Photophysical Decay Processes of Toluene in Dilute Solution

By Robert B. Cundall,* Licinio C. Pereira and David A. Robinson

Dept. of Chemistry, University of Nottingham, Nottingham NG7 2RD

Fluorescence yields, fluorescence lifetimes and triplet yields have been measured for dilute solutions of toluene in methylcyclohexane over the temperature range 213 to 333 K. Fluorescence and intersystem crossing for this system are independent of temperature and a radiationless $S_1 \rightarrow S_0$ decay occurs by a single temperature dependent process. The rate constant for this latter process has an activation energy of 0.17 eV and an A factor of 8×10^9 s^{-1}. The data are compared with those for benzene. The differences are explained on the basis of the effect of methyl substitution on the energy and symmetry of aromatic ring.

Toluene is a benzenoid hydrocarbon, a class of molecule for which the sums of the fluorescence and triplet yields are often less than unity. The quantum yield deficit, assigned to a radiationless $S_1 \rightarrow S_0$ process has been measured for [$^2H_6$]-benzene,[1] benzene,[2] *o*-xylene,[3] tetralin,[4] and phenylcyclohexane[5] in the liquid phase and is greater than 30 %, at room temperature, in all cases. For benzene in dilute solution in cyclohexane, internal conversion is responsible for most of the de-excitation of the first excited singlet state (*ca.* 70 %). It is necessary to measure the triplet yield, ϕ_T, fluorescence yield, ϕ_{FM}, and the fluorescence lifetime, τ_M, in order to establish the mechanism for internal conversion. A study of the effect of temperature on these quantities gives information on the characteristics of the radiative and radiationless transitions involved. An extension of the range of temperature into the region below room temperature is particularly important to ascertain whether non-radiative processes are reduced to a limiting minimum.

In this work ϕ_T has been measured in dilute solutions of toluene in methylcyclo-hexane and, combined with ϕ_{FM} and τ_M measured previously, parameters for the different processes for relaxation of the S_1 state evaluated.

EXPERIMENTAL

Triplet yields were determined by the *cis-trans* isomerisation of but-2-ene technique.[6] General techniques and materials were as described previously.

RESULTS

Fluorescence lifetimes obtained [7] between -70 and $+70°C$ are included in fig. 1. The experimental error on the values is believed to be within ± 2 %. The temperature dependence of the measured lifetime is very marked, changing from 20 ns at 65°C to 67 ns at $-70°C$. The plot of τ_M against T tends to a limiting value at low temperature. This is confirmed by the measured fluorescence lifetime of 70 ns observed in methylcyclohexane glass at 77 K. The value of 40 ns for τ_M at room temperature agrees with published measurements of 34 ns in cyclohexane,[9] 33.6 ns in ethanol,[10] 38.4 ns in n-nonane,[11, 12] and 39.2 ns in hexane.[13] Corrections were applied for variation in optical density and refractive index with temperature in the determination of fluorescence yields. The determined values

of ϕ_{FM} as a function of temperature are presented in fig. 2. The value of 0.14 for ϕ_{FM} in methylcyclohexane at 25°C is similar to those of Lumb and Weyl [14] (0.12 in n-hexane) and Berlman (0.14 in cyclohexane,[9] after correction by a factor of 0.83 as suggested in Birks [15] and Demas and Crosby [16]). Our results may not be directly
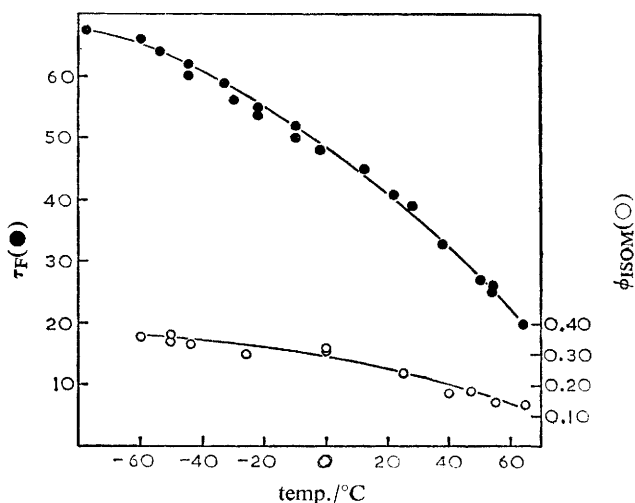

FIG. 1.—Variation of fluorescence lifetime (τ_M) and but-2-ene isomerization yield (ϕ_{ISOM}) with temperature in toluene solutions.
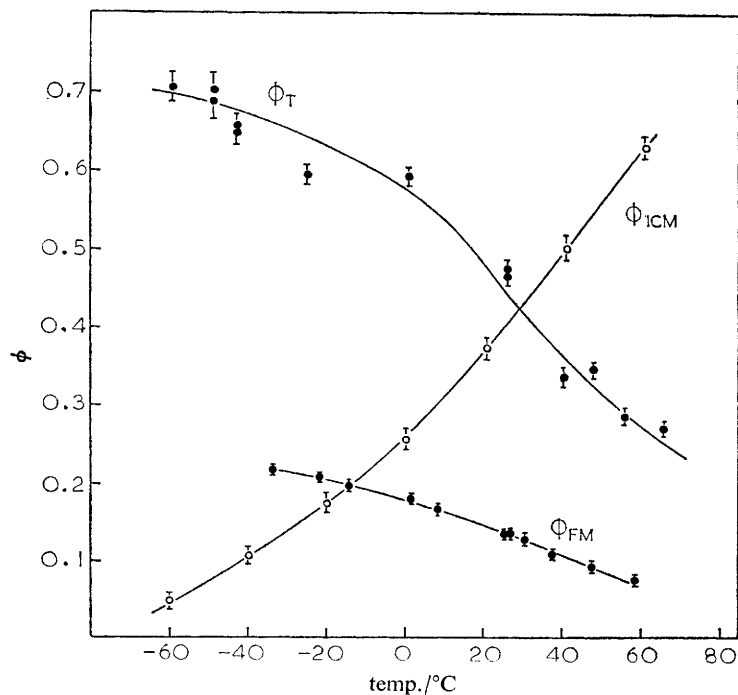

FIG. 2.—Variation of triplet yield (ϕ_T) fluorescence yield (ϕ_{FM}), and internal conversion (ϕ_{ICM}) with temperature for toluene solutions.

comparable with those of other authors, if the fluorescence quantum yield variation with solvent, reported [17] for benzene and [7] for *o*-xylene, tetralin, and benzene, also occurs with toluene.

The refractive index, at 36 000 cm^{-1}, used in the normalisation of the fluorescence yields to a medium of unit refractive index was calculated from the Selmeier-Drude equation using constants determined by Lauer.[18] According to Lumb [19] application of this correction to yields measured in an apparatus with optical arrangement similar to that used in our experiments gives

$$\phi_{FM} = k_{FM}/(k_{FM} + \Sigma k_{IM})$$

where the radiative rate constant k_{FM} in a medium of refractive index n is given by [20] $k_{FM} = k^{\circ}_{FM}n^2$ and Σk_{IM} is the sum of the rate constants for the non-radiative processes involving the first excited singlet state.

Triplet state yields were measured by the addition of sufficient *cis*-but-2-ene to the toluene solution to quench effectively all the triplet states present. The concentrations used were : (i) below room temperature, $\geqslant 0.08$ M, (ii) room temperature, 0.10-0.12 M, and (iii) above room temperature, $\geqslant 0.12$ M. All of the experiments were carried out using the analytically convenient *cis*→*trans* conversion. Cundall and Tippett [21] showed that the probabilities for the olefin triplet relaxing to either of the isomeric forms after sensitization in liquid benzene were equal and the triplet yield is twice the olefin isomer yield. The triplet yield at 20°C is 0.48, similar to the value of 0.53 in cyclohexane at 20°C measured by Sandros [22, 23] using the sensitised phosphorescence of biacetyl. The difference may be real and due to solvent effects, or simply experimental uncertainty. Both of these values are considerably higher than those reported [24, 25] using stilbene isomerization measurements.

The sum of fluorescence and triplet yields is less than unity but greater than that for benzene in methylcyclohexane at any particular temperature. Data for the quantum yield deficient ϕ_{IC} attributed to internal conversion, are also shown in fig. 2.

At the toluene concentrations used only monomeric excited states will participate in decay from the excited singlet state.[13, 26, 27] The fraction of excited singlet molecules in the monomeric form, f_M, may be estimated from a knowledge of the intrinsic monomer lifetime τ_M, the intrinsic excimer lifetime τ_D, the concentration c, and the half value concentration, c_h by the equation

$$f_M = \tau_M c_h/(\tau_M c_h + \tau_D c).$$

Published data show this fraction to be 0.997 at room temperature. In a 0.05 M toluene solution at -60°C 13 % of the excited singlet molecules exist as excimers. Triplet yields measured using 0.01 M toluene solutions at -60°C showed no difference between the two concentrations within experimental error. At the lower concentration and temperature f_M is 0.975 and the view that the decay processes studied arise exclusively from monomeric excited states is supported.

DISCUSSION

Precise values of the energies of electronically excited states of toluene are not available. The 0—0 band for $S_0 \rightarrow S_1$ absorption in n-hexane [28] is at 37 200 cm^{-1}, about 1200 cm^{-1} less than for benzene under the same conditions. The 0—0 band for toluene phosphorescence in various rigid media is between 28 780 and 28 920 cm^{-1} [30-32] and the origin of the $S_0 \rightarrow T_1$ oxygen induced absorption band in chloroform is 29 000 cm^{-1}.[33] Both the $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ separations are 500-700 cm^{-1} below those for benzene under similar conditions. No experimental information

about the second triplet level T_2 of toluene is available though, by analogy with benzene [34-36] and the effect of methyl substitution on the first excited singlet and triplet states, it is expected to have an energy similar to S_1.

Toluene belongs to the C_{2v} point group and in the ground state has A_1 symmetry, the first excited singlet state is B_1, the first triplet state is A_1 and second excited triplet state, which is E_{1u} in benzene, may have A_1 or B_1 symmetry.[37] The effect of methyl substitution on the vibrational modes of the aromatic ring reduces the number of symmetry classes from 12 to 4 and increases the number of vibrations of any class capable of coupling to promote a transition.

On all but seven of the aromic ring vibrations the effect on the energy levels in going from benzene to toluene is slight. The symmetry classes and energies (cm^{-1}) of these 7 vibrations for C_{2v} toluene and D_{6h} benzene are as follows [38] :

	benzene		toluene	
	S_0	S_1		S_0
e_{2u}	405	243	b_2	254
e_{2g}	610	521	a_1	778
a_{2u}	674	513	b_2	497
e_{1g}	848	584	b_2	754
a_{1g}	992	923	a_1	506
e_{1u}	1029	940	b_1	388
e_{2g}	3044	3080	a_1	1299

The lower energies and consequently higher Boltzmann factors for these vibrations will contribute to the differences in photophysical behaviour between benzene and toluene. The energies of the other aromatic ring vibrations are similar in benzene and toluene and cause no difference in photophysical behaviour, other than reducing symmetry.

THE S_0—S_1 RADIATIVE TRANSITION

Methyl substitution of the aromatic chromophore reduces structure, slightly increases extinction coefficients, and gives rise to a prominent 0—0 band in the absorption spectrum, largely by second order inductive changes in the $^1A_{1g}$ and $^1B_{2u}$ states by interaction with the higher $^1E_{1u}$ state.[39]

Using the data of Petruska [39] we calculate that the ground state of toluene is a composite with 0.06 % $^1E_{2g}$ and 0.08 % $^1B_{1u}$ parent state character. The nominal $^1B_{2u}$ state has 0.06 % $^1A_{2g}$, 0.11 % $^1E_{2g}$ and 0.70 % $^1E_{2u}$ character. The $^1A_{1g} \rightarrow {}^1E_{1u}$ transition is allowed and the low but significant $^1E_{1u}$ character of the S_1 state is responsible for observation of the 0—0 transition.

The radiative rate constants for excited singlet monomer, k_{FM}, are calculated from the fluorescence quantum yields and lifetimes, table 1. The slight temperature dependence of k_{FM} arising from the effect upon refractive index disappears when the intrinsic radiative rate constant, k_{FM}°, given by [20] $k_{FM} = k_{FM}^\circ n^2$ is calculated.

TABLE 1.—TEMPERATURE DEPENDENCE OF RATE CONSTANTS FOR PRIMARY PHOTOPHYSICAL PROCESSES FOR TOLUENE IN METHYLCYCLOHEXANE

temp./°C	$10^{-7}k_{ISCM}$/s^{-1}	$10^{-5}k_{ICM}$/s^{-1}	$10^{-6}k_{FM}$/s^{-1}	$10^{-6}k_{FM}^\circ$/s^{-1}
−60	1.08	7.7	4.05	——
−40	1.08	18	4.00	1.71
−20	1.11	33	3.92	1.82
0	1.17	54	3.90	1.75
20	1.15	93	3.79	1.72
40	1.16	160	3.70	1.68
60	1.12	280	——	1.71

INTERSYSTEM CROSSING

The results in table 1 show that the intersystem crossing rate constant k_{ISCM} (ϕ_T/τ_M) is independent of temperature in contrast with benzene where there is a slight temperature dependence.

The rate constants for intersystem crossing at 25°C are 7.7×10^6 s^{-1} for benzene and 1.14×10^7 s^{-1} for toluene. The difference may arise from a greater density of vibrational states in the triplet manifold of correct symmetry for the transition and an increase in the Franck-Condon overlap or state mixing arising from substitution in the benzene ring.

Vibrations of symmetry e_{2g}, e_{1g}, b_{2g} and b_{1g} will promote the S_1—T_2 transitions in benzene. There are no simple vibrations of b_{1g} symmetry in benzene though this can arise from a vibrational combination, e.g., e_{1g}, e_{2g} and S_1—T_2 transition would require an appreciable activation energy. The rate constant k_{ISCM} for benzene, previously fitted to a simple Arrhenius function is better described by $k_{ISCM} = k_{ISCM}^{\circ} + A_{ISCM} \exp(-E_{ISCM}/kT)$ where the temperature independent k_{ISCM}° represents the S_1—T_1 process and the exponential function that for the S_1—T_2 process. A limiting yield of 0.2 for the fluorescence of benzene is achieved at low temperatures [40] and the triplet yield is then probably 0.8. In toluene intersystem crossing does not depend on temperature, transitions from S_1 to T_1 can occur from the lowest vibrational levels of S_1. Transitions to T_2 may require no vibrational coupling, or changes of symmetry from some of the very low energy vibrations may be active in promoting this transition.

INTERNAL CONVERSION, THE RADIATIONLESS $S_1 \rightarrow S_0$ PROCESS

The yield for internal conversion decreases with lowering of temperature and $\phi_{FM} + \phi_T$ tends to unity. A temperature dependent rate constant k_{ICM} is deduced from ϕ_{ICM}/τ_M, table 1. If a simple Arrhenius expression $k_{ICM} = A_{ICM} \exp(-E_{ICM}/kT)$ is valid $E_{ICM} = 0.17(3)$ eV and $A_{ICM} = 8 \times 10^9$ s^{-1}. Comparable values for benzene and toluene deduced from data in the literature, assuming that k_{FM} and k_{ISCM} are temperature independent, are presented in table 2.

TABLE 2.—ARRHENIUS RATE PARAMETERS FOR INTERNAL CONVERSION OF THE FIRST EXCITED SINGLET STATES OF BENZENE AND TOLUENE IN DILUTE SOLUTION

	A_{ICM}/s^{-1}	E_{ICM}/eV mol^{-1}	solvent	ref.
toluene	8×10^9	0.17(3)	methylcyclohexane	this work
	8×10^{10}	0.23	hexane	10*
	4.7×10^9	0.18	hexane	13*
	2×10^{11}	0.25	ethanol	10*
	2.5×10^{12}	0.32	cyclohexane	23
benzene	8×10^{12}	0.325	cyclohexane	2
	1.2×10^{12}	0.35	hexane	10*
	2×10^{12}	0.29	cyclohexane	23

* Values calculated assuming that the temperature dependent part of the non-radiative processes involving the excited singlet state is internal conversion.

The nature of the internal conversion process is uncertain. The possibility of a transition occurring through a valence isomer [41] has been considered and the existence of a reactive diradical " pre-fulvene ", which relaxes to either an aromatic molecule or metastable valence isomer, formed from the S_1 excited state postulated.[42] The

differences in the values of activation energies and A factors for benzene and toluene are larger than expected for internal conversion involving pre-fulvene formation. The activation energy for formation of m-xylene [3] from excited o-xylene (~ 0.4 eV) which almost certainly occurs through a pre-fulvene or benzvalene type structure, compares with values 0.33 and 0.17 eV for the internal conversion of benzene and toluene.

Callomon, Parkin, and Lopez-Delgado [43] suggest that a (σ, π^*) state rather than pre-dissociation, may be involved in the onset of diffuseness in the vibrational structure of the S_1 absorption and fluorescence spectra and non-radiative relaxation in benzene. The absence of appreciable photochemical reaction in benzene after excitation at wavelengths longer than 210 nm is consistent with the observation of a high energy for the isomerization of o-xylene through a metastable intermediate.[3] Of six possible (σ, π^*) states whose energies are unknown (A_{1u}, A_{2u}, or E_{2u}), $^3E_{2u}$ (σ, π^*) is regarded as most probable because of its weak mixing with the $^1B_{2u}$ state and in-sensitivity of the radiationless process to vibrational symmetry. The operator governing the transition is the e_{1g} component of the pure electronic spin orbit coupling Hamiltonian.

Our results for benzene and toluene in solution suggest that a singlet state is involved. The values for the pre-exponential factors, are larger than expected for spin forbidden intersystem crossing and butene isomerization measurements indicate that the transition does not involve triplets with energies greater than 3.4 eV. A similar conclusion can be drawn from the results with biacetyl [22, 23]; in this case the $^3(\sigma, \pi^*)$ triplet energy would need to be below 2.4 eV. There is no evident reason why a triplet state of toluene not readily formed from the $^3A_1$ state, should be so short lived as to be undetectable by triplet scavengers.

The effect of methyl substitution on the (σ, π^*) state is uncertain but is probably more pronounced than for (π, π^*) states since the C—C bond is linked to the σ m.o of the aromatic ring. Changes in the energy of the (σ, π^*) level may be responsible for the lower activation energy for internal conversion in toluene compared with benzene. Further data for internal conversion in other substituted benzenes should give more indication of the critical factors which affect this process.

The postulate of a $^1(\sigma, \pi^*)$ state does not solve the problem of the third process for deactivation of the $^1(\pi, \pi^*)$ states of aromatic hydrocarbons since the nature of the $^1(\sigma, \pi^*) \rightarrow$ ground state transition is unexplained. If a $^1(\sigma, \pi^*)$ state is lower in energy than the $^1(\pi, \pi^*)$ states there may be favourable overlap for internal conversion.

CONCLUSIONS

1. The decay of the first singlet excited state of dilute toluene in methylcyclo-hexane involves fluorescence, intersystem crossing $S_1 \rightarrow T_1$, and internal conversion $S_1 \rightarrow S_0$. The first two processes are insensitive to temperature, but internal conversion is strongly dependent on temperature, tending to zero for $T < -60°C$.

2. A comparison of toluene and benzene shows that:

(a) for $S_0 \rightarrow S_1$ radiative transitions the 0—0 transition is more allowed in toluene due to a significant $^1E_{1u}$ character of S_1.

(b) Intersystem crossing in benzene has a slight temperature dependence, toluene does not. For benzene this is tentatively explained in terms of a temperature independent $S_1 \rightarrow T_1$ transition and a temperature dependent $S_1 \rightarrow T_2$ process. In toluene a $S_1 \rightarrow T_2$ process may be independent of temperature or have an activation energy too low to be apparent in the temperature range studied.

The higher value for k_{ISCM} of toluene, compared with benzene, may arise from a

greater density of vibrational states in the triplet manifold of correct symmetry and state mixing arising from substitution.

(c) For internal conversion, changes in a (σ, π^*) level due to methyl substitution may be responsible for the lower activation energy for this process in excited toluene molecules.

[1] R. B. Cundall, L. C. Pereira, D. A. Robinson, *Chem. Phys. Letters*, 1972, **13**, 253.
[2] R. B. Cundall and D. A. Robinson, *J.C.S. Faraday II*, 1972, **68**, 1145.
[3] R. B. Cundall, D. A. Robinson and A. J. R. Voss, to be published.
[4] R. B. Cundall and L. C. Pereira, *Chem. Phys. Letters*, 1972, **16**, 371.
[5] R. B. Cundall and D. A. Robinson, *J.C.S. Faraday II*, 1972, **68**, 1323.
[6] R. B. Cundall, *Progr. Reaction Kinetics*, 1963, **2**, 165.
[7] R. B. Cundall and L. C. Pereira, *J.C.S. Faraday II*, 1972, **68**, 1152.
[8] R. B. Cundall and G. B. Evans, *J. Sci. Instr. Ser.* 2, 1968, **1**, 305.
[9] I. R. Berlmann, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic Press, New York, 1965) (2nd edn. 1971).
[10] J. R. Greenleaf and T. A. King, *Proc. Int. Conf. Luminescence*, Budapest, 1968, p. 212.
[11] C. D. Amata, M. Burton, W. P. Helman, P. K. Ludwig and S. A. Rodemeyer, *J. Chem. Phys.*, 1968, **48**, 2375.
[12] P. K. Ludwig and C. D. Amata, *J. Chem. Phys.*, 1968, **49**, 326.
[13] J. R. Greenleaf, M. D. Lumb and J. B. Birks, *J. Phys. B.*, 1968, **1**, 1157.
[14] M. D. Lumb and D. A. Weyl, *J. Mol. Spectr.*, 1967, **23**, 365.
[15] J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley-Interscience, New York, 1970).
[16] J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
[17] J. W. Eastman and S. J. Rehfeld, *J. Phys. Chem.*, 1970, **74**, 1438.
[18] J. L. Lauer, *J. Chem. Phys.*, 1948, **16**, 212.
[19] M. D. Lumb, *Rev. Fis. Quim., Eng. Univ. Lourenço Marques*, 1970.
[20] J. B. Birks and D. J. Dyson, *Proc. Roy. Soc. A*, 1963, **275**, 135.
[21] R. B. Cundall and W. Tippett, *Trans. Faraday Soc.*, 1970, **66**, 350.
[22] K. Sandros, *Acta. Chem. Scand.*, 1968, **23**, 2815.
[23] K. Sandros, *Acta. Chem. Scand.*, 1971, **25**, 3651.
[24] V. M. Berenfel'd and V. A. Krongauz, *Teor. i eksp. Khim.*, 1967, **3**(1), 117-118.
[25] V. M. Berenfel'd and V. A. Krongauz, *Izvest. Akad. Nauk. S.S.S.R. Ser. Fiz.*, 1968, **32**(9), 1575-9.
[26] J. B. Birks, *Int. Conf. Luminescence*, Chicago, ed. E. C. Lim, (Benjamin, New York, 1969).
[27] F. Hirayama and S. Lipsky, *J. Chem. Phys.*, 1969, **51**, 1939.
[28] *U.V. Atlas of Organic Compounds* (Butterworths, London, 1966).
[29] S. Stokes, *J. Chem. Phys.*, 1963, **39**, 2309.
[30] Y. Kanda and H. Sponer, *J. Chem. Phys.*, 1958, **28**, 798.
[31] D. S. McClure, *J. Chem. Phys.*, 1949, **17**, 905.
[32] Y. Kanda and R. Shimada, *Spectrochim. Acta*, 1961, **17**, 279.
[33] D. F. Evans, *Nature*, 1956, **178**, 534; *J. Chem. Soc.*, 1957, 1351; 1959, 2753.
[34] S. D. Colson and E. R. Bernstein, *J. Chem. Phys.*, 1965, **43**, 2661.
[35] D. R. Kearns, *J. Chem. Phys.*, 1962, **36**, 1608.
[36] E. R. Bernstein and S. D. Colson, *J. Chem. Phys.*, 1966, **45**, 3873.
[37] G. R. Bailey, C. K. Ingold, H. Poole and C. L. Wilson, *J. Chem. Soc.*, 1948, 406.
[38] E. W. Schmid, J. Brandmuller and G. Nonnenmacker, *Z. Elektrochem.*, 1960, **64**, 726.
[39] J. Petruska, *J. Chem. Phys.*, 1961, **34**, 1120.
[40] J. W. Eastman, *J. Chem. Phys.*, 1968, **49**, 4617.
[41] A. A. Lamola, G. S. Hammond and F. B. Mallory, *Photochem. Photobiol.*, 1965, **4**, 259.
[42] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47. I, Jano and Y. Mori, *Chem. Phys. Letters*, 1968, **2**, 185.
[43] J. H. Callomon, J. E. Parkin and R. Lopez-Delgado, *Chem. Phys. Letters*, 1972, **13**, 125.