ENERGY TRANSFER PROCESSES IN *N*-TRIMETHYLBORAZINE

C. D. DEJARDINS, F. GREIN, M. E. MACBEATH, J. PASSMORE and I. UNGER

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick (Canada)

(Received May 14, 1972)

SUMMARY

N-Trimethylborazine quenches the singlet state of benzene excited at 267 nm, but does not affect the triplet state of benzene. There is no evidence for chemical reaction between *N*-trimethylborazine and benzene or between *N*-trimethylborazine and biacetyl. *N*-Trimethylborazine excited at 221 nm does not exhibit any fluorescence or phosphorescence in either gas phase or in glassy matrix. Theoretical calculations predict that the singlet state of benzene lies at lower energies than that of *N*-trimethylborazine hence the quenching of the singlet state of benzene by *N*-trimethylborazine should not result in the production of the first excited singlet of *N*-trimethylborazine.

INTRODUCTION

The replacement of a carbon atom by a nitrogen atom in the benzene ring causes the rate of radiationless processes to increase as is evidenced by the decrease of the yield of radiative processes[1-3]. On going from benzene and benzene derivatives to borazine and its derivatives radiative processes disappear entirely[4,5]; however, it is not clear what sort of non-radiative processes take over, particularly where the exciting wavelength is longer than 184.9 nm.

In a previous communication[6] we reported on the energy transfer processes occurring in benzene–borazine mixture excited at 258 nm. The data in ref. 6 showed that borazine accepted triplet energy from benzene, but did not quench the first excited singlet state of benzene. We report here the results of a similar study with the donor–acceptor pair being benzene–*N*-trimethylborazine (*N*-tmb) with initial donor excitation into the singlet state.

EXPERIMENTAL MATERIALS

N-Trimethylborazine was prepared by a modification of the method of Hohnstedt and Haworth[7] with a yield better than 60%. The reaction was carried

out at atmospheric pressure by passing dry N_2 continuously through the reaction vessel sweeping out the diborane by-product after passing through a mercury bubbler. The product was twice distilled under vacuum (10^{-2} Torr) through a $-23°$ C into a $-7.8°$ C trap.

The sharp melting point of the crystalline solid($-7.8°$ C), infra-red spectrum[8], and vapour pressure measure (8.13 Torr at $23°$ C) confirmed the identity and purity of the product.

The benzene used was fluorometric grade obtained from the Hartmann-Leddon Co. Chromatographic analysis showed it to be 99.9% pure and it was used without further purification. The biacetyl, purchased from the Aldrich Chemical Co., was stored in a dark reservoir and purified prior to use by bulb to bulb distillation *in vacuo*. All materials were thoroughly out-gassed before use.

The high vacuum line employed in this study was a grease and mercury-free system equipped with Hoke packless diaphragm metal valves. All emission measurements were taken on a modified Aminco Bowman spectrophotofluorimeter. Details about the light source, slit widths, band pass *etc.* have been given previously[9]. The cell was a cuvette flow-through type and mixing was accomplished by means of an all-glass pump.

For photolysis, a Beckman F076 cell with path length of 5 cm and fused silica windows was used. A custom made Hanovia low pressure mercury lamp with a Corning No. 7910 filter was used to obtain the 253.7 nm line. The source for the photolysis at 436 nm was a compact arc Hg–Xe 1000 W lamp from Hanovia (No. 1-5080-000). The beam from this lamp passed through two $1/4$ m Ebert Monochromators (Jarrell-Ash, Model 82-410) before entering the cell.

The ultra-violet (u.v.) absorption spectra were taken on a Coleman Model EPS-3T Hitachi Ratio Recording Spectrophotometer, using the Beckman cell described above.

The infra-red (i.r.) spectra were taken on a Perkin-Elmer Model 457 Grating Infrared Spectrophotometer. A 10 cm gas cell with NaCl windows was used for these spectra.

The attempt to obtain the phosphorescent spectrum of *N*-tmb at 77 K was made using a solid solution in 3:1 isopentane–methylcyclohexane. The solution was out-gassed and hermetically sealed in a specially constructed sample tube with quartz viewing section. To record the spectrum on the spectrophotofluorimeter, described above, the flow through gas cell was replaced by the cryostat and a rotating shutter, the whole arrangement flushed with dry nitrogen to prevent fogging.

THEORETICAL

CNDO–CI calculations, using singly excited configurations only, were performed on *N*-trimethylborazine, and on borazine for comparison. The method

used is essentially the CNDO/2 method of Pople *et al.*[10], followed by configuration interaction (CI). The parameterization of Del Bene and Jaffé[11] was adopted, with the bonding parameters BETA $= -12$ eV for H and -17 eV for C, the electron repulsion integrals $W = 12.85$ for H, 11.11 for C (and 12.01 for N). The two-centre repulsion integrals γ_{AB} were obtained by a modification of the Mataga–Nishimoto[12] formula due to Weiss[13] in the following way:

$$\gamma_{AB} = \frac{e^2 C}{r_{AB} + \Gamma C}$$

where r_{AB} is the distance between the centers (e^2/r in eV). $\Gamma = [0.5 W_A + 0.5 W_B]^{-1} e^2$, with the constant $C = 1.7469$. The off-diagonal Hamiltonian matrix elements were weighted differently for σ- and π-type interactions using the weighting factor 0.585 for the π-type elements[11]. The covergence tolerance of the charge density was set equal to 0.005. With the bonding parameters of B and N equal to -17 eV and -25 eV respectively, according to the CNDO/2 parameterization, the computed excitation energies are too high. Therefore, adjustments had to be made, and values close to -14 eV for B and -20 eV for N (with an average of -17, equal to the C-bonding parameter) were found to be more satisfactory.

Electron repulsion parameters W can be obtained as the difference between the valence state ionization potential and the electron affinity. Assuming a trigonal valence state for B (trtrtr) and a trtrtrπ^2 valence state for N, using data published by Hinze and Jaffé[14] gives excitation energies which are too high. Therefore, a trtrπ model for B ($W = 6.91$) and a tr^{2}trtrπ model for N ($W = 12.01$[11]) was chosen as a basis. Both the BETA and the W parameters were optimized such that the computed excitation energy for the transition from the ground state to the lowest excited singlet state of borazine would be about 6.28 eV.

For borazine the B–N, B–H and N–H bond lengths were taken to be 1.44, 1.19 and 1.0 Å, respectively; the bond angles 120° corresponding to a planar structure. For *N*-tmb the same B–N and B–H distances were taken. The N–C distance was assumed to be 1.48 Å, the C–H distance 1.08 Å. Tetrahedral bond angles were used for the $-CH_3$ groups, with one H above the borazine plane, the other two symmetrically below the plane.

Results for the three lowest singlet and triplet excitation energies for $\pi \rightarrow \pi^*$ excitation are given in Table 1 using three sets of parameters (I to III). The symmetry designations are those of the D_{3h} group for borazine, and the C_{3v} group for *N*-tmb. In set I the "standard" parameters were chosen. In set II the W parameters and in set III the BETA parameters were optimized as mentioned above. (With the set III parameters a doubly degenerate excited state of $\pi \rightarrow \sigma^*$ character moves between the $\pi \rightarrow \pi^*$ states, with energy 6.62 eV for borazine, and 6.39 eV for *N*-tmb.) In the fourth row of the Table results are given according to Peyerimhoff and Buenker[15], who performed *ab initio* SCFMO–CI calculations. All their energies are significantly higher than ours. Recent experimental results

TABLE 1

SINGLET AND TRIPLET EXCITATION ENERGIES ΔE FOR BORAZINE (Bo),
N-TRIMETHYLBORAZINE (N-tmb) AND BENZENE (Be)

Molecule	Ref.	Singlet ΔE (eV)			Triplet ΔE (eV)		
		$^1A_2'$, $^1A_2$	$^1A'_1$, $^1A_1$	$^1E'$, ^1E	$^3E'$, ^3E	$^3A_1'$, $^3A_1$	$^3A_2'$, $^3A_2$
Bo	I	6.36	7.08	7.24	6.00	6.21	6.36
	II	6.29	6.58	6.87	6.05	6.28	6.29
	III	6.27	7.00	7.13	5.89	6.13	6.27
	(f)	6.97	8.75	9.57	7.30	6.46	8.52
	(g)	6.28	6.56	7.55	—	—	—
N-tmb	I	5.81	6.48	6.66	5.49	5.69	5.81
	II	5.75	6.00	6.32	5.53	5.73	5.75
	III	5.75	6.43	6.59	5.40	5.63	5.75
	(h)	5.11	5.46	5.93	5.11	5.11	5.08
Be		4.69	5.50	6.51	4.05	3.41	4.69
		(4.71)	(6.09)	(6.93)		(3.66)	

Parameters:		BETA		W	
	Ref.	B	N	B	N
	I	−14	−20	6.91	12.01
	II	−14	−20	3.5	10
	III	−14.5	−18.8	6.91	12.01

for the singlet excitation energies of borazine according to Kaldor[16] are reproduced in the fifth row. In the last row we give N-tmb results calculated by Perkins and Wall[17] using the PPP method.

Excitation energies for benzene, calculated by our CNDO–CI program with the parameterization as described above, are shown in Fig. 1 for comparison (with the experimental values in parentheses). The benzene wavefunction consisted of 16 configurations, the borazine and N-tmb wavefunctions of 30 configurations. Electric dipole transitions to the A-states of borazine and to the A_2 state of N-tmb are symmetry forbidden.

Calculated oscillator strengths for the $^1E'$ states of borazine are around 1, for the $^1A_1$ and ^1E states of N-tmb these are 0.0001 and 0.48, respectively.

Our calculated singlet excitation energies for N-trimethylborazine are 5.75 to 5.8 eV, about 0.5 eV lower than for borazine. Similarly, the triplet excitation energies for N-tmb (5.4 to 5.5 eV) are about 0.5 eV lower. In a previous paper[6] we calculated 5.6 to 5.7 eV as the lowest triplet excitation energy of borazine, using a PPP–CI method. Experimentally, form the observed quenching of the triplet state of benzene by borazine, it was placed as no higher than 4.9 eV (112 kcal/mole). The observed quenching of the singlet state of benzene by N-tmb using an excitation wavelength of 267 nm (4.65 eV) would suggest that the lowest excited singlet

	Borazine	*Benzene*	*N-trimethylborazine*	
6.3	S (calc.)			
5.9	T (calc.)			
			S (calc.)	5.7
			T (calc.)	5.4
4.9	T (obs.)			
		S (obs.) 4.7	S (obs.)	4.7
		T (obs.) 3.6		

Fig. 1. Excitation energies of borazine and *N*-trimethylborazine (energies in eV; S for singlet T for triplet state).
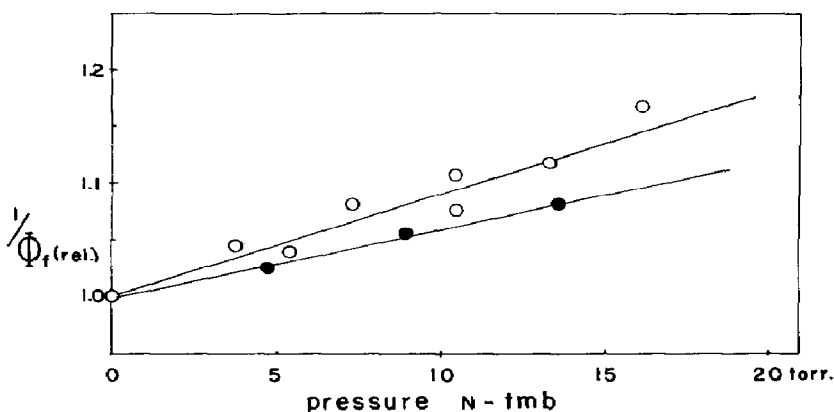

Fig. 2. Variation of the reciprocal of the relative quantum of fluorescence $(1/\Phi_f)$ of benzene excited by 267 nm radiation as a function of *N*-trimethylborazine pressure. ● = 20 Torr benzene; ○ = 10 Torr benzene.

state of *N*-tmb is no higher than 4.65 eV (*vs.* 5.75 calculated). Again a discrepancy between observed and calculated excitation energies is found. However, it should be pointed out that the theory qualitatively agrees with the experiment. A quenching of singlet benzene by borazine (which has the higher excitation energies) has not been observed.

Figure 1 shows the calculated energy levels in eV, with the discrepancies indicated by arrows. Since there is no obvious way of theoretically accounting for such low excitation energies, one may tentatively conclude that the triplet state of borazine and the singlet state of *N*-tmb involved in the quenching do not correspond to a planar ring structure.

RESULTS AND DISCUSSION

The absorption spectrum of *N*-trimethylborazine[18] is very similar to that of borazine and is red shifted ∽ 30 nm compared to that of borazine. Based on the above and on theoretical considerations one would expect the lowest excited states of *N*-tmb to lie at lower energy levels than those of borazine.

The addition of *N*-tmb to benzene excited at 267 nm quenches the fluorescence of benzene and the usual Stern–Volmer relationship $1/\Phi_f$ *vs.* *N*-tmb pressure is obeyed (see Fig. 2). That this effect is due to energy transfer rather than chemical or photochemical reaction is corroborated by the following experiments:

(a) mixtures of *N*-tmb and benzene were exposed in the spectrophotofluorimeter for 1/2 h with the fluorescence intensity being noted at the beginning and end of each run. No change in the fluorescent intensity was observed;

(b) u.v. absorption spectra of pure benzene and pure *N*-tmb were recorded, the gases were then mixed, allowed to stand, and the absorption spectrum of the mixture was obtained. The spectrum of the mixture was simply the superimposed spectra of the two molecules. No new bands were observed;

(c) a procedure similar to (b) above was carried out using i.r. absorption as monitor. Again no new bands were recorded;

(d) a mixture of *N*-tmb–benzene was exposed to 253.7 nm radiation for 4 h. The i.r. absorption spectrum of the mixture was taken prior to and after the photolysis. There was no change in the spectrum.

Since benzene does not exhibit any phosphorescent emission in the gas phase, its triplet state was therefore monitored by the sensitized emission of biacetyl technique[19]. Prior to using this technique the effect of *N*-tmb on biacetyl excited directly at 436, 405 and 365 nm was examined. *N*-tmb had no effect on the emission yield of biacetyl excited at 436 and 405 nm but increases the emission yield of biacetyl at 365 nm (see Fig. 3).
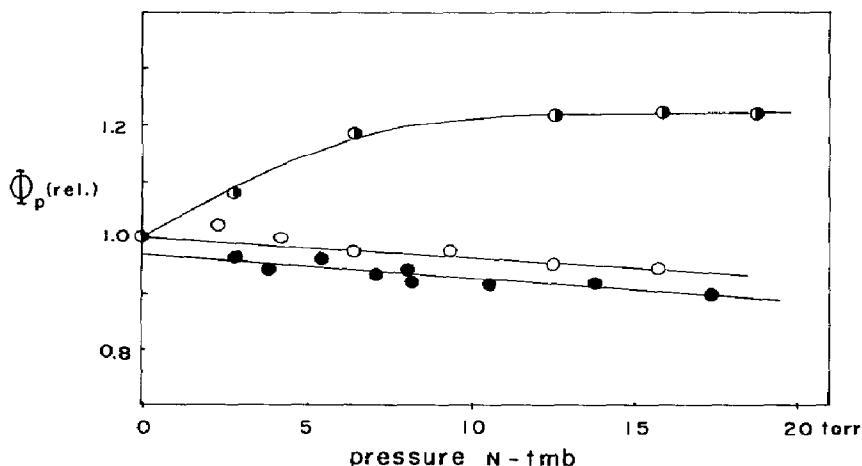

Fig. 3. Variation in the relative quantum yield of phosphorescence of biacetyl (BiA) as a function of *N*-trimethylborazine pressure at three different wavelengths: $\pmb{\mathbb{O}}$ = λ_{ex} 365 nm, BiA = 10.5 Torr; $\circ$ = λ_{ex} 405 nm, BiA = 12.5 Torr; $\bullet$ = λ_{ex} 436 nm, BiA = 10.0 Torr.

This behaviour is typical of molecules which act as vibrational quenchers of excited biacetyl but which do not exhibit electronic energy transfer reactions with biacetyl[20]. Experiments (a), (b), (c) and (d), described above, were carried out for mixtures of N-tmb, biacetyl and benzene and showed that there was no ground state or excited state reaction between the three molecules. N-tmb was added to a mixture consisting of 20 Torr of benzene, excited at 267 nm, and 0.15 Torr of biacetyl. The benzene sensitized emission yield of biacetyl (benzene triplet yield) decreased (see Fig. 4); the decrease in the benzene triplet yield corresponded to the decrease in the benzene singlet yield, and the slope of the line in Fig. 2 is equal to the slope of the line in Fig. 4. Since the benzene triplet is produced from the benzene singlet any process which depletes the yield of benzene singlets will deplete by a corresponding amount the yield of benzene triplets. Thus we conclude that, unlike the case of borazine[6], there is no energy transfer from triplet benzene to N-tmb, or at best that such a process must be very inefficient. The following mechanism is consistent with the known photochemistry of benzene[21] and our experimental observations:

$$\text{B} + hv \rightarrow {}^1\text{B} \tag{Ia}$$
$$ {}^1\text{B} \rightarrow \text{B} + hv^1 \tag{1}$$
$$ {}^1\text{B} \rightarrow \text{B} \tag{2}$$
$$ {}^1\text{B} + \text{N} \rightarrow \text{B} + \text{N}^* \tag{3}$$
$$ {}^1\text{B} \rightarrow {}^3\text{B} \tag{4}$$
$$ {}^3\text{B} + \text{N} \rightarrow \tag{5}$$
$$ {}^3\text{B} \rightarrow \text{B} \tag{6}$$

In the above mechanism B and N represent benzene and N-tmb molecules respectively, superscripts indicate spin multiplicity, hv^1 represents a fluorescence photon
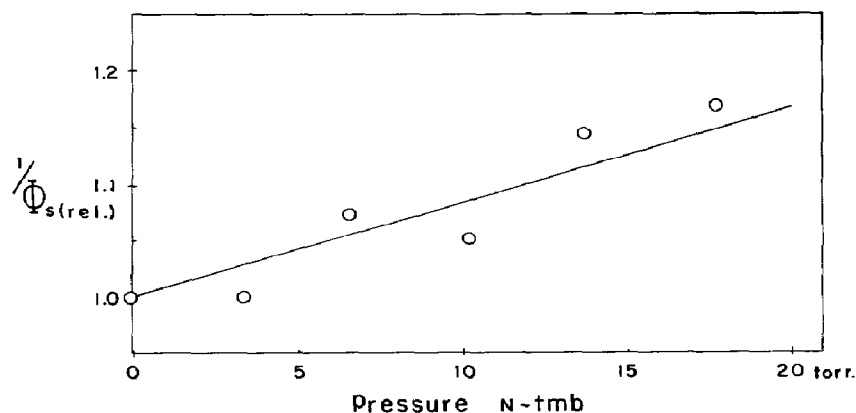

Fig. 4. Variation of the reciprocal of the relative quantum yield of sensitized emission of biacetyl as a function of N-trimethylborazine pressure. Benzene pressure $= 20$ Torr; biacetyl pressure $= 0.18$ Torr. Excitation wavelength $= 267$ nm.

and N* denotes a non-Frank–Condon state of *N*-tmb. Application of the steady state treatment to this mechanism yields:

$$1/\Phi_B = 1 + \frac{k_2}{k_1} + \frac{k_4}{k_1} + \frac{k_3[N]}{k_1} \tag{7}$$

where Φ_B is the fluorescent yield of benzene. Equation (7) predicts a linear relationship between $1/\Phi_B$ and [N] which is observed experimentally. The fluorescence lifetime of benzene has been established by a variety of techniques to be $\simeq 75$ nsec [22–24]. This gives a value for k_1 of 1.33×10^7 sec^{-1}. The slope in Fig. 2 is k_3/k_1 which gives k_3 (calc.) $= 2.16 \times 10^9$ mole^{-1} l sec^{-1}. Since theory predicts the energy of the first singlet of *N*-tmb to lie above the first singlet energy of benzene, the molecule which has been labelled N* in the scheme given above is very likely a non-planar isomer of *N*-tmb, possibly analogous to the isomers of benzene which are produced when that molecule is irradiated in 253 nm region[25, 26].†

Attempts were made to experimentally locate the first singlet and triplet states of *N*-tmb by exciting the molecule directly at 221 nm both in the gas phase and in a glassy matrix (3:1 isopentane–methyl-cyclohexane). In neither case was any fluorescence or phosphorescence observed. Similarly no emission was observed when a mixture of 8 Torr of *N*-tmb and 10 Torr biacetyl was irradiated at 221 nm thus indicating that the reaction:

$$^3N\text{-tmb} + \text{Biacetyl} \rightarrow {}^3\text{Biacetyl} + N\text{-tmb} \tag{8}$$
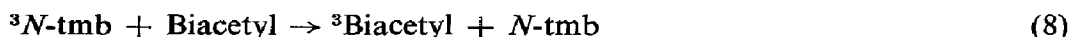
was not occuring.** These findings suggest that both the first excited singlet and triplet (if formed at all) of *N*-tmb must be very short lived. This is in keeping with the known photochemistry of borazine and its derivatives[27], and with the observation that methyl substitution on benzene-like molecules lowers the rates of emission[28].

† It should be noted that an alternative explanation for the quenching of benzene fluorescence is possible. Energy transfer from benzene to a first singlet of *N*-tmb which has energy close to that of benzene may be occurring. An extremely weak absorption band has recently been observed by us at 250–270 nm ($\sim$4.6 eV) for a cyclohexane solution of *N*-tmb. At this time we are not able to unambiguously assign this transition and it could be due to a singlet triplet absorption or an impurity since concentrated solutions are required in order to observe the absorption.
** This experiment is not definitive since biacetyl triplets produced by reaction (8) would be expected to be very hot vibrationally and would dissociate rapidly[21].

REFERENCES

1 T. Brewer and S. H. Jones, *J. Phys. Chem.*, 75 (1971) 3769.
2 J. Lemaire, *J. Phys. Chem.*, 71 (1967) 612.
3 W. Roebke, *J. Phys. Chem.*, 74 (1970) 4198.
4 M. Oertel and R. R. Porter, *Inorg. Chem.*, 9 (1970) 904.
5 G. Lee and R. F. Porter, *Inorg. Chem.*, 6 (1967) 648.
6 W. F. Young, F. Grein, J. Passmore and I. Unger. *Can. J. Chem.* 49 (1971) 233.
7 L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, 82 (1960) 89.
8 W. C. Price, R. D. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 9 (1950) 131.
9 M. E. MacBeath and I. Unger, *Can. J. Chem.*, 48 (1970) 1607 and references therein.
10 J. A. Pople, D. F. Santry and G. A. Segal, *J. Chem. Phys.*, 43 (1965) S129; J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 43 (1965) S136; J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 44 (1966) 3289.
11 J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, 48 (1968) 1807.
12 N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt)*, 13 (1957) 140.
13 K. Weiss, personel communication.
14 J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, 84 (1962) 540.
15 S. D. Peyerimhoff and R. J. Buenker, *Theoret. Chim. Acta*, 19 (1970) 1.
16 A. Kaldor, *J. Chem. Phys.*, 55 (1971) 4641.
17 P. G. Perkins and D. H. Wall, *J. Chem. Soc. (A)*, (1966) 235.
18 C. W. Rector, G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.*, 17 (1949) 460.
19 H. Ishikawa and W. A. Noyes Jr, *J. Chem. Phys.*, 37 (1962) 583.
20 J. G. Calvert and J. N. Pitts, Jr, *Photochemistry*, Wiley, New York, 1966, p. 328.
21 D. Phillips, J. Lemaire, C. S. Burton and W. A. Noyes, Jr, *Adv. Photochem.*, 5 (1968) 329.
22 W. H. Smith, *J. Chem. Phys.*, 54 (1971) 4169.
23 B. K. Selinger and W. R. Ware, *J. Chem. Phys.*, 53 (1970) 3160.
24 C. S. Burton and H. E. Huziker, *J. Chem. Phys.*, 52 (1970) 3302.
25 L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, 90 (1968) 3291.
26 J. N. Pitts, Jr, J. K. Foote and J. K. S. Wan, *Photochem. Photobiol.*, 4 (1965) 323.
27 R. I. Porter, personal communication in press in *J. Am. Chem. Soc.*
28 A. Reiser and L. J. Leyshon, *J. Chem. Phys.*, 56 (1972) 1011.