment of the very weak bands to  $S_0 \rightarrow T_1$  absorption of the diazirines, we designed kinetic tests which involved an investigation of the rate constants for quenching of a series of triplets of well-defined triplet energy by diazirines and by conventional treatment (for estimation of  $E_T$ , see ref. 6) of the data to extract the triplet energies of the diazirines. The diazirines 1 and 2 were employed as quenchers of the triplet states of a series of donors of known and well-defined triplet energy, employing conventional time-resolved laser spectroscopy. The results of these investigations are summarized in Fig. 3. The triplet energy of a quencher, in the absence of special quenching mechanisms, such as exciplex formation, can be evaluated from plots such as those in Fig. 3 by various fitting techniques. In the simplest case [7] the data can be fitted to an exponential expression such as the equation

$$k_q = k_{\text{diff}} \left\{ 1 + \exp \left( - \frac{\Delta E_T}{RT} \right) \right\}^{-1} \quad (1)$$

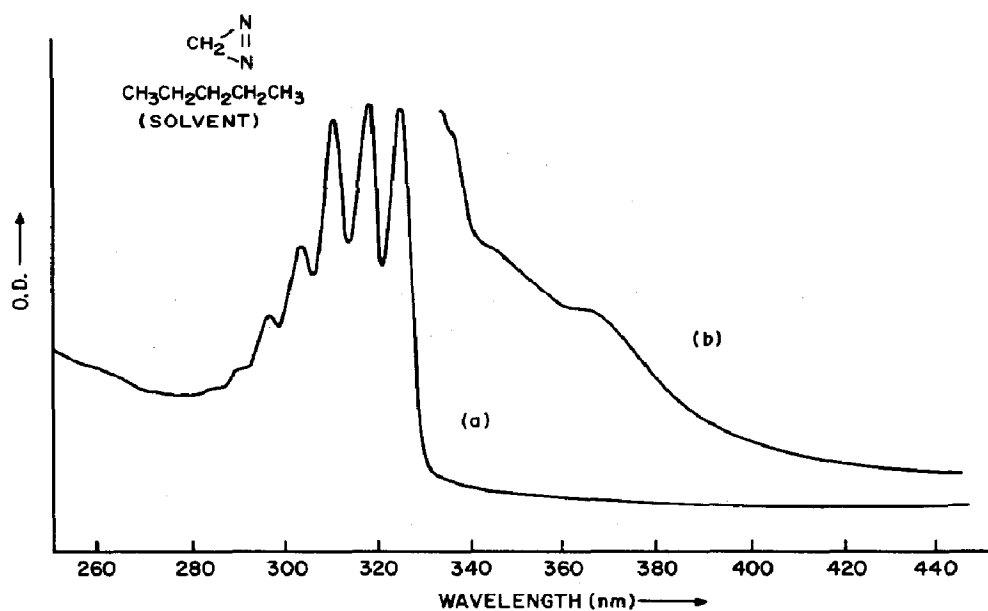


Fig. 1. Absorption spectra of diazirine 1 in *n*-pentane. (a) About 0.005 M; cell path length, 1 cm. (b) About 0.02 M; cell path length, 10 cm. (12 scans.)

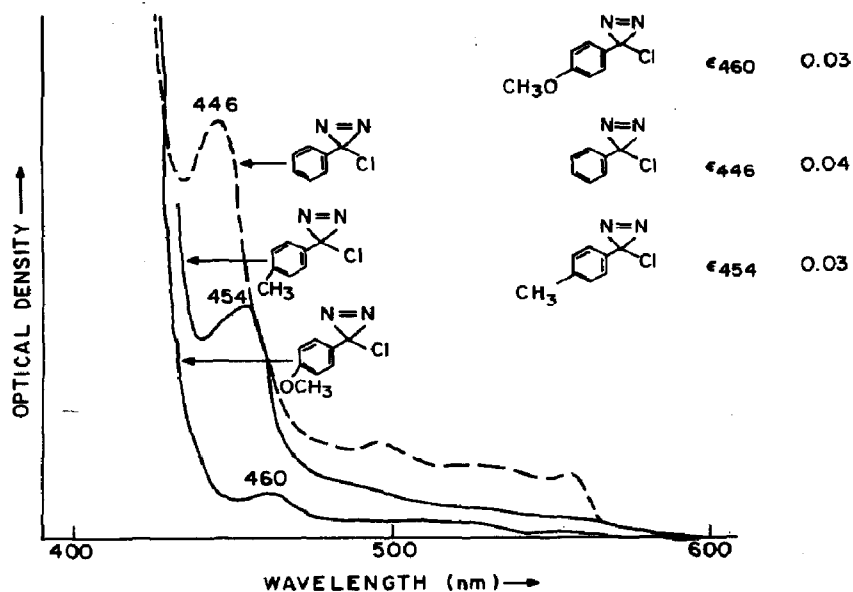


Fig. 2.  $S_0 \rightarrow T_1$  absorption spectra of 2 (about 1.6 M), 3 (about 0.6 M) and 4 (about 0.1 M) in *n*-pentane (cell path length, 10 cm).

TABLE 1

Triplet energies of diazirines studied

Compound	Structure	$E_T$ (kcal mol <sup>-1</sup> )	
		$S_0 \rightarrow T_1$ transition (nm)	Triplet quenching
1	<chem>C1=NN1</chem>	$77 \pm 1$ (~370)	$73 \pm 3$
2	<chem>ClC1(Cl)N=N1C2=CC=CC=C2</chem>	$64 \pm 1$ (446)	$63 \pm 0.5$
3	<chem>CC1=CC=C(C=C1)C2(Cl)N=N2</chem>	$62 \pm 1$ (454)	—
4	<chem>COC1=CC=C(C=C1)C2(Cl)N=N2</chem>	$62 \pm 1$ (460)	—

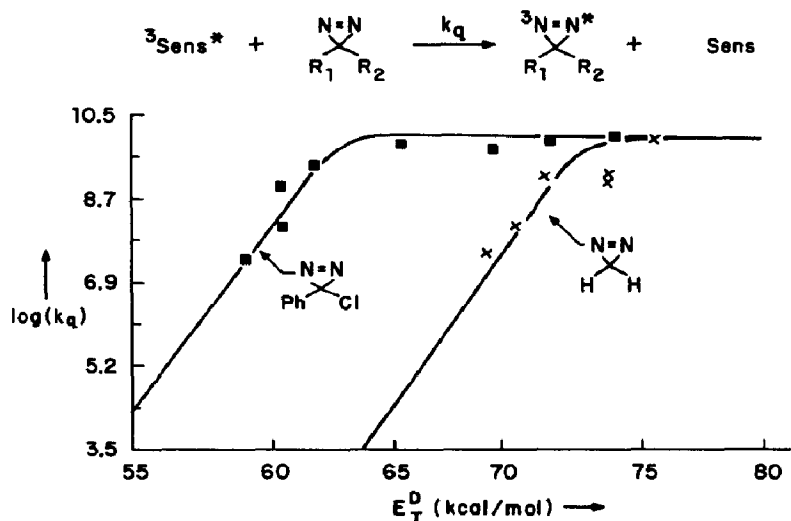


Fig. 3. Rate constants for quenching of triplet sensitizers by diazirine 1 (x) and by 2 (■) in acetonitrile at ambient temperature. The full lines are calculated from eqn. (1) with  $E_T^1 = 73 \text{ kcal mol}^{-1}$  and  $E_T^2 = 63 \text{ kcal mol}^{-1}$ .

where  $k_q$  is the observed rate constant for quenching of the triplet donor,  $k_{\text{diff}}$  is the rate constant for diffusion in the solvent acetonitrile at ambient temperatures  $T$  and  $\Delta E_T$  is the energy difference between the donor triplet and the diazirine triplet. The basic idea behind eqn. (1) is that thermal equilibrium exists in the encounters of a triplet donor and a ground state acceptor, and that only the Boltzmann distribution law determines the probability that the donor or the acceptor will leave the solvent cage with electronic excitation. If eqn. (1) is appropriate for the analysis, the only unknowns are the triplet energies of the diazirines ( $E_T^1$  and  $E_T^2$ ).

From the fitting of the data in Fig. 2, the values of  $E_T^1$  and  $E_T^2$  are found to be  $73 \pm 3 \text{ kcal mol}^{-1}$  and  $63 \pm 0.5 \text{ kcal mol}^{-1}$  respectively. These values may be compared with the energies corresponding to the *maxima* of the very weak absorptions of 1 and 2,  $77 \pm 1 \text{ kcal mol}^{-1}$  and  $64 \pm 1 \text{ kcal mol}^{-1}$  respectively. The error in the energy derived from the maxima in the absorption spectra is estimated to be about  $2 \text{ kcal mol}^{-1}$ . The fitting for 2 is good, and the error in the fitting is estimated to be about  $0.5 \text{ kcal mol}^{-1}$ . Since the experiment is difficult for 1, which is a gas at room temperature, the fitting is less good. The error in the fitting is estimated to be about  $3 \text{ kcal mol}^{-1}$ . The error in the donor triplet energy is about  $0.5 \text{ kcal mol}^{-1}$ . Since the absorption maximum is only an approximation to the 0-0 band (which is the more accurate measure of  $E_T$ ), and the UV absorptions and the quenching measurements are in different solvents, *n*-pentane and acetonitrile, the agreement between the spectroscopic and the kinetic values of  $E_T$  are considered to be acceptable, *i.e.* the very weak absorption bands are confirmed as resulting from  $S_0 \rightarrow T_1$  absorption of the diazirines. Table 1 summarizes the results.

### 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  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , which is the largest bimolecular rate constant observed in this experiment.

### Acknowledgments

The authors thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research.

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