Translated from *Uspekhi Khimii*, **55**, 1633-1666 (1986) U.D.C. 535.37

The Luminescence-spectroscopic Properties of Aromatic Radicals and Biradicals

V.A.Smirnov and V.G.Plotnikov

The luminescence-spectroscopic characteristics (the parameters of the absorption and luminescence spectra and the lifetimes and conditions in the observation of luminescence) of the radical products of the photolysis of aromatic compounds, namely abstraction radicals, hydro-radicals, radical-ions, and biradicals, are examined.
The bibliography includes 158 references.

CONTENTS

I.	Introduction	929
II.	General characteristics of the luminescence of polyatomic molecular systems	931
III.	The benzyl radical	933
IV.	Radicals of the benzyl type	936
V.	Hydro-radicals	937
VI.	Heteroradicals	938
VII.	Radical-ions	942
VIII.	Biradicals	

I. INTRODUCTION

The study of the luminescence-spectroscopic properties of polyatomic molecular systems can yield information about the nature and characteristics of the processes involved in the evolution of electronically excited molecular states. A number of problems of practical importance have made such research particularly timely. Among these we may mention the problem of the selection and creation of active media for lasers based on solutions of organic compounds, the development of methods of synthesis of effective organic phosphors and scintillators, the development of systems for the photochemical recording of information, the creation of photostable and radiation-chemically stable systems, etc.

The luminescence-spectroscopic properties of organic molecules have been so far studied in adequate detail and at sufficient depth and the general characteristics of their dependence on the electronic structure of the molecules have been established.[1-5] The principal stages in the development of such investigations are associated with the development of orbital models to describe the electronically excited molecular states, the study of the fine structure of vibronic states, and the development of theoretical ideas about the nature and characteristics of non-radiative conversion processes.

The problem of the determination of a relation between luminescence-spectroscopic properties and the structure of radicals and biradicals derived from organic compounds, which are the primary products of the photochemical and radiation-chemical reactions, has been solved to a much lesser extent. It is essential that they be solved because luminescence (together with EPR) is one of the main procedures whereby the decomposition products of the initial compounds can be detected. Furthermore, a luminescence analysis makes it possible to determine the electronic state in which the decomposition product is formed and hence to understand the mechanism of the process.

We may mention further that at advanced stages of photolytic (or radiolytic) processes, the radicals and biradicals themselves react and the mechanisms of such reactions cannot be understood without the knowledge of the nature of their electronic states.

The present review gives a systematic account of experimental luminescence-spectroscopic data for the radicals, biradicals, and radical-ions derived from aromatic compounds together with their interpretation based on molecular orbital ideas concerning the nature of the electronically excited states and the general characteristics of the processes involved in radiative and non-radiative evolution. Since these ideas and characteristic features have been described in a number of reviews in recent years,[2,4,5] in the present review we will confine ourselves to a brief description.

II. GENERAL CHARACTERISTICS OF THE LUMINESCENCE OF POLYATOMIC MOLECULAR SYSTEMS

The electronic states of radicals and biradicals, like those of molecules, can be classified in terms of the multiplicity of the given states. The electronic states of molecules and biradicals can be of the singlet (S) and triplet (T) types, because these systems contain an even number of electrons. In the majority of molecules, the ground state is of the singlet type (S_0) and the electronically excited state with the lowest energy is of the triplet type. The ground state of the majority of known biradicals is of the triplet type. In conformity with the fact that radicals contain an odd number of electrons, they can have either doublet (D) or quartet (Q) electronic states. The ground state of known radicals derived from organic compounds is of the doublet type (D_0). The lowest electronically excited state in most cases is a D state, while Q states have a higher energy.

Another important characteristic feature of excited states is their orbital nature. Ideas concerning the orbital nature of the electronic transitions and electronically excited states, which have been developed in detail for planar π-electron systems, can be used without any changes for planar radicals and biradicals. Accordingly, $S_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{\pi\pi^*}$, $T_{n\pi^*}$, etc. states are possible in biradicals, whereas $D_{\pi\pi^*}$, $D_{n\pi^*}$, $Q_{\pi\pi^*}$, $Q_{n\pi^*}$ states are possible in radicals. For systems

with a non-planar structure, states of the $n\pi^*$ and $\pi\pi^*$ types cannot, strictly speaking, be separated even in terms of the Condon approximation. However, when the deviations of the geometrical structure of the system from planarity are small or when the π and n orbitals are separated by large energy gaps, the lowest excited states of the system can be approximately classified as $\pi\pi^*$, $n\pi^*$, etc. states.[6] As for molecules, we shall retain designations of the type S_0, T_0, and D_0 for the ground state, because they are adequate for the description of the luminescence-spectroscopic properties (we may note that they can be specified in greater detail for the purpose of the EPR method). Here we shall also not dwell on the differentiation of the $\pi\pi^*$ and $n\pi^*$ states of molecular systems containing l and ν orbitals.[4]

Two principal channels leading to the decomposition of electronically excited states of photostable polyatomic systems are known to exist, namely the photon emission process (luminescence) and non-radiative conversion processes in which the energy of the electronic excitation is converted into the vibrational energy of the nuclei of the system. The probability of both is governed significantly by the orbital nature and multiplicity of the combining states and (especially for the conversion processes) by the transition energy. The general features which determine the probability of the radiative processes and the non-radiative conversion processes as a function of the structure of the molecular system have been to a large extent elucidated for π-electron molecules. Some of them can be transferred to polyatomic radicals and biradicals without significant changes, while others must be somewhat modified taking into account the characteristic features of the structures of these systems and the form of their energy spectra. Here we shall discuss briefly these features emphasising their similarity and differences in the case of molecules, radicals, and biradicals.

(a) Radiative Transitions

The probability of radiative transitions between states of identical multiplicity (fluorescence in the case of emission) is determined by the orbital nature of the transition. Since the expressions for the probability of a radiative transition in molecules, radicals, and biradicals, contain isotypical matrix elements of the dipole moment of the transition, the features found for molecular systems can be used also for radicals and biradicals. In the case of the symmetry-allowed $\pi \rightarrow \pi^*$ transitions ($D_0 \rightarrow D_{\pi\pi^*}$, $T_0 \rightarrow T_{\pi\pi^*}$, $S_0 \rightarrow S_{\pi\pi^*}$) the dipole moment of the transition $e\langle\pi|\mathbf{r}|\pi^*\rangle$ (where $\mathbf{r}$ is the radius-vector of the electron and e its charge) is approximately 1 a.u., the oscillator strength $f \cong 0.1-1$ and the radiative lifetime τ_r of the excited state is $\sim 10^{-8} - 10^{-9}$ s. If the $\pi \rightarrow \pi^*$ transition is symmetry-prohibited, its probability may be found to be non-zero only on going outside the framework of the Condon approximation. The oscillator strength is then reduced to approximately $10^{-3} - 10^{-4}$ and τ_r is increased to $\sim 10^{-6}$ s.[7]

The $n \rightarrow \pi^*$ electronic transition is allowed in terms of the Condon approximation only when the n orbital contains an admixture of an atomic s orbital. The oscillator strength of such a transition is approximately 10^{-3} and $\tau_r \cong 10^{-6}$ s.[8] For the symmetry-prohibited $n \rightarrow \pi^*$ transitions, the oscillator strength is $\sim 10^{-4} - 10^{-5}$ and the lifetime is $\sim 10^{-5}$ s.[9] We may note that, when the steric structure of the system deviates from planarity, the $n\pi^*$ and $\pi\pi^*$ states of the corresponding planar configuration are mixed and the probability of a transition genealogically related to the $n \rightarrow \pi^*$ transition increases.

The probability of multiplicity-prohibited transitions depends on the energy of the spin-orbital coupling of states of different multiplicity, which depends in its turn on the orbital nature of the interacting states. The matrix elements for the spin-orbital coupling of states (of identical orbital nature) of planar molecular systems are small, because they contain only the three-centre one-electron integrals and two-electron integrals. They are estimated as approximately 0.1 cm^{-1}.[10,11] The matrix elements of the spin–orbital coupling of electronic states of different orbital nature (for example, $n\pi^*$ and $\pi\pi^*$) include one-centre one-electron integrals, which are proportional to Z^4, where Z is the effective charge of the atomic nucleus carrying the n electrons. For this reason, the matrix elements $|\langle S_{\pi\pi^*}|\hat{H}_{SO}|T_{n\pi^*}\rangle|$ and $|\langle S_{n\pi^*}|\hat{H}_{SO}|T_{\pi\pi^*}\rangle|$ are relatively large, amounting to approximately 100 cm^{-1}.[12] The matrix elements $|\langle D_{n\pi^*}|\hat{H}_{SO}|Q_{\pi\pi^*}\rangle|$ and $|\langle D_{\pi\pi^*}|\hat{H}_{SO}|Q_{n\pi^*}\rangle|$ can reach values of the same order of magnitude. Such a large difference between the coupling energies of states of the same and different orbital nature and the difference between the probabilities of the multiplicity-allowed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions lead to significant differences between the probabilities of the multiplicity-prohibited $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Since the $T_{n\pi^*}(Q_{n\pi^*})$ states are linked by a comparatively strong spin–orbital coupling with the $S_{\pi\pi^*}(D_{\pi\pi^*})$ states and the probability of the $S_0 \rightarrow S_{\pi\pi^*}(D_0 \rightarrow D_{\pi\pi^*})$ transitions is high, the radiative lifetime of the $T_{n\pi^*}(Q_{n\pi^*})$ states is comparatively short. For molecular systems, it amounts to approximately $10^{-4} - 10^{-3}$ s.[1-4] For reasons which are clear from the foregoing, the radiative lifetime corresponding to the $T_{\pi\pi^*} \rightarrow S_0$ and $Q_{\pi\pi^*} \rightarrow D_0$ transitions is, unlike the previous case, large, amounting to 0.1–10 s.[1-4]

(b) Non-radiative Conversion Processes

Such processes are understood as processes involving the conversion (total or partial) of the electronic excitation energy of the system into vibrational energy. Two types of conversion processes are distinguished in molecular systems: the internal conversion processes ($S-S$ and $T-T$) and intersystem crossing processes: singlet–triplet ($S-T$) and triplet–singlet ($T-S_0$) (degradation processes). The internal conversion processes take place as a consequence of non-adiabatic interaction, while intersystem crossing processes are possible only with participation of spin–orbital coupling.

The probability of internal conversion processes diminishes exponentially with increase of the transition energy.[13] If the transition energy exceeds approximately 2.5 eV, the probability of this process is less than the probability of emission and intersystem crossing. In this case the contribution of the internal conversion process may be neglected in the description of the evolution of the electronically excited state. Such a situation is observed in reality for many polyatomic aromatic molecules in the transition between the lowest excited S_1 state and the ground S_0 state.[14] In molecules containing a comparatively small number of atoms (for example, in benzene and its simplest derivatives) the $\pi \rightarrow \pi^*$ electronic excitation entails an appreciable decrease of the lengths of the C–H bonds whose stretching vibrations play the role of promoting vibrations in the internal conversion process. This leads to such a significant increase of the probability of the internal conversion that it becomes close to the probability of emission and $S-T$ conversion even for transitions with energies exceeding approximately 2.5 eV.[13]

If the transition energy is 1.5–2.5 eV, then the probability of internal conversion for polyatomic molecules and molecules with a comparatively small number of atoms is similar to, as regards order of magnitude, or exceeds the probability of emission and $S-T$ conversion. In this case the internal conversion process competes with other processes leading to the decomposition of the excited state and the role of conversion increases with decrease of the transition energy.

Finally, if the transition energy is less than approximately 1 eV, the main pathway to the decomposition of the excited state becomes the internal conversion process whose rate constant exceeds 10^{11} s^{-1} and it suppresses the emission process. This energy range is characteristic of transitions between the electronically excited states of molecular systems: the very low (approximately 10^{-4}) quantum yields of the fluorescence in the highest excited states are due to this factor (Kasha's rule[1]). The internal conversion process is characterised by an isotope effect (H/D) whose magnitude increases sharply (exponentially) with the increase of the transition energy. If the conversion process competes with the emission process, then the isotope effect affects also the fluorescence yield.[15]

Thus, since, as shown below, the energy of the long-wavelength multiplicity-allowed transition is much smaller for radicals and biradicals than for molecules, the internal conversion process (D_1-D_0 or T_1-T_0) in radicals may compete with the fluorescence process and the fluorescence quantum yield should be sensitive to isotopic H/D substitution; such a situation has indeed been observed experimentally. As for molecules, the yield of the fluorescence from the highest excited states of radicals and biradicals cannot be high.

The probability of the intersystem crossing (degradation) processes depends on the energy of the spin–orbital coupling of the combining states and diminishes exponentially with increase of the transition energy. Since the energy of the spin–orbital coupling of states of different orbital nature is relatively high (see above), the probability of the conversion processes $S_{\pi\pi^*} \rightsquigarrow T_{n\pi^*}$ and $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ is also high and the rate constant is approximately $10^{10}-10^{11}$ s^{-1} for molecules.[2,4] If there is a possibility of processes of this type, the fluorescence quantum yield is very low, (approximately $10^{-3}-10^{-4}$). In conformity with the fact that the spin–orbital coupling of states of an identical orbital nature is weak, the probability of the $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ and $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ conversion processes is appreciably lower and amounts to approximately $10^{7}-10^{9}$ s^{-1}.[2,4] Consequently processes of this kind can compete with the fluorescence process but do not lead to the complete suppression of the latter. The relations between the processes involved in the evolution of excited states described above serve as a basis for a systematic treatment of molecules in terms of their luminescence-spectroscopic properties.[16,17] These features can be transferred without any changes to the $S \rightarrow T$ and $T \rightarrow S$ transitions in biradicals and the $D \rightarrow Q$ transitions in radicals. In particular, it is shown below that, when there is a possibility of intersystem crossing between the excited states of different orbital nature, the fluorescence yield of biradicals is very low.

In the case of intersystem non-radiative transitions to the ground state where the probability of the transition depends on the spin–orbital coupling, the dependence of such probability on the transition energy, which has been studied in detail both experimentally and theoretically for molecular systems,[2,4,18,19] becomes of primary importance. A sharp decrease of the phosphorescence yield with decrease of the energy of the $T \rightarrow S_0$ transition is a consequence of this dependence. Such behaviour also obtains in the case of radicals and biradicals.

Thus one may expect that, if the energies of the excited states of radicals and biradicals are relatively low, the quantum yield of their luminescence should be smaller than for molecules.

III. THE BENZYL RADICAL

The luminescence of radicals of the benzyl type (the triphenylmethyl radical) was first observed in 1944.[20] This radical was formed chemically in solution in the ether–isopentane–alcohol (EPA) mixture; on cooling the solution to 90 K, the absorption and luminescence spectra of the radical were recorded.

The benzyl radical is the simplest odd alternant aromatic hydrocarbon and its structure has been thoroughly investigated.[21] It is illustrated in Fig. 1*a*. Three of the four electrons of the methyl carbon atom are located in the hybrid sp^3 orbitals forming two C–H bonds and one C–C bond; the fourth electron is involved in π conjugation.

Numerous theoretical calculations by various methods[22–25] indicate the occurrence of prohibited electronic transitions in the range 400–500 nm (2.5–3 eV) and of allowed transitions in the ultraviolet region of the spectrum at 250–350 nm (3.5–5 eV).

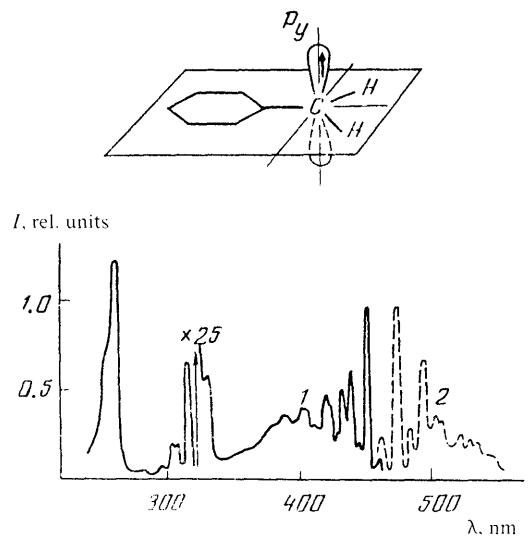


Figure 1. *a*) The structure of the benzyl radical; *b*) the excitation (curve *1*) and luminescence (curve *2*) spectra of the benzyl radical in a vitreous solution at 77 K.[41]

The absorption spectrum (the luminescence excitation spectrum) of the benzyl radical (Fig. 1) has three distinct bands in the region of 450, 320, and 250 cm, which correspond to different electronic transitions. The characteristics of these bands are presented in Table 1. The most probable extinction coefficients are $\varepsilon_1 \cong 50$ litre mol^{-1} cm^{-1} in the long-wavelength band, $\varepsilon_2 \cong (1-5) \times 10^3$ litre mol^{-1} cm^{-1} in the region of 320 nm, and $\varepsilon_3 \cong 10^4$ litre mol^{-1} cm^{-1} in the short-wavelength region. The weak absorption band in

the region of 450 nm was first observed in the photolysis of toluene in solution in the isopentane–methylcyclohexane glass at 77 K.[26] It has been noted[27] that the extinction coefficient of the benzyl radical can vary with solvent polarity: with increase of the polarity, the ratio $\varepsilon_{258}/\varepsilon_{318}$ diminishes: at room temperature it is 4.4 in cyclohexane, 3.3 in alcohol, and 2.5 in water.

Table 1. The maxima (λ, nm) and extinction coefficients (ε, litre mol^{-1} cm^{-1}) of the first, second, and third absorption bands of the benzyl radical.

Matrix	T, K	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	Refs.
Methanol	298	—	—	318	1 500	—	—	[27]
Water	293	450	50	317.5	5 500	258	14 000	[28]
Alcohols	298	—	—	318	1 100	—	—	[29]
Cyclohexane	293	—	—	317	12 000	—	—	[30]
Gas phase	293	—	—	305.3	10^a	253	—	[31]
3-Methylpentane	77	453	30	318	1 100	—	—	[32]
3-Methylpentane	77	450	68	318	920	250	1 900	[33]
3-Methylpentane	77	—	—	318	1 000	258	*	[35]
3-Methylpentane	77	—	—	317.5	12 000	—	—	[37]
2-Methyltetrahydrofuran	77	420	400	320	18 000	—	—	[34]
Ether–isopentane–alcohol	77	—	—	318.2	19 200	—	—	[36]

* $\varepsilon_2/\varepsilon_3$=4,5.

Table 2. The energies of the long-wavelength 0–0 transition (E_{00}) in the benzyl radical.

E_{00}, cm^{-1}	Solvent	State	T, K	Refs.
21 805	—	gas	293	[38]
22 324	—	gas	293	[39]
22 001.7	—	gas	293	[46]
22 002	—	gas	293	[42]
22 001.5	—	gas	293	[41]
21 575	Paraffin	gl	77	[26]
21 552	3-MP	pc	77	[41]
21 647	MCH	pc	88	[43]
21 679	CP	pc	88	[43]
21 685	MCP	pc	88	[43]
21 667	CH	pc	77	[48]
21 662	CH	pc	77	[42]
21 626	n-Pn	pc	77	[44]
22 007	neon	—	4.2	[45]

Notation: gl = vitreous state (glass), pc = polycrystalline state, 3-MP = 3-methylpentane, MCH = methylcyclohexane, CP = cyclopentane, MCP = methylcyclopentane, CH = cyclohexane, and n-Pn = n-pentane.

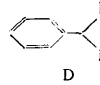
The luminescence of the benzyl radical was first observed in an electric discharge in toluene vapour.[38,39] It was subsequently observed in solutions in glasses[40,41] and in polycrystalline hydrocarbons[42–44] at 77 K and also in a neon matrix at liquid helium temperature.[45] Table 2 presents the energies of the 0–0 transitions of benzyl radicals under different conditions. In the gaseous phase the energy of 22002 cm^{-1} (454.5 nm) appears to be the most likely. The same transition energy has been found also in an inert gas (neon) matrix at 4.2 K. A shift of the 0–0 transition towards lower energies by 300–400 cm^{-1} (~10 nm) has been observed in the condensed phase. Deuteriation of the radical reduces the energy of the 0–0 transition by 90–100 cm^{-1} in both gaseous[48] and condensed[43] phases.

According to theoretical calculations, bands corresponding to two $\pi \rightarrow \pi^*$ electronic transitions, having similar energies but associated with excited electronic levels of different symmetry (A_2 and B_2), should occur in the long-wavelength part of the spectrum; according to some calculations, the lowest excited level has the A_2 symmetry,[49,50] while in other studies the lowest excited state is said to have the B_2 symmetry.[24]

A calculation carried out[23] taking into account only singly excited configurations has led to the conclusion that this state has the B_2 symmetry; allowance for doubly excited configurations lowers the energy of the states with the A_2 symmetry. It is now regarded as established that the lowest excited state has the A_2 symmetry both in solid solutions[51] and in the gaseous phase[47,52] and that the splitting between the excited 1^2A_2 and 2^2B_2 states is 430–485 cm^{-1} for the benzyl radical and 355–370 cm^{-1} for the perdeuteriobenzyl radical.

Thus the 1^2A_2–1^2B_2 optical transition is responsible for the fluorescence of the benzyl radical. This transition is symmetry-prohibited and the extinction coefficient is approximately 50 litre mol^{-1} cm^{-1} (Table 1) and, when account is taken of the fact that the energy of this transition is ~2.5 eV and that the radical contains relatively few atoms, competition is to be expected between the internal conversion and $D_1 \rightarrow D_0$ fluorescence processes. Experimental data have confirmed this: the fluorescence quantum yield of the benzyl radical is 0.39, while deuteriation increases it to 0.47.[53]

Table 3. The fluorescence lifetimes (μs) of the benzyl radicals in glasses at 77 K and in the gas phase.

Radical	Matrix					
	3-MP (Ref.33)	EPA (Ref.43)	3-MP (Ref.54)	methanol (Ref.54)	3-MH (Ref.54)	gas (Ref.56)
	1.44	1.28	1.45	1.5	1.18	0.88
	—	—	1.80	—	—	—
	—	—	1.52	—	—	—
	—	—	1 54	—	—	—
	1.73	—	1.26	—	—	—
	3.21	—	—	—	—	—
	3.26	—	3.22	—	—	—
	3.93	2.97	3.65	3.69	—	1.34

Notation: EPA = ether–isopentane–alcohol and 3-MH = 3-methylhexane; for the significance of the remaining symbols, see the footnote to Table 2.

Table 3 presents the fluorescence lifetimes of the benzyl radical and its deuteriated analogues in glassy solvents at 77 K. These times are of the order of 10^{-6} s, which

corresponds to the symmetry-prohibited $\pi \rightarrow \pi^*$ transition. Estimation of the oscillator strength from the formula $f = 1.5\tau_f^{-1}\nu^{-2}$, where $\nu = 22600$ cm^{-1} is the average transition frequency, yields $f = 8 \times 10^{-4}$;[54] the extinction coefficient estimated from this oscillator strength is 68 litre mol^{-1} cm^{-1}.[33]

The quartet states of the benzyl radical lie above the lowest excited doublet states. Theoretical calculations lead to the following energies of the lowest quartet states of the benzyl radical: 3.65 eV (29450 cm^{-1}),[23] 3.92 eV (31630 cm^{-1}),[24] and 3.89 eV (31380 cm^{-1}),[25] while the energy of the doublet–doublet transition is 2.67 eV (21550 cm^{-1}). The intersystem doublet–quartet conversion $D_{\pi\pi^*}$–$Q_{\pi\pi^*}$ in the benzyl radical cannot compete with the D–D internal conversion process whose rate constant exceeds 10^{11} s^{-1} for the energy of the transition between the states less than 1 eV; for this reason, the Q–D phosphorescence of the benzyl radical has not been observed.

IV. RADICALS OF THE BENZYL TYPE

This Section deals with the properties of aromatic radicals containing an unpaired electron at the α-carbon atom of an aliphatic substituent. These include radicals arising from the decomposition of alkylbenzenes and their homologues—radicals of the diphenylmethane and triphenylmethane series. Their luminescence-spectroscopic characteristics are presented in Table 4. The unpaired electrons in these radicals participate in π conjugation and their lowest electronically excited states are $\pi\pi^*$ states, although they contain an admixture of the $\sigma\pi^*$ states in the case of nonplanar systems.

Table 4. The 0–0 transition energies and the fluorescence lifetimes (τ_f) of radicals of the benzyl type.

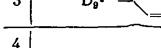
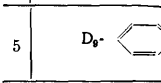
No.	Radical or initial molecule	E_{00}, cm^{-1}	τ_f, s	Solvent	State*	Refs.
1		22 002	—	—	gas	[42]
		21 662	—	CH	pc	[42]
		—	1.45	3-MP	gl	[54]
		—	1.44	Et	gl	[60]
2		21 368	—	Et	gl	[57]
		21 322	—	3-MP	gl	[41]
		21 345	—	n-Hx	pc	[58]
		—	1.19	3-MP	gl	[53]
		—	1.21	EPA	gl	[53]
		—	1.33	Et	gl	[60]
3		—	2.85	3-MP	gl	[33]
4		20 964	—	n-Hx	pc	[58]
		20 942	—	Et	gl	[57]
		—	0.79	EPA	gl	[53]
		—	0.87	3-MP	gl	[33]
		—	0.87	Et	gl	[60]
5		—	1.02	3-MP	gl	[33]
6		21 053	—	n-Hx	pc	[58]
		21 008	—	Et	gl	[57]
		—	0.79	3-MP	gl	[33]
		—	0.8	Et	gl	[60]
		—	0.75	EPA	gl	[53]
7		20 963	—	n-Hx	pc	[58]
		20 202	—	Et	gl	[57]
		—	0.62	3-MP	gl	[33]

Table 4 (contd.).

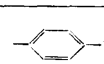
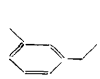
No.	Radical or initial molecule	E_{00}, cm^{-1}	τ_f, s	Solvent	State*	Refs.
8		20 222	—	n-Hx	pc	[58]
9		21 231	—	n-Hx	pc	[58]
		21 008	—	Et	gl	[57]
10		20 141	—	n-Hx	pc	[58]
		20 121	—	Et	gl	[57]
11		21 008	—	n-Hx	pc	[58]
		21 231	—	Et	gl	[57]
12		20 408	—	n-Hx	pc	[58]
		20 408	0.54	3-MP	gl	[33]
		20 408	—	Et	gl	[57]
		—	0.56	EPA	gl	[52]
		—	0.62	Et	gl	[60]
13		20 471	—	n-Hx	pc	[58]
		20 367	0.5	3-MP	gl	[33]
		20 416	—	pc	pc	[59]
		—	0.53	Et	gl	[60]
		—	0.52	EPA	gl	[53]
		—	0.48	3-MP	gl	[54]
14	D_{13}- 	—	0.59	3-MP	gl	[33]
15		20 964	—	n-Hx	pc	[58]
16		20 450	—	n-Hx	pc	[58]
17		19 493	—	n-Hx	pc	[58]
18		20 450	—	n-Hx	pc	[58]
19		19 399	—	n-Hx	pc	[58]
20		19 861 / 19 646	—	n-Hx	pc	[58]
		—	0.35	IP	gl	[60]
		—	0.16	Et	gl	[60]
21		18 921	—	n-Hx	pc	[58]
		18 762	0.24	3-MP	gl	[33]
		—	0.16	Et	gl	[60]
22		21 400	—	3-MP	gl	[61]
23**		21 689	—	—	gas	[62]
24**		21 460	—	—	gas	[62]
25**		21 325	—	—	gas	[62]
26		21 395	—	CP	pc	[63]
		21 400	—	CH	pc	[63]
		21 395	—	MCP	pc	[63]
		21 377	—	MCH	pc	[63]
27		21 144	—	CP	pc	[63]
		21 155	—	CH	pc	[63]
		21 310 / 21 207 / 21 155	—	MCP	pc	[63]
		21 366 / 21 252	—	MCH	pc	[63]

Table 4 (contd.).

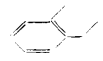
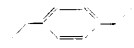
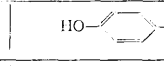
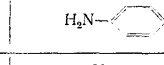
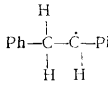
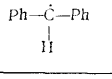
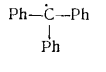
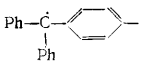
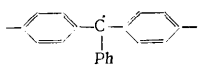
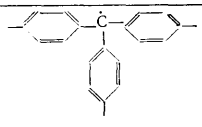
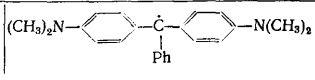
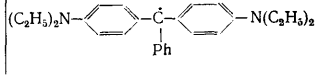
No.	Radical or initial molecule	E_{00}, cm^{-1}	τf, s	Solvent	State*	Refs.
28		21 115 21 105 21 162 21 070	— — — —	CP CH MCP	pc pc pc	[63] [63] [63]
29		20 960 20 940 20 880 20 910 20 803 20 980 20 979	— — — — — — —	MCP MCH CP n-Hx n-Hp 2,2,4-TMP pc	pc pc pc pc pc pc pc	[64] [64] [64] [64] [64] [64] [64]
30		21 354 21 320	— —	MCP MCH	pc pc	[64] [64]
31		21 191 21 269 21 200 21 167 21 165 21 172	— — — — — —	MCP MCH CH n-Hx n-Hp 2,2,4-TMP	pc pc pc pc pc pc	[64] [64] [64] [64] [64] [64]
32		20 835	—	3-MH	gl	[65]
33		21 053	—	3-MH	gl	[65]
34		24 096	—	3-MH	gl	[65]
35		20 120	—	Et	gl	[66]
36		19 050	—	Et	gl	[66]
37		21 500	—	MCH	gl	[67]
38		19 120 — —	— 0.44 0.41	Et Et IP	gl gl gl	[68] [60] [69]
39		19 474 19 410 19 455 19 400 19 342 19 361 19 286 — —	— — — — — — — 0.28 0.33	MCH + IP EPA Et Tol + EPA Bz n-Hx pc Et IP	gl gl gl pc pc pc pc gl gl	[69] [20] [68] [70] [71] [71] [71] [70] [70]
40		16 700	—	Tol + EPA	pc	[70]
41		16 400	—	Tol + TEA	pc	[70]
42		16 400	—	Tol + TEA	pc	[70]
43		17 094 17 182 17 330 17 036	— — — —	Bz n-Hx Et pc	pc pc gl pc	[71] [71] [71] [71]
44		17 035 17 065 17 065 17 575	— — — —	Bz n-Hx Et pc	pc pc gl pc	[71] [71] [71] [71]

Table 4 (contd.).

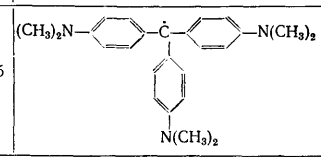
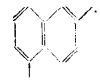
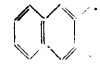
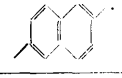
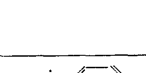
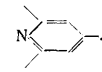
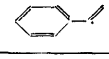
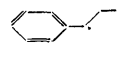
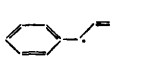
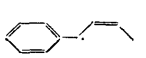
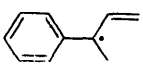
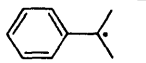
No.	Radical or initial molecule	E_{00}, cm^{-1}	τf, s	Solvent	State*	Refs.
45		16 640 16 680 17 035 16 530	— — — —	Bz n-Hx Et pc	pc pc gl pc	[71] [71] [71] [71]
46		17 012 16 593	— —	n-Hx —	pc gas	[72] [73]
47		16 722 17 017	— —	n-Hx —	pc gas	[72] [73]
48		17 010	—	—	gas	[74]
49		16 760	—	—	gas	[74]
50		16 774	—	—	gas	[74]
51		16 648	—	—	gas	[74]
52		16 648	—	—	gas	[74]
53		16 828	—	—	gas	[74]
54		16 816	—	—	gas	[74]
55		29 573	0.005–0.02	—	gas	[75]
56		— 17 600 17 600 17 520	21×10^{-3} 21.1×10^{-3} 16.8×10^{-3} $2\cdot10^{-3}$	PVA EPA Et CH	gl gl gl l	[76] [77] [77] [78]
57		21 360 21 900	— —	argon 3-MH	— gl	[159] [159]
58		21 900	—	3-MH	gl	[159]
59		17 000	—	n-Pn	pc	[79]
60		21 100	—	MCH + IP	gl***	[80]
61		21 435	—	MCH + IP	gl	[160]

Table 4 (contd.).

No.	Radical or initial molecule	E_{00}, cm^{-1}	τf, s	Solvent	State*	Refs.
62		18 975	—	MCH + IP	gl	[160]
63		18 940	—	MCH + IP	gl	[160]
64		19 085	—	MCH + IP	gl	[160]
65		21 390	—	MCH + IP	gl	[160]

Notation: Et = ethanol, n-Hx = n-hexane, IP = isopentane, n-Hp = n-heptane, TMP = trimethylpentane, Tol = toluene, TEA = triethylamine, Bz = benzene, PVA = poly(vinyl alcohol), and l = liquid state; for the significance of the remaining abbreviations see the footnotes to Tables 2 and 3.

*In the gas phase and for solution No.56 in CH room temperature was used; the temperature for specimens Nos.1–22, 32–47, 56, and 59–66 was 77 K; the temperature for specimen No.57 in argon and No.59 was 20 K; the temperature for specimens Nos.26–31 was 88 K.

**Here R = CH_3, C_2H_5, or n-C_3H_7.

***Thermoluminescence was observed on raising the temperature above 77 K.

It is seen from Table 4 that the introduction of alkyl substituents into the aromatic ring of the benzyl radical reduces the energy of the first excited $D_{\pi\pi^*}$ state; the decrease is 2760 cm^{-1} for hexamethylbenzene. The probability of the radiative transition increases with increase of the number of aliphatic substituents as a consequence of the removal of the symmetry prohibition, which entails an increase of the fluorescence quantum yield[33] and a decrease of the lifetime of the excited state. As for the benzyl radical, the D_1–D_0 internal conversion process competes with the emission process, which is the reason for the effect of isotope substitution on the fluorescence lifetime.

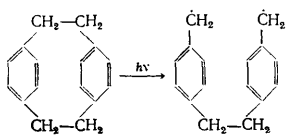
The photolysis of certain compounds (pentamethylbenzene, ethylmethylbenzenes), in solid matrices gives rise to nonequivalent radicals and at least two sets of vibrational bands appear in the luminescence spectrum, while a doublet with a splitting of 100–200 cm^{-1} corresponds to the 0–0 transition (Table 4). However, only one set of vibrational bands is manifested in a gas discharge regardless of the nature of the second alkyl substituent.[62] This suggests that the radical is formed in the discharge as a result of the dissociation of a C–H with minimal energy. The same result has been obtained also in the condensed phase.[63] It has been shown in relation to reactions involving the abstraction of a halogen atom on electron capture in γ-irradiated frozen solutions[61] that, if a radical with an unpaired valence at the β-carbon atom of the alkyl substituent is formed initially, it rearranges to a more stable radical via the dissociation of the α-C–H bond even in a vitreous solution.

An interesting effect of the dissociated halide ion on the luminescence-spectroscopic properties of benzyl type radicals has been observed.[55,57,61,76] A halide ion adjoining the radical induces a bathochromic shift of the spectrum (by 140 cm^{-1} for Cl^{-1}), a change in the vibrational structure of the fluorescence spectrum of the radical, and a decrease of the fluorescence lifetime. New bands due to radical–halide ion charge-transfer complex appear in the absorption spectrum in the region of 265, 362, 413, and 500 nm for F^-, Cl^-, Br^-, and I^- respectively. This effect is absent in polar matrices, since the halide ion is solvated by solvent molecules.

The fluorescence of the diphenylmethyl and triphenylmethyl radicals is displaced to the red region relative to the benzyl radical (Table 4) and the energy of the 0–0 transition for the diphenylmethyl radical (19120 cm^{-1}) is smaller than for the triphenylmethyl radical (19400 cm^{-1}). This is apparently associated with the fact that the diphenylmethyl radical has a structure closer to planarity. It has been noted[70] that methyl substituents in the *para*-position significantly reduce (by 3000 cm^{-1}) the energy of the 0–0 transition for triphenylmethyl radicals. This appears doubtful, since the introduction of even the amino-group shifts the 0–0 transition band by a smaller amount (by 2400 cm^{-1}).[71] In the benzyl radical the methyl, hydroxy-, and amino-substituents in the *para*-position lower the 0–0 transition energy by 250, 1500, and 2500 cm^{-1} respectively (Table 4).

The luminescence of other radicals of the benzyl type is known only for methylnaphthalenes.[72–74] In the photolysis of methylnaphthalene in n-paraffin matrices at 77 K, a luminescence, attributed to methylnaphthyl radicals, appears in the red region.[72] Luminescence attributed to methylnaphthyl radicals has also been observed in an electric discharge in ethyl- and dimethyl-naphthalene vapours.[73,74] Both in the gas discharge and in the condensed phase, the energy of the 0–0 transition is in the region of approximately 17000 cm^{-1} (~590 nm), but in the case of the gas discharge the 0–0 transition of the α-methylnaphthyl radicals has a lower energy than for the β-methylnaphthyl radical, while in solid n-hexane the opposite effect has been observed. The results of theoretical calculations are also ambiguous.[82,83] It may be that the experimental results do not provide an unambiguous answer owing to the inaccurate identification of the products, since the hydronaphthyl radicals, examined below, may be present in the specimen.

An interesting example is provided by the product of the photolysis of (2,2)-*p*-cyclophane in vitreous solutions,[81] which was formed via the reaction



It can exist in two configurations, one of which corresponds to a biradical (a radical pair) and the other to two benzyl radicals linked by the $-CH_2-CH_2-$ group. Together with the band characteristic of the benzyl radical, a structureless band in the range 500–700 nm, attributed to the emission from the radical pair, appears in its luminescence spectrum. On decrease of the viscosity of the matrix, the intensity of the long-wavelength band diminishes, because the conformational transformations of the photolysis product are facilitated.

Table 4 presents data for the acenaphthyl and α-styryl radicals (Nos.59 and 60). These hydrocarbon radicals are not of the benzyl type, because their unpaired electron occupies the sp^2-hybrid orbital of the carbon atom, i.e. is an *n* electron. The lowest excited states of these radicals are therefore $n\pi^*$ states, have a long radiative lifetime,

and their fluorescence quantum yield cannot be high. The luminescence in the range 588–640 nm, manifested in the photolysis of the acenaphthene in n-pentane at 20 K, has been observed[79] and has been attributed to the luminescence of the acenaphthyl radical. A luminescence has been observed[80] which the authors attributed to the α-styryl radical, whose absorption bands are in the region of 320 and 480 nm.[84] However, special investigations[65] failed to confirm these observations. Thus there are at present no reliable data on the luminescence of hydrocarbon radicals from $D_{n\pi^*}$ states owing to its low yield, as in the case of the luminescence observed for the $S_{n\pi^*}$ molecular states.

V. HYDRO-RADICALS

Hydro-radicals are formed by the addition of a hydrogen atom to the aromatic ring of a π-electron molecule. Such radicals have been investigated in detail by EPR.[85] The luminescence of a hydro-radical was first observed in solid solutions.[86,87]

The simplest hydro-radical is the cyclohexadienyl radical arising following the addition of a hydrogen atom to a benzene molecule, its structure being illustrated in Fig. 2. The cyclohexadienyl radical can be regarded as a polyene chain made up of five carbon atoms. Accordingly, its lowest excited state is of the $D_{\pi\pi^*}$ type and the probability of the long-wavelength electronic transition is high.

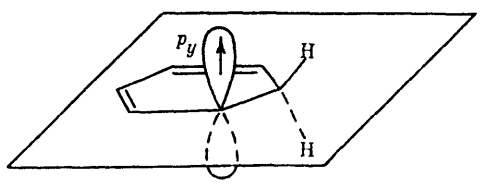
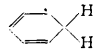
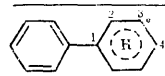
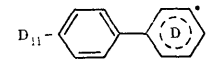
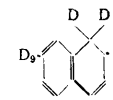
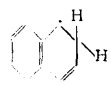
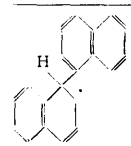
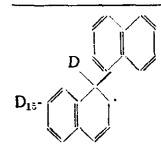


Figure 2. The structure of the cyclohexadienyl radical.

The luminescence of the cyclohexadienyl radical was observed after the laser excitation of crystalline benzene subjected to preliminary radiation by fast electrons at liquid helium temperature.[88] Its fluorescence band has undergone a 2500 cm^{-1} bathochromic shift compared with the benzyl radical. In conformity with the fact that the $D_{\pi\pi^*} \rightarrow D_0$ transition is allowed, the luminescence lifetime is approximately 2 ns (Table 5). The effect of isotope substitution on the fluorescence lifetime indicates the competition of D_1–D_0 internal conversion and emission processes; this is consistent with the finding that the transition energy is approximately 2 eV.

The biphenyl and naphthalene molecules contain non-equivalent carbon atoms; for this reason, the hydro-radicals formed by the addition of hydrogen at these positions have different absorption and luminescence spectra. Different 0–0 transition energies of the hydrobiphenyl radical, with maximum differences of 200 cm^{-1}, correspond to four different isomers.[89] The 0–0 transition energies of the isomers of the hydrobiphenyl radical have been calculated theoretically,[89] the results being in good agreement with experimental data. The 1-hydrobiphenyl radical has the highest energy of the first excited state. This can be accounted for by the fact that there is no interaction between the benzene rings in this radical.

Table 5. The 0–0 transition energies and fluorescence lifetimes of hydro-radicals.

Radical	E_{00}, cm^{-1}	τ_f, ns	Solvent	State	T, K	Refs.
	17 902 18 127	2±1 —	Bz cyclohexa-1,4-diene	pc pc	4.2 4.2	[88] [88]
	18 041	6±1	Bz-d_6	pc	4.2	[88]
	14 943 15 004 15 126 15 142	—	biphenyl	cr	4.2	[89]
	15 029 15 088 15 211 15 228	—	biphenyl-d_{10}	cr	4.2	[89]
	19 530 18 557 18 530 18 484	— 40 120	BA, Et + EE naphthalene naphthalene	gl cr cr	77 4.2 77	[86,87] [90] [91]
	18 653 18 631	—	naphthalene-d_8	cr	4.2	[90]
	21 460	—	BA, Et + EE	gl	77	[86,87]
	14 125 14 094 14 079 14 063	—	naphthalene	cr	4.2	[92]
	14 180 14 150 14 136 14 121	—	naphthalene-d_8	cr	4.2	[92]

Notation: BA = vitreous boric acid, EE = diethyl ether, and cr = crystal; for the significance of the remaining abbreviations, see the footnotes to Tables 2–4.

In the naphthalene molecule there are two non-equivalent positions to which correspond two isomers: the α- and β-hydronaphthyl radicals,[86,87] differing in the absorption, luminescence, and EPR spectra. A photochromic interconversion of the α- and β-radicals has been observed in solid solutions.[86,87]

In the case of a naphthalene single crystal irradiated by fast electrons, the luminescence of only one α-hydronaphthyl radical was observed. In the crystal field the radical occupies two non-equivalent positions; the splitting between the levels amounts to 27 cm^{-1}.[90] Binaphthyl hydro-radicals

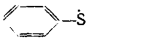
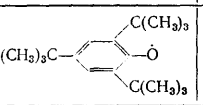
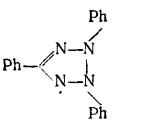
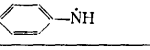
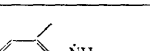
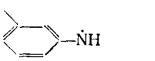
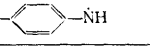
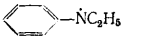
having four non-equivalent positions have also been observed in the single crystal; for this reason four vibrational band progressions are manifested in their fluorescence spectra.

The luminescence properties of a small number of hydroradicals, presented in Table 5, have now been investigated.

VI. HETERORADICALS

Aromatic radicals having an unpaired electron at a heteroatom (heteroradicals) are widely known in the literature and have been investigated both by EPR and by optical absorption spectroscopy. Many of these radicals are stable[93] but the luminescence properties have been investigated only for four types of heteroradicals; thiophenoxy-, phenoxy-, verdazyl, and anilino-radicals (Table 6).

Table 6. The 0–0 transition energies and fluorescence lifetimes of heteroradicals.

No.	Radical	E_{00}^{*}, cm^{-1}	τ_f, ns	Solvent	Refs.
1***		25 000 15 650 15 650 15 650 25 000 25 000	— — $(29.3\pm0.5)\cdot10^3$ $(51.4\pm0.5)\cdot10^3$ $(73\pm5)\cdot10^3$ $(60\pm5)\cdot10^3$	EPA EPA 3-MP EPA 3-MP EPA	[94] [94] [95] [95] [95] [95]
2		25 000	—	Bz	[96]
3		20 600 12 500	— —	Et Et	[99] [99]
4		24 400	12±2	EE	[98]
5		25 000	—	EE	[98]
6		24 700	—	EE	[98]
7		24 300	—	EE	[98]
8		24 000	12±2	EE	[98]

*The fluorescence band maxima are quoted for No.3; the accuracy of the measurement for Nos.4–8 is to within ±300 cm^{-1}.

**Room temperature for No.2 and 77 K (vitreous state) in the other cases.

***Laser generation was achieved with *p*-aminothiophenoxy-radicals (S.Ishizaka and M.Kotani, Chem.Phys.Letters, 1985, 117, 251).

The thiophenoxy-radical (the phenylsulphyl radical). The luminescence of the thiophenoxy-radicals has been investigated after the photolysis of frozen solutions of thiophenol or diphenyl disulphide in EPA or 3-MP at 77 K.[94] A characteristic feature of the luminescence of this radical consists in the fact that emission has been observed in two parts of the spectrum, at 400–500 and 640–700 nm, and is due to two different electronic transitions (D_2–D_0 and D_1–D_0). The lifetime of the red fluorescence is 30–50 μs whilst that of the blue fluorescence is 60–70 ps.[95] The opposite shifts of the red and blue fluorescence bands in different solvents show that the long-wavelength fluorescence corresponds to the $D_{n\pi^*}$–D_0 transition, while the short-wavelength fluorescence corresponds to the $D_{\pi\pi^*}$–D_0 transition. The spectroscopic behaviour of this radical constitutes an instance of the deviation from Kasha's rule, which is rare even for molecules. The deviation is caused by the fact that the rate constant for the D_2–D_1 internal conversion between the $\pi\pi^*$ and $n\pi^*$ levels is small both as a consequence of the orbital nature of the transition and as a consequence of the relatively large transition energy (1.15 eV).

The phenoxy-radical. The luminescence of the 2,4,6-tri-t-butylphenoxy-radical, obtained chemically in solution in benzene, has been observed at room temperature in the range 400–450 nm.[96] However, it is known[97] that, apart from the absorption band in the range 350–400 nm, the phenoxy-radical has a long-wavelength absorption band in the range 500–700 nm and for this reason the fluorescence is apparently caused by a transition of the $\pi\pi^*$ type from the second doublet level. The structure of the phenoxy-radical is illustrated in Fig. 3*a*.

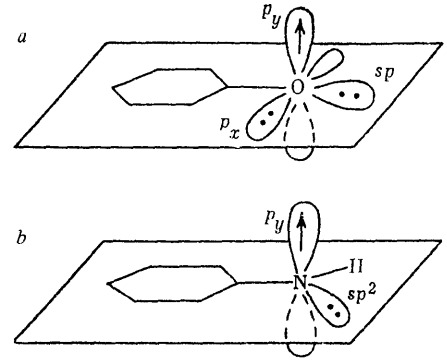


Figure 3. The structure of the phenoxy-radical (*a*) and the phenylaminyl radical (*b*).

The phenylaminyl radical (the anilino-radical). The luminescence of the phenylaminyl radical has been observed after the photolysis of aniline in glassy solutions in ether and MCH at 77 K[98] (Fig. 4). The absorption spectrum of this radical has two bands: a weak band in the region of 400 nm and a more intense band in the region of 300 nm.[100] For the sterically hindered 2,4,6-tri-t-butylphenylaminyl radical, obtained photochemically in solution in hexane at room temperature,[101] the extinction coefficients ε_{400} = 670 litre mol^{-1} cm^{-1} and ε_{300} = 4700 litre mol^{-1} cm^{-1} have been measured. The short luminescence lifetime of the radical (Table 6) made it possible to assign it to a $D_{\pi\pi^*}$–D_0 fluorescence. The phenylaminyl radical is isoelectronic

with the phenoxyradical (Fig. 3b), but absorption and emission by the phenylaminyl radical in the long-wavelength region have not so far been observed.

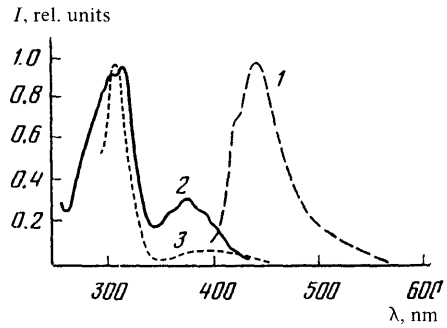


Figure 4. The excitation (curve 2) and luminescence (curve 1) spectra of the phenylaminyl radical in ether at 77 K [98] and the absorption spectrum (curve 3) of the phenylaminyl radical in heptane at room temperature.[101]

The phenoxy- and aminyl radicals are isoelectronic with the benzyl radical (cf. Figs. 1 and 3), but their luminescence properties are significantly different (cf. Figs. 1 and 4). This can be explained by the inclination of the axis of the p_y orbital in the heteroradical relative to the plane of the ring or by its strong conjugation with a carbon atom of the ring and the formation of a structure close to one of the quinonoid type.

The verdazyl radical. The luminescence of the stable triphenylverdazyl radical (Table 6, No. 3) has been investigated in solution in ethanol, isoctane, diisopropyl ether, benzene, and poly(ethylene glycol) at 77 K.[99] The radical, obtained chemically, has two absorption bands with maxima at 400 and 700 nm, to which correspond two luminescence bands in the region of 485 and 800 nm (in ethanol). In the other solvents enumerated above, the short-wavelength luminescence maxima are at 472, 497, and 478 nm respectively, while in acetonitrile the maximum is at 518 nm.

VII. RADICAL-IONS

The luminescence of radical-ions was first observed for the radical-cations of triphenylmethane dyes in vitreous solutions at 77 K.[102] The most intense investigations of the luminescence of the radical-ions of aromatic compounds have been carried out recently. The results are presented in Table 7.

Halogenobenzenes. The luminescence properties of the radical-cations of halogenobenzenes have been studied in detail in the gas phase. The luminescence spectra were then compared with the photoelectron spectra.

Fig. 5 presents the photoelectron spectrum of 1,2,4-trifluorobenzene on irradiation with light corresponding to the He(I) line.[103] The $\tilde{X}$ band in this spectrum corresponds to the formation of a radical-cation in the ground state, while the $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, etc. bands correspond to excited states of the radical-cation. During photoionisation, the radical-cations are formed in an excited state and their transition to the ground state is accompanied by luminescence. The lowest excited state $\tilde{A}$ is located near $\tilde{X}$ and is due to the splitting of the ground state in asymmetric (with not more than a twofold symmetry axis) halogeno- or alkyl-benzenes. The luminescence (doublet–doublet $\pi \rightarrow \pi^*$ fluorescence) of such radical-cations is observed in the $\tilde{B} \rightarrow (\tilde{X}, \tilde{A})$, $\tilde{C} \rightarrow (\tilde{X}, \tilde{A})$, etc. transitions, but is not observed for the $\tilde{A} \rightarrow \tilde{X}$ transition as a consequence of the smallness of the energy gap. The energies of the electronic levels of certain radical–cations are presented in Fig. 6.[104,106] Using the method based on the coincidences of photoelectrons and luminescence photons,[105] it has now been possible to observe luminescence from the $\tilde{C}$ and $\tilde{D}$ levels and to estimate the lifetimes of the highest electronic states, which proved to be several times shorter than for the $\tilde{B}$ level.

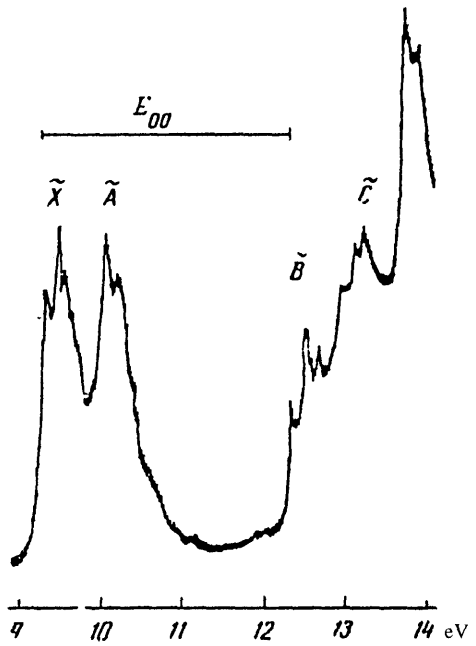


Figure 5. Photoelectron spectrum of 1,2,4-trifluorobenzene.[103]

The fluorescence of the radical-cations derived from halogenobenzenes has also been investigated in inert (argon and neon) matrices at temperatures close to liquid helium temperature.[110,111] In solid argon the excitation and luminescence lines of the radical-cations are broader and are displaced towards the red region relative to the neon matrix.[112,113] This is due to the higher energy of the interaction of the radical-cations with the argon atoms than with the neon atoms. The luminescence spectra of the radical-cations obtained in the neon matrix are close to the spectrum in the gas phase. The vibrational structures of the absorption and luminescence are similar, which indicates only a small change in the geometrical parameters of the system on electronic excitation.

Polarisation studies of the fluorescence of the radical-cations in a neon matrix at helium temperatures have been carried out.[114] For molecules with the D_{6h} and D_{3h} symmetries, where the ground state is degenerate, the luminescence is polarised with a degree of polarisation $P = I_{\parallel}/I_{\perp} = 4/3$. For low symmetry radical-cations, for example 1,2,4,5-$C_6H_2F_4^+$, two sets of vibrational bands are observed in the emission spectrum. One set, with a degree of polarisation $P = 3.0$, corresponds to a transition to the lowest non-degenerate state $\tilde{X}^2B_2$. The second system of bands is displaced to the red region and perpendicular polarisation ($P = 0.5$) predominates in it. This system has been attributed to the transition $\tilde{B}^2B_2$–$\tilde{A}^2B_1$.

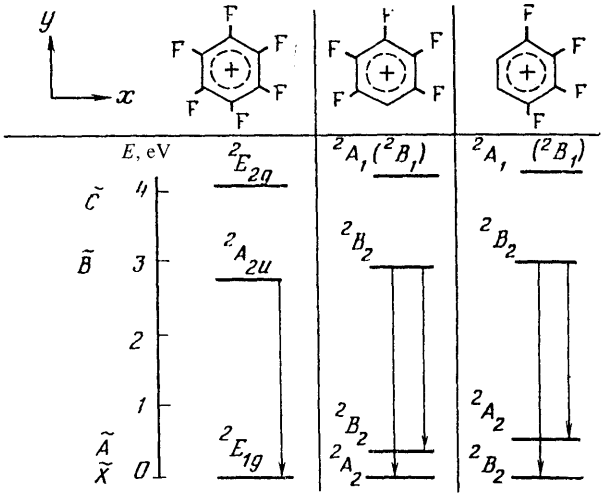


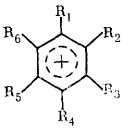
Figure 6. Schematic illustration of the electronic states and the radiative transitions of the radical-cations of fluorobenzenes.[104,106]

The luminescence quantum yield varies from unity in perfluorobenzene to approximately 10^{-2} in difluorobenzene, while the luminescence lifetimes amount to tens of nanoseconds, which shows that the transition of the $\pi \rightarrow \pi^*$ type is allowed.[106] Such behaviour of the luminescence yield can be accounted for by the increase of the $D_{\pi\pi^*}$–D_0 internal conversion rate constant with increase of the number of C–H oscillators in the system.[13] This is one of the causes of the low luminescence yield of the benzene radical-cation (see below).

The rate constant for the non-radiative decomposition of the excited states increases with increased amount of the vibrational energy in the excited state and with decrease of the transition energy.[105,106] Luminescence investigations have established the following features of the vibrational relaxation in the radical-cations of halogenobenzenes:[114,115] (1) the lifetimes of vibrationally excited states are in the range from 200 ps to less than a picosecond; (2) the rate of relaxation increases with increase in the amount of vibrational energy but not monotonically; (3) the rate of vibrational relaxation increases with decrease in the symmetry of the system. Theoretical studies of the Jahn–Teller effect in symmetrical radical-cations of halogenobenzenes have been made.[117–119]

For a long time it has not been possible to observe the luminescence of the benzene radical-cation. The reason for this is that the lowest excited level has the $^2E_{2g}$ symmetry and the radiative transition $^2E_{2g} \rightarrow {}^2E_{1g}$ is prohibited and non-radiative processes predominate. Luminescence has been observed in an argon matrix at 12 K;[111] it is manifested on laser excitation in the form of three weak peaks at 19770, 19140, and 18290 cm^{-1} (at 19860, 19270, and 18400 cm^{-1} for deuteriobenzene). The luminescence can be accounted for by the fact that in an argon matrix the $^2A_{2u}$ and $^2E_{2g}$ excited levels are inverted, which produces the radiative transition $^2A_{2u} \rightarrow {}^2E_{1g}$. The benzene radical-cations are unstable; on irradiation with light from a mercury lamp, they rapidly decompose and their fluorescence vanishes.

Table 7. The 0–0 transition energies and fluorescence lifetimes and quantum yields (q) of the radical-cations of substituted benzene derivatives.



No.	Substituents	E_{00}, cm^{-1}	τ_f, ns	q	Solvent	State*	Refs.
1	R_1=R_2=R_3=R_4=R_5=R_6=H	19 770	—	—	Ar	—	[111]
2	R_1=R_2=R_3=R_4=R_5=R_6=D	19 860	—	—	Ar	—	[111]
3	R_1=R_3=F, R_2=R_4=R_5=R_6=H	— 23 230 — 22 998	<10 <6 <15 <0.1	0.003 0.002 0.006 —	— — — Ne	gas gas gas —	[106] [107] [105] [104]
4	R_1=R_2=R_3=F, R_4=R_5=R_6=H	22 460 22 288 — **	— 51±2 48±4 <15	— — 0.74 0.11	— Ne — —	gas – gas gas	[113] [124] [105] [105]
5	R_1=R_2=R_4=F, R_3=R_5=R_6=H	24 177 24 278 24 274 —	10 10±2 16±5 15	— — 0.05 0.14	Ne — — —	— gas gas gas	[124] [107] [104, 106] [105]
6	R_1=R_3=R_5=F, R_2=R_4=R_6=H	21 774 21 867 21 869 — 21 855	53±2 58±2 57±4 59±3 —	— — 0.87 1.0 —	Ne — — — —	— gas gas gas gas	[124] [107] [104, 106] [105] [119]
7	R_1=R_3=R_5=F, R_2=R_4=R_6=D	21 934 21 831 —	— — 57±2	— — 0.87	— Ne —	gas – gas	[129] [110] [106
8	R_1=R_2=R_3=R_4=F, R_5=R_6=H	23 192 23 277 23 292 — 23 298	44±2 50±2 51±2 50±3 —	— — 0.43 0.90 —	Ne — — — —	— gas gas gas gas	[104] [107] [104, 106[[105] [113]
9	R_1=R_3=R_4=R_5=F, R_2=R_6=H	23 232 23 321 23 324 24 072 24 440 —	43±2 59±2 53±3 — — 50±3	— — 0.52 — — 0.99	Ne — — Ar — —	— gas gas – gas gas	[124] [107] [104, 106] [112] [112] [105]
10	R_1=R_2=R_4=R_5=F, R_3=R_6=H	24 358 24 438 24 443 22 903 23 321 —	30±2 30±2 35±3 — — 32±2	— — 0.21 — — 0.61	Ne — — Ar — —	— gas gas – gas gas	[124] [107] [104, 106] [112] [112] [105]
11	R_1=R_2=R_4=R_5=F, R_3=R_6=D	—	38±3	0.74	—	gas	[105]

Table 7 (contd.).

No.	Substituents	E_{00}, cm^{-1}	τ_f, ns	q	Solvent	State*	Refs.
12	$R_1=R_2=R_3=R_4=R_5=F$, $R_6=H$	23 014	40±2	—	Ne	—	[124]
		33 137	47±2	—	—	gas	[107]
		23 097	51±4	0.52	—	gas	[104, 106]
		22 810	—	—	—	—	[112]
		23 096	—	—	—	gas	[112]
		—	48±3	0.98	—	gas	[105]
13	$R_1=R_2=R_3=R_4=R_5=R_6=F$	21 645	48±2	—	—	gas	[107]
		21 600	54±4	0.41	—	gas	[104, 106]
		21 372	—	—	Ar	—	[112]
		21 606	—	—	—	gas	[112]
		—	49±3	1.0	—	gas	[105]
		21 557	42	—	Ne	—	[124]
		21 617	—	—	—	gas	[128]
14	R_1=Cl, $R_2=R_4=R_6=H$, $R_3=R_5=F$	19 220	6	—	—	gas	[125]
15	R_1=Cl, $R_2=R_3=R_6=F$, $R_4=R_5=H$	21 080	21±3	—	—	gas	[125]
16	R_1=Cl, $R_2=R_4=R_5=F$, $R_3=R_6=H$	21 640	6	—	—	gas	[125]
17	R_1=Cl, $R_2=R_3=R_4=R_5=F$, $R_6=H$	20 600	27±2	—	—	gas	[125]
18	R_1=Cl, $R_2=R_3=R_5=R_6=F$, $R_4=H$	—	52±2	—	—	gas	[125]
19	$R_1=R_3$=Cl, $R_2=R_5=R_6=H$, $R_4=F$	19 940	8±2	—	—	gas	[125]
20	$R_1=R_3$=Cl, $R_2=F$, $R_4=R_5=R_6=H$	18 540	14±3	—	—	gas	[125]
21	$R_1=R_3$=Cl, $R_2=R_4=R_6=H$, $R_5=F$	17 205	8±2	—	—	gas	[125]
22	$R_1=R_4$=Cl, $R_2=F$, $R_3=R_5=R_6=H$	19 620	6	—	—	gas	[125]
23	$R_1=R_3$=Cl, $R_2=R_4=F$, $R_5=R_6=H$	19 855	29±3	—	—	gas	[125]
24	$R_1=R_3$=Cl, $R_2=R_5=F$, $R_3=R_6=H$	18 940	38±2	—	—	gas	[125]
25	$R_1=R_4$=Cl, $R_2=R_5=F$, $R_3=R_6=H$	19 955	6	—	—	gas	[125]
26	$R_1=R_3$=Cl, $R_2=R_4=R_6=F$, $R_5=H$	20 035	38±3	—	—	gas	[125]
27	$R_1=R_3=R_5$=Cl, $R_2=F$, $R_4=R_6=H$	17 080	22±2	—	—	gas	[125]
28	R_1=Cl, $R_2=R_3=R_4=R_5=R_6=F$	19 990	43±3	—	—	gas	[125]
		19 914	37±2	—	Ne	—	[124]
29	$R_1=R_3=R_5$=Cl, $R_2=R_4=R_6=H$	15 265	19	—	Ne	—	[124]
		15 398	—	—	—	—	[129]
30	$R_1=R_3=R_5$=Cl, $R_2=R_4=R_6=F$	16 948	—	—	—	gas	[127]
		16 636	—	—	Ar	—	[126]
		16 785	29±5	—	Ne	—	[126]
		16 950	34±3	—	—	gas	[125]
		—	35±3	0.66	—	gas	[131]
31	$R_1=R_3=R_5$=Cl, $R_2=R_4=R_6=D$	15 270	—	—	Ne	—	[110]
32	$R_1=R_2=R_4=R_5$=Cl, $R_3=F$, $R_6=H$	17 135	—	—	—	gas	[125]
33	$R_1=R_3=R_4=R_5=F$, $R_2=R_6$=Br	14 745	—	—	—	gas	[116]
34	$R_1=R_4$=Br, $R_2=R_3=R_5=R_6=F$	14 870	—	—	—	gas	[116]
35	$R_1=R_3=R_5$=Br, $R_2=R_4=R_6=F$	13 510	—	—	—	gas	[116]
		—	6	0.52	—	gas	[131]
36	R_1=CH_3, $R_2=R_4=R_6=F$, $R_3=R_5=H$	22 636	41±2	—	Ne	—	[124]
37	R_1=CH_3, $R_2=R_3=R_5=R_6=F$, $R_4=H$	23 360	43±2	—	—	gas	[108]

Table 7 (contd.).

No.	Substituents	E_{00}, cm^{-1}	τ_f, ns	q	Solvent	State*	Refs.
38	R_1=CH_3, $R_2=R_3=R_4=R_5=R_6=F$	21 750	40±2	—	Ne	—	[124]
		—	43±2	—	—	gas	[108]
39	R_1=CH_3, $R_2=R_5$=Cl, $R_3=R_4=R_6=H$	19 690	6	—	—	gas	[108]
40	R_1=CH_3, $R_2=R_4=R_6=H$, $R_3=R_5$=Cl	17 490	10±2	—	—	gas	[108]
41	R_1=CF_3, $R_2=R_3=R_5=R_6=F$	23 030	—	—	Ne	—	[113]
		—	45±2	—	—	gas	[108]
42	$R_1=R_4$=CF_3, $R_2=R_3=R_5=R_6=F$	—	11±3	—	—	gas	[108]
43	$R_1=R_3=R_5$=CH_3, $R_2=R_6=H$, $R_4=F$	21 468	0.01	—	Ne	—	[124]
44	$R_1=R_3=R_5$=CH_3, $R_2=R_6=F$, $R_4=H$	22 086	27±2	—	Ne	—	[124]
45	$R_1=R_3=R_5$=CH_3, $R_2=R_4=R_6=F$	21 140	35±2	—	Ne	—	[124]
		—	37±2	—	—	gas	[108]
46	R_1=OH, $R_2=R_3=F$, $R_3=R_4=R_6=H$	23 785	13±3	—	—	gas	[109]
47	R_1=OH, $R_2=R_4=R_6=H$, $R_3=R_5=F$	21 990	36±4	—	—	gas	[109]
		21 908	—	—	Ne		[133]
48	R_1=OH, $R_2=R_3=R_4=F$, $R_5=R_6=H$	23 790	26±3	—	—	gas	[109]
49	R_1=OH, $R_2=R_4=R_5=F$, $R_3=R_6=H$	24 240	6	—	—	gas	[109]
50	R_1=OH, $R_2=R_3=R_5=R_6=F$, $R_4=H$	21 860	41±4	—	—	gas	[109]
		21 798	40	—	Ne	—	[133]
51	R_1=OH, $R_2=R_3=R_4=R_5=R_6=F$	22 410	33±3	—	—	gas	[109]
		22 407	32±2	—	Ne	—	[124, 130]
52	R_1=CN, $R_2=R_3=R_4=R_5=R_6=F$	—	6	—	—	gas	[108]
53	R_1=NH_2, $R_2=R_3=R_4=R_5=R_6=F$	***	—	—	—	gas	[108]
54	R_1=NO_2, $R_2=R_3=R_4=R_5=R_6=F$						
55	R_1=OCH_3, $R_2=R_3=R_4=R_5=R_6=F$						
56	R_1=$COCH_3$, $R_2=R_3=R_4=R_5=R_6=F$						
57	R_1=CHO, $R_2=R_3=R_4=R_5=R_6=F$						

*Liquid helium temperature obtained in inert gas (Ar and Ne) matrices and room temperature was used in the gas phase.

**Fluorescence of the $\tilde{C} \rightarrow \tilde{X}$ transition.

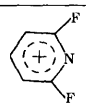
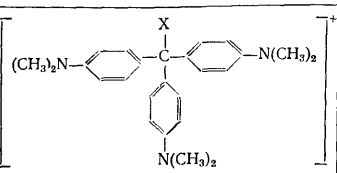
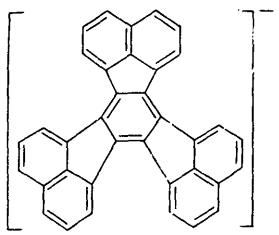
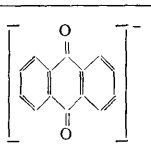
***Only luminescence was noted for the radical-cations Nos. 53–57.

Other substituted benzenes. Apart from halogenobenzenes, the luminescence of radical-cations of halogenated alkylbenzenes, alkylphenols, and alkylbenzonitrile derivatives has now been investigated (Table 7). In addition, the luminescence in the gas phase of the radical-cations of pentafluorobenzene with the following substituents has also been reported: NH_2, NO_2, OCH_3, COOH, and CHO,[108] although spectroscopic data have not been presented. The energies of the 0–0 transitions for the radical-cations of phenols and methyl-substituted benzenes lie in the same range as for halogenobenzenes and the luminescence lifetimes are also similar; there are no quantum yield data. The methyl and hydroxy-substituents influence the spectroscopic characteristics similarly to a fluorine atom but their effect on non-radiative processes is apparently significantly

different. It has been noted[108] that the gas-phase luminescence of the radical-cations of xylenes and pentamethylbenzenes has not been observed. The same communication quotes a list of 42 aromatic compounds for which the luminescence of radical-cations could not be observed in the range 300–850 nm on ionisation of these compounds in the gas phase with an electron beam having an energy of 20–40 eV.

Complex aromatic molecules. The fluorescence of the radical-cations of molecules more complex than those of substituted benzenes has been observed for the leuco-base of Crystal Violet (Table 8). The study of two-step photoionisation and photodissociation reactions of aromatic amines in solutions in ethanol at 77 K led to the observation[102] of the luminescence of the photolysis product, which was modified on replacement of the methyl hydrogen atom in the leuco-base by the OH or CN group. The luminescence band with a maximum near 17000 cm^{-1} and the absorption band at 21000 cm^{-1}, which the authors[102] attributed to the radical-cation of the leuco-base of Crystal Violet, proved to be the most stable under these conditions.

Table 8. The 0–0 transition energies and fluorescence lifetimes and quantum yields of the radical-ions of aromatic compounds.

No.	Radical-ion	E_{00}, cm^{-1}	τ, s	q	Solvent**	Refs.
1		27 158	—	—	Ne	[132]
2		17000*	—	—	Et	[102]
3		15 700 14 500	10^{-11} $2.6\cdot10^{-3}$	10^{-3} 10^{-4}	2-MTHF 2-MTHF	[120] [121]
4		20 000	—	—	Et + KOH	[122]

Notation: 2-MTHF = 2-methyltetrahydrofuran; for the significance of the remaining abbreviations, see the footnotes to Tables 2–5.

*The fluorescence maximum is indicated.
**The helium temperature was used for specimen No.1, while in the remaining cases the temperature was 77 K.

Interesting studies of the luminescence properties of the decacyclene radical-anion (Table 8, No.3) have been carried out.[120,121] The phosphorescence from a quartet level, i.e. a radiative quartet–doublet transition, was observed for the first time in these investigations. The decacyclene radical-anion absorbs intensely in the infrared with a maximum at 4950 cm^{-1} and absorbs in the visible region at 16500 cm^{-1}. If a solution of decacyclene radical-anions in 2-methyltetrahydrofuran (in which neutral molecules are also present) at 77 K is excited with light at a wavelength longer than that of the singlet–singlet absorption of the neutral molecule (E_{S_1} = 21400 cm^{-1}), then fluorescence attributed to the D_2–D_0 transition and phosphorescence with $\tau_p = 2.6 \times 10^{-3}$ s, attributed to the Q_1–D_0 transition of the radical-anion, are observed. The electronic levels of the decacyclene radical-anion are illustrated schematically in Fig.7 and the main spectroscopic characteristics are listed in Table 8 (No.3).

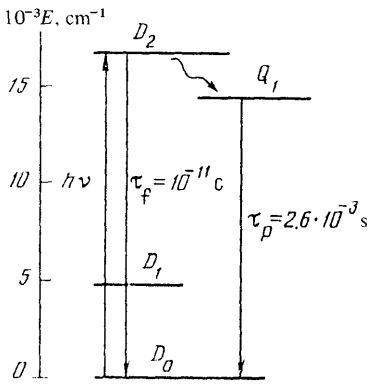


Figure 7. Schematic illustration of the electronic states of the decacyclene radical-anion.[120,121]

The luminescence of the radical-anions has also been observed for anthraquinone.[122] In ethanol to which a 0.1 M KOH solution has been added, anthraquinone is reduced to the radical-anion having a characteristic absorption at 480 nm. A broad luminescence band with a maximum at 540 nm (at room temperature) has been attributed to the fluorescence of the anthraquinone radical-anion, since its excitation spectrum coincided with the absorption spectrum, while the absorption and fluorescence spectra exhibit mirror symmetry. On reducing the temperature to 77 K, the bands undergo a bathochromic shift, which may be associated with dimerisation.

Attention should be drawn to a study[123] whose authors investigated the luminescence of an anthracene solution in a 1:2 mixture of acetic and sulphuric acids. In such a solution it is possible to photoinduce anthracene radical-cations having absorption bands at 315, 352, and 720 nm and an EPR spectrum, which vanish in the dark in the course of several minutes. The luminescence in the range 550–600 nm, excited by light with a wavelength shorter than 500 nm, is correlated with this behaviour. This emission has been attributed to the fluorescence of the anthracene radical-cation. Such interpretation requires further confirmation, because, as noted by the authors

themselves,[123] it has been found that the luminescence spectrum depends on the exciting light wavelength, which means that either different products emit or charge-transfer complexes or exciplexes are formed, so it cannot be regarded as unambiguously established that the observed emission is due to the anthracene radical-cations.

VIII. BIRADICALS

Carbenes. The luminescence of aromatic biradical species was observed for the first time for diphenylcarbene,[134] whose structure is illustrated in Fig. 8*a*.[135] It has been shown by EPR[136] that the benzene rings are located in the same plane and that the angle between them is 140–150°. The unpaired electrons are present in two orbitals, one of which is located in the plane of the rings, while the other is at right angles to this plane. The spins of these electrons are parallel; the ground state of carbene is a triplet, which has been demonstrated by EPR also for other aromatic carbenes.[137] The unpaired electron present in the 2*p* orbital perpendicular to the molecular plane is conjugated to the π-electron system and for this reason the luminescence-spectroscopic properties of diphenylcarbene should resemble those of the benzyl and diphenylmethyl radicals. Indeed the absorption spectrum of diphenylcarbene contains a weak band in the region of 450 nm and a more intense band in the region of 300 nm,[134,138,139] whose extinction coefficients have been estimated[140] as ε_{301} = 2500 litre mol^{-1} cm^{-1} and ε_{465} = 300 litre mol^{-1} cm^{-1}. The long-wavelength absorption is polarised along the line connecting the benzene rings[139] so that one can claim that they correspond to the $T_0 \rightarrow T_{\pi\pi^*}$ transition.

The luminescence spectrum of diphenylcarbene is presented in Fig. 8*a* (curve 2). Since the carbene has a triplet ground state, the observed luminescence has been identified as triplet–triplet fluorescence, which has been confirmed by the mirror symmetry of the absorption spectrum (or the excitation spectrum) and the luminescence spectrum and also by the short luminescence lifetime.[134,135,140]

The electron present in the orbital in the molecular plane is an *n* electron and can participate in $n \rightarrow \pi^*$ transitions. In the spectra of aromatic aldehydes and ketones the absorption bands corresponding to the $n \rightarrow \pi^*$ transitions are in the region of 300–400 nm[1–4] and the extinction coefficient corresponding to the $n \rightarrow \pi^*$ transitions is small (~100 litre mol^{-1} cm^{-1}). In the spectra of carbenes the bands corresponding to the $n \rightarrow \pi^*$ transitions are apparently in the same range 300–400 nm, but the absorption is relatively weak and is masked by the more intense absorption corresponding to the $\pi \rightarrow \pi^*$ transitions, which determine the luminescence properties of aromatic carbenes.

It has not yet been discovered what influence is exerted on the spectroscopic properties of carbenes by the lowest singlet state having the same electronic configuration as the ground triplet state. Direct photolysis of diazodiphenylmethane results in the formation of diphenylcarbene in the lowest singlet state, from which it passes to the ground triplet state after a period of approximately 10^{-11} s.[141] The energy gap S_1–T_0, estimated from the equilibrium constants of the chemical reactions of diphenylcarbene, is only 3–5 kcal mol^{-1}[(1 – 2) × 10^3 cm^{-1}].[141–143] For such a small energy gap, it is naturally impossible to expect an appreciable yield of the phosphorescence corresponding to the S_1–T_0 transition. Theoretical estimation of the S_1–T_0 gap leads to 10–20 kcal mol^{-1} [(3.5–7) × 10^3 cm^{-1}].[144] Such a large discrepancy between the experimental and theoretical values is associated both with the approximate character of the quantum-chemical methods used in the calculation and the fact that the experimental values do not correspond to the equilibrium configuration of the system.

The lifetime of diphenylcarbene at the $T_{\pi\pi^*}$ excited level at 77 K is approximately 10^{-7} s; the introduction of heavy atoms (in the form of ethyl iodide) into the solution does

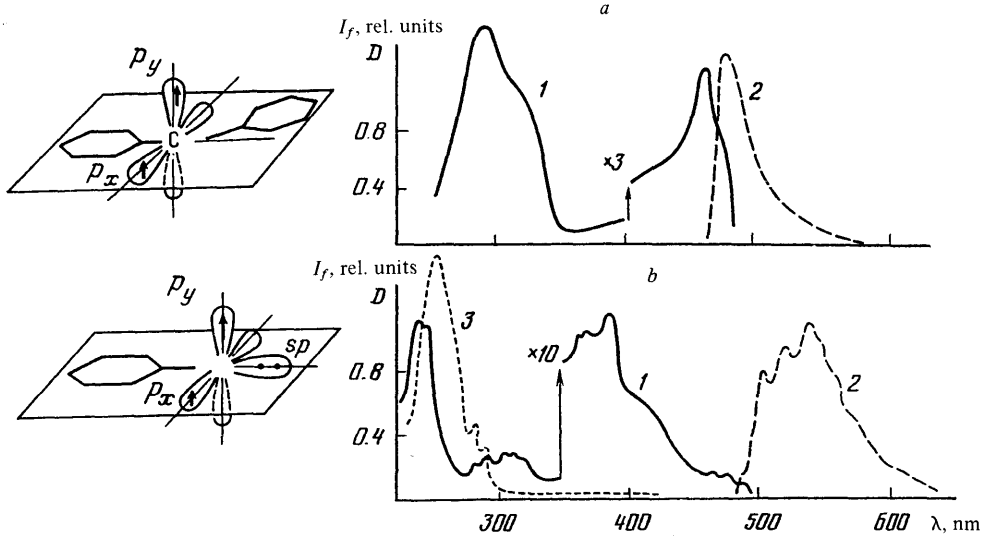


Figure 8. a) The structure of the excitation (curve *1*) and the luminescence (curve *2*) spectra of diphenylcarbene;[134,135] b) the structure and the absorption (curve *1*) and luminescence (curve *2*) spectra of phenylnitrene and the absorption spectrum of the initial phenyl azide (curve *3*).[149]

not entail sharp changes in this value. Hence one may conclude that the probability of the intersystem crossing $T_{\pi\pi^*} \rightarrow S_1$ is small because the energy gap is approximately 2.5 eV and the conversion does not compete with the luminescence.

Fluorescence has been observed also for many *para*-substituted dephenylcarbenes (Table 9). If the substituent is a nitro-group, then there is no fluorescence.[135,158] This finding can be accounted for by the fact that in nitro-derivatives the $S_{n\pi^*}$ states lie below the $T_{\pi\pi^*}$ state and the $T_{\pi\pi^*}$–$S_{n\pi^*}$ conversion suppresses the fluorescence, similarly to the situation which obtains in molecules as a consequence of the $S_{\pi\pi^*}$–$T_{n\pi^*}$ conversion.[2-5]

Table 9. The 0–0 transition energies and the fluorescence lifetimes and quantum yields of the biradicals of aromatic compounds at 77 K.

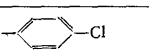
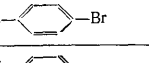
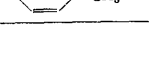
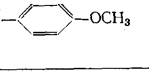
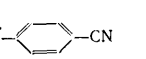
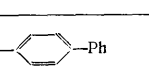
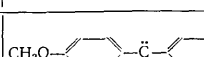
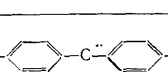
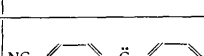
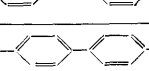
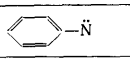
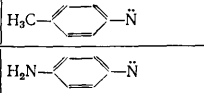
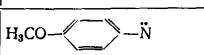
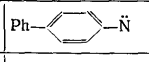
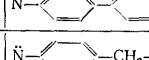
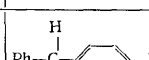
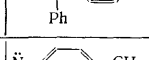
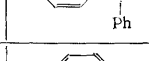
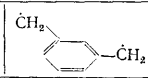
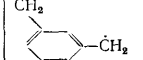
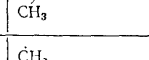
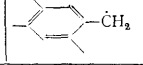
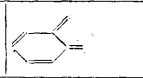
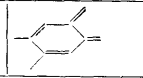
No.	Biradical	E_{00}, cm^{-1}	τ_f, ns	q	Solvent	State	Refs.
1	Ph–Ċ–Ph	20 830	—	—	MCH, EPA	gl	[134, 135]
		—	108	—	MC	gl	[145]
		—	87	0.25	Et	gl	[145]
		—	72	—	Et + EtI	gl	[145]
		—	4*	—	3-MP	gl	[143]
		20 750	123	0.2	MCH	gl	[152]
		20 830	113.6	0.2	Et	gl	[158]
		20 660	94.3	0.32	Et + EtI	gl	[158]
		21 410	73.3	—	MCH + EtI	gl	[158]
2		20 530	—	—	MCH	gl	[135]
3		20 490	—	—	MCH	gl	[135]
4		20 530	—	—	MCH	gl	[135]
5		20 200	—	—	MCH	gl	[135]
		20 450	77.1	0.27	MCH	gl	[158]
		20 200	79.4	0.14	Et	gl	[158]
		20 325	74.5	0.17	Et + EtI	gl	[158]
		20 280	76.4	—	MCH + EtI	gl	[158]
6		19 600	84	0.61	MCH	gl	[158]
		19 600	74.6	0.78	Et	gl	[158]
		19 570	66.4	0.19	Et + EtI	gl	[158]
		19 400	74.8	—	MCH + EtI	gl	[158]
		19 600	91.7	0.51	MCH-*d*	gl	[158]
7		18 020	—	—	MCH	gl	[135]
		17 540	—	—	EE + IA	gl	[146]
8		19 725	—	—	MCH	gl	[135]
		19 840	66.8	0.47	MCH	gl	[158]
		19 880	72.1	0.27	Et	gl	[138]
9		20 080	11.4	0.02	MCH	gl	[158]
		20 040	11.4	0.06	Et	gl	[158]
		20 120	11.7	0.05	Et + EtI	gl	[158]
10		19 000	69.5	0.38	MCH	gl	[158]
		18 870	65.9	0.23	Et	gl	[158]
		18 870	59.6	0.2	Et + EtI	gl	[158]
11		17 240	—	—	Et	gl	[146]
12		20 570	—	—	Et	gl	[149, 153]
13		20 970	—	—	Et	gl	[149, 153]
14		20 330		—	Et	gl	[149]
15		21 460	—	—	Et	gl	[149]

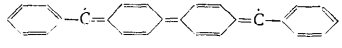
Table 9 (contd.).

No.	Biradical	E_{00}, cm^{-1}	τ_f, ns	q	Solvent	State	Refs.
16		18 800	2	—	Et + EE	gl	[149, 157]
17		16 220	18	—	Et + EE	gl	[157]
18		20 820	—	—	Et	gl	[153]
19		21 300	—	—	Et	gl	[153]
20		20 570	—	—	Et	gl	[153]
21		23 000	7*	—	Bz	l	[151]
22		22 370	—	—	n-Pn	pc	[155]
23		22 100	—	—	n-Pn	pc	[155]
24		22 430	—	—	n-Pn	pc	[155]
25		24 130	—	—	n-Pn	pc	[155]
26		24 100	—	—	n-Pn	pc	[155]
27		23 850	—	—	n-Pn	pc	[155]
28		19 685	—	—	MTHF	gl	[161]

Notation: EtI = ethyl iodide, MCH-*d* = deuteriated MCH, and IA = isopropyl alcohol; for the significance of the remaining abbreviations, see the footnotes to Tables 2–8.

*Room temperature.

Dicarbene (Table 9, No.11), whose luminescence has been observed,[146] constitutes a special case. Formally it should have a sextet ground state, but, as a consequence of π-conjugation, it passes to a triplet state, which corresponds to a quinonoid structure:



For this reason, the luminescence of dicarbene is also $T_{\pi\pi^*} \rightarrow T_0$ fluorescence.

Nitrenes. The electronic structure of nitrenes resembles that of carbenes (Fig. 8*b*). The unpaired electrons are in two 2*p* orbitals, one of which (p_x) is in the molecular plane, while the other (p_y) is perpendicular to this plane. Furthermore, a nitrene contains an unpaired electron pair which

occupies a hybrid *sp* orbital located also in the molecular plane. Aromatic nitrenes are usually formed on photolysis of light-sensitive compounds such as azides and their chemical and certain spectroscopic properties have therefore been surveyed in a number of reviews and monographs,[147,148] but the luminescence properties of nitrenes have been investigated only recently.

The absorption spectrum of phenylnitrene, obtained on photolysis of phenyl azide in a solid solution at 77 K, is illustrated in Fig. 8*b*.[149] As in the spectrum of the benzyl radical, three bands are observed: an intense band in the region of 240 nm, a less intense one in the region of 300 nm, and a weak band in the region of 350–450 nm. As in carbenes, absorption bands in the range 300–400 nm, masked by the absorption due to the $\pi-\pi^*$ transitions, should correspond to the $n \rightarrow \pi^*$ transitions from the p_x and *sp* orbitals. Theoretical estimates of the transition energies in phenylnitrene[150] describe fairly satisfactorily the experimental absorption spectrum.[149–151]

The luminescence spectrum of phenylnitrene is represented by curve *2* in Fig. 8*b*. The fact that the luminescence is due to the corresponding nitrenes has been confirmed by the agreement between the dynamics of the behaviour of the absorption and luminescence spectra, the mirror symmetry of the spectra, and the coincidence of the luminescence excitation spectrum with the absorption spectrum of nitrene.[149] The luminescence lifetime is approximately 10^{-8} s and, when account is taken of the fact that nitrenes have a triplet ground state,[141] one may conclude that the observed emission represents the triplet–triplet fluorescence of nitrenes.

Phenylnitrene is isoelectronic with the benzyl radical (cf. Figs. 1 and 8) and their luminescence-spectroscopic properties are very similar, which significantly distinguishes phenylnitrenes from the phenoxy- and aminyl heteroradicals.

The addition of the methyl group to the *para*-position causes a hypsochromic and not a bathochromic shift of the band corresponding to the 0–0 transition in phenylnitrene, in contrast to aromatic molecules. This phenomenon had been observed earlier for radical-ions and had been explained by the inductive effect.[152] The inductive effect is associated with the redistribution of the electron density in the excited state: when it increases at the site of the addition of the substituent, the transition energy rises, i.e. the hypsochromic shift of the 0–0 transition is observed. When alkyl substituents are introduced into simple aromatic molecules, the hyperconjugation effect, which always leads to a bathochromic shift of the absorption band, usually predominates. In this case the inductive effect predominates in the nitrene.

The luminescence properties of aromatic nitrenes are presented in Table 9; in many respects they resemble those of carbenes. Phenylnitrenes with alkyl electron-donating substituents fluoresce, while electron-accepting substituents (the nitro- and acetyl group) quench the fluorescence of nitrene.[149] As in the case of carbenes, the presence of *n* electrons in the substituent gives rise to the possibility of an intense $T_{\pi\pi^*}-S_{n\pi^*}$ conversion and leads to the quenching of the fluorescence.

It follows from Table 9 that a dinitrene with strong conjugation between the nitrene groups (4,4-dinitrenobiphenyl, Table 9, No. 17) also fluoresces, which is due to its biradical quinonoid structure. In the case of weakly conjugated systems, such as triphenylmethanes, the individual molecular fragments make independent contributions to the absorption spectra. However, the fluorescence quantum yield of dinitrenotriphenylmethane (Table 9, No. 20) is an order of magnitude lower than for the mononitrene (Table 9, No. 19), while the fluorescence of trinitrenotriphenylmethane has not been observed at all.[153] This can be explained both by the mutual quenching of the fluorescence due to the individual fragments, analogous to concentration-induced quenching, and by the formation of states with higher multiplicity.

Xylylenes. Xylylenes constitute yet another class of biradical species for which luminescence has been observed.[154,155] The photolysis of methylated benzenes in MCH at 77 K [154] led to the observation of the luminescence of the product in the range 400–440 nm, which differs from the luminescence of benzyl radicals and was attributed to *ortho*- and *meta*-xylylenes (such products did not appear for toluene and *p*-xylene). Subsequently xylylenes were synthesised chemically and their luminescence, whose characteristics are presented in Table 9 (Nos. 22–27), was investigated.[155] It is noteworthy that only *meta*-xylylene and its methyl derivatives (Table 9, Nos. 22–24) are true biradical species, while *ortho*-xylylenes (or *para*-xylylenes) have the configuration shown in Table 9 (Nos. 25–27). According to theoretical calculations,[155,156] *meta*-xylylenes have a triplet lowest state so that the observed luminescence can be attributed to triplet–triplet fluorescence. Theoretical estimates of the transition energy agree well with experimental data.[155]

The triplet–triplet fluorescence of the biradical benzene isomer 2,4-dimethylenecyclobutane-1,3-diyl, obtained by the photolysis of an azo-compound, has been observed.[161] This biradical is unstable even at 77 K and decomposes spontaneously; its concentration diminishes by a factor of two over a period of 30 h.

---o0o---

The studies of the luminescence-spectroscopic properties of the radical products of aromatic compounds have shown that all the rules of the luminescence-spectroscopic systematic treatment developed in recent years for molecular systems[1–5] are applicable to them. Apart from the general selection rules as regards multiplicity and symmetry, account must be taken of the influence of the orbital nature of the excited states in the radiative and non-radiative transitions. The characteristics of the structure of certain radical compounds and the development of modern research methods (laser excitation, accumulation of spectra) made it possible to observe interesting phenomena in the luminescence spectra; quartet–doublet phosphorescence, the Jahn–Teller effect, fluorescence from the highest excited states, laser generation based on the fluorescence of radicals, and vibrational structure in luminescence spectra. The luminescence of radicals of the benzyl type has been most fully investigated and described in the literature; the luminescence of radical-ions of complex aromatic systems, such as naphthalene, biphenyl, etc., as well as the luminescence properties of the heteroradicals have been studied to a much lesser extent.

REFERENCES

1. M. Kasha, Discuss. Faraday Soc., 1950, 9, 14.
2. S. P. McGlynn, T. Azumi, and M. Konoshita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Izd. Mir, Moscow, 1972, p. 448.
3. R. N. Nurmukhametov, "Pogloshchenie i Lyuminestsentsiya Aromaticheskikh Soedinenii" (The Absorption and Luminescence of Aromatic Compounds), Izd. Khimiya, Moscow, 1971, p. 216.

4. V.G.Plotnikov, Uspekhi Khim., 1980, **49**, 327 (Russ.Chem.Rev., 1980(2)].
5. J.B.Birks (Editor), "Organic Molecular Photophysics", Wiley, London–New York, 1975, pp.415, 645.
6. V.M.Komarov, V.G.Plotnikov, and L.G.Belousova, Optika i Spektrosk., 1970, **29**, 1006.
7. A.C.Albrecht, J.Chem.Phys., 1963, **38**, 354.
8. A.Kaito, M.Hatano, and A.Tajiri, J.Amer.Chem. Soc., 1977, **98**, 5241.
9. J.W.Sidman, Chem.Rev., **58**, 689.
10. H.F.Hameka and L.J.Osterhoff, Mol.Phys., 1958, 1, 358.
11. E.Clementi, Mol.Phys., 1961, **6**, 439.
12. V.G.Plotnikov, Optika i Spektrosk., 1967, **22**, 735.
13. V.G.Plotnikov and B.A.Dolgikh, Optika i Spektrosk., 1977, **43**, 882.
14. V.L.Ermolaev and E.B.Sveshnikova, Acta Phys. Polon., 1968, **34**, 771.
15. A.E.W.Knight and B.K.Selinger, Chem.Phys. Letters, 1971, **12**, 419.
16. R.N.Nurmukhametov, V.G.Plotnikov, and D.N.Shigorin, Zhur.Fiz.Khim., 1966, **40**, 1154 [Russ.J.Phys.Chem., 1966(5)].
17. D.N.Shigorin and V.G.Plotnikov, Dokl.Akad.Nauk SSSR, 1977, **234**, 121.
18. G.W.Robinson and R.P.Frosch, J.Chem.Phys., 1962, **38**, 1187.
19. W.Sibrand, J.Chem.Phys., 1967, **47**, 2411.
20. G.M.Lewis, D.Lipkin, and T.T.Magel, J.Amer. Chem.Soc., 1944, **66**, 1579.
21. K.Higasi, H.Baba, and A.Rembaum, "Quantum Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1967, p.82.
22. H.C.Longuet-Higgins and J.A.Pople, Proc.Phys. Soc., 1955, **A68**, 591.
23. Y.A.Kruglyak and E.V.Mozdor, Theor.Chim.Acta, 1969, **15**, 374.
24. Y.Mori, Bull.Chem.Soc.Japan, 1961, **34**, 1035.
25. J.Baudet and G.Berthier, J.Chim.Phys., 1963, **60**, 1161.
26. G.Porter and E.Strachan, Spectrochim.Acta, 1958, **12**, 299.
27. T.O.Meiggs, L.I.Grossweiner, and S.I.Miller, J.Amer.Chem.Soc., 1972, **94**, 7986.
28. H.C.Christensen, K.Sehested, and E.J.Hart, J.Phys.Chem., 1973, **77**, 983.
29. R.L.McCarthy and A.MacLachlan, Trans.Faraday Soc., 1960, **56**, 1187.
30. R.J.Hugemann and H.A.Schwarz, J.Phys.Chem., 1967, **71**, 2694.
31. F.Bayrakceken and J.E.Nicholas, J.Chem.Soc., 1970, B, 691.
32. E.J.Land, in "Progress in Reaction Kinetics" Vol.3 (Edited by G.Porter), Pergamon Press, Oxford, 1965, p.369.
33. A.B.Bromberg, D.M.Fridrich, and A.C.Albrecht, Chem.Phys., 1974, **6**, 353.
34. W.H.Hamill, J.P.Guarino, M.P.Ronayne, and J.A.Ward, Discuss.Faraday Soc., 1963, **36**, 4323.
35. G.Porter and M.I.Savadatti, Spectrochim.Acta, 1966, **22**, 803.
36. J.E.Hodgkins and E.D.Megarity, J.Amer.Chem. Soc., 1965, **87**, 5322.
37. J.B.Gallivan and W.H.Hamill, Trans.Faraday Soc., 1965, **61**, 1960.
38. H.Schüler and J.Kusjakov, Spectrochim.Acta, 1961, **17**, 356.
39. A.T.Watts and S.Walker, J.Chem.Soc., 1962, 4323.
40. L.Grajcar and S.Leach, Compt.rend., 1961, **252**, 1014.
41. P.M.Johnson and A.C.Albrecht, J.Chem.Phys., 1968, **48**, 851.
42. L.Grajcar and S.Leach, J.Chim.Phys., 1964, **61**, 1523.
43. J.Ripoche, Spectrochim.Acta, 1967, **23A**, 1003.
44. Kh.I.Mamedov and M.M.Khalimov, Optika i Spektrosk., 1978, **44**, 697.
45. C.L.Angell, E.Hedaya, and D.McLeod, J.Amer. Chem.Soc., 1967, **89**, 4214.
46. G.Porter and B.Ward, J.Chim.Phys., 1964, 61, 1517.
47. C.Cossart-Magos and S.Leach, J.Chem.Phys., 1972, **56**, 1534.
48. L.Watmann-Grajcar, J.Chim.Phys., 1969, **66**, 1023.
49. A.Hinchliffe, R.E.Stainbank, and M.A.Ali, Theor. Chim.Acta, 1966, **5**, 95.
50. N.M.Chang, H.H.Jaffe, and C.A.Masmanidis, J.Phys. Chem., 1975, **79**, 1118.
51. D.M.Friedrich and A.C.Albrecht, Chem.Phys., 1974, **6**, 366.
52. C.Cossart-Magos and S.Leach, J.Chem.Phys., 1976, **64**, 4006.
53. T.Okamura and I.Tanaka, J.Phys.Chem., 1975, **79**, 2728.
54. J.D.Laposa and V.Morrison, Chem.Phys., Letters, 1974, **28**, 270.
55. M.Irie, M.Shimizu, and H.Yoshida, J.Phys.Chem., 1976, **80**, 2008.
56. T.Okamura, T.R.Charlton, and B.A.Thrush, Chem.Phys.Letters, 1982, **88**, 369.
57. T.Izumida, T.Ichikawa, and H.Yoshida, J.Phys. Chem., 1980, **84**, 60.
58. C.Branciard-Larcher, E.Migirdicyan, and J.Baudet, Chem.Phys., 1973, **2**, 95.
59. S.Leach and E.Migirdicyan, Chem.Phys.Letters, 1967, **1**, 21.
60. T.Okamuza, K.Obi, and I.Tanaka, Chem.Phys. Letters, 1974, **26**, 218.
61. T.Saito and H.Yochida, Bull.Chem.Soc.Japan, 1974, **47**, 3167.
62. T.F.Bindley, A.T.Watts, and S.Walker, Trans. Faraday Soc., 1962, **58**, 849.
63. A.Pellois, J.-C.Navatte, and J.Ripoche, Compt. rend., 1969, **268b**, 1134.
64. R.Collores, A.Moison-Pellois, and J.Ripoche, Compt.rend., 1970, **270b**, 211.
65. T.Izumida, K.Inoue, S.Noda, and H.Yoshida, Bull.Chem.Soc.Japan, 1981, **54**, 2517.
66. V.A.Smirnov, S.B.Brichkin, and S.P.Efimov, Optika i Spektrosk., 1983, **55**, 773.
67. V.B.Nazarov, V.A.Smirnov, and M.V.Alfimov, Dokl.Akad.Nauk SSSR, 1976, **227**, 908.
68. T.Izumida, Y.Tanabe, T.Ichikawa, and H.Yoshida, Bull.Chem.Soc.Japan, 1979, **52**, 235.
69. S.Leach, in "Luminescence of Organic and Inorganic Materials" (Edited by H.P.Kallman and G.M.Spruch), Wiley, New York–London, 1962, p.176.
70. T.L.Chu and S.I.Weissman, J.Chem.Phys., 1954, 22, 21.
71. D.N.Shigorin and Yu.I.Kozlov, Optika i Spektrosk., 1961, **10**, 600.
72. Kh.I.Mamedov and I.K.Nasibov, Optika i Spektrosk., 1971, **30**, 1052.
73. A.T.Watts and S.Walker, Trans.Faraday Soc., 1964, **60**, 484.

74. A.T.Watts and S.Walker, J.Chem.Soc., 1964, 2348.
75. H.H.Nelson, L.Pasternack, and J.R.McDonald, Chem.Phys., 1983, **74**, 227.
76. H.Hiratsuka, T.Yamazaki, H.Takahashi, T.Hikida, Y.Mori, Chem.Phys.Letters, 1983, **101**, 341.
77. K.Obi and H.Yamaguchi, Chem.Phys.Letters, 1978, **54**, 448.
78. R.Mehnert, O.Brede, and W.Helmstreit, Z.Chem., 1975, **15**, 448.
79. Kh.I.Mamedov and S.G.Shchukyurov, Optika i Spektrosk., 1972, **33**, 1109.
80. B.Brocklehurst, J.S.Robinson, and D.N.Tawn, Chem.Phys.Letters, 1972, **12**, 610.
81. S.Ishikawa, J.Nakamura, and S.Nagakura, Bull. Chem.Soc.Japan, 1980, **53**, 2476.
82. P.Carsky and R.Zahradnik, J.Phys.Chem., 1970, **74**, 1249.
83. P.Jorgensen and J.Bellum, Molec.Phys., 1973, **26**, 725.
84. T.Shida and W.H.Hamill, J.Amer.Chem.Soc., 1966, **88**, 3689.
85. S.Ya.Pshezhetskii, A.G.Kotov, V.K.Milinchuk, V.A.Roginskii, and V.I.Tupikov, "EPR Svobodnykh Radikalov v Radiatsionnoi Khimii" (The EPR of Free Radicals in Radiation Chemistry), Izd.Khimiya, Moscow, 1972.
86. V.A.Smirnov, O.M.Andreev, and M.B.Alfimov, Chem.Phys.Letters, 1974, **28**, 84.
87. O.M.Andreev, V.A.Smirnov, and M.V.Alfimov, Khim.Vys.Energii, 1975, **9**, 512.
88. S.J.Sheng, J.Phys.Chem., 1978, **82**, 442.
89. T.Nakayama, S.J.Sheng, and K.Takagi, J.Phys. Chem., 1981, **85**, 174.
90. C.W.Jacobsen, H.-K.Hond, and S.J.Sheng, J.Phys. Chem., 1978, **82**, 1537.
91. T.Chong, Y.Shibata, and N.Itoh, Phys.Stat.Solid., 1979, **A27**, 599.
92. T.Nakayama and S.J.Sheng, J.Phys.Chem., 1979, **83**, 2869.
93. A.L.Buchachenko and A.M.Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Izd.Khimiya, Moscow, 1973.
94. P.G.Russel, J.Phys.Chem., 1975, **79**, 1353.
95. M.Jinguji, T.Imamura, K.Obi, and I.Tanaka, Chem.Phys.Letters, 1984, **109**, 31.
96. T.Okamura and R.W.Yip, Bull.Chem.Soc.Japan, 1978, **51**, 937.
97. C.D.Cook and B.E.Noreross, J.Amer.Chem.Soc., 1959, **81**, 1176.
98. V.A.Smirnov, S.B.Brichkin, and S.P.Efimov, Khim.Vys.Energii, 1984, **18**, 60.
99. L.N.Ganyuk, N.F.Guba, and V.D.Pokhodenko, Teor.Eksper.Khim., 1982, **18**, 361.
100. E.J.Land and G.Porter, Trans.Faraday Soc., 1963, **59**, 2027.
101. E.J.Land and G.Porter, J.Chem.Soc., 1961, 3540.
102. M.A.Pak, D.N.Shigorin, and G.A.Ozerova, Dokl. Akad.Nauk SSSR, 1969, **186**, 369.
103. M.Allan and J.P.Maier, Chem.Phys.Letters, 1975, **34**, 442.
104. C.Cossart-Magos, D.Cossart, and S.Leach, Molec. Phys., 1979, **37**, 793.
105. J.P.Maier and F.Thommen, Chem.Phys., 1981, **57**, 319.
106. S.Leach, G.Dujardin, and G.Taieb, J.Chim.Phys., 1980, **77**, 705.
107. M.Allan, J.P.Maier, and O.Marthaler, Chem.Phys., 1977, **26**, 131.
108. J.P.Maier, O.Marthaler, and M.Mohraz, J.Chim. Phys., 1980, **77**, 661.
109. J.P.Maier, O.Marthaler, and M.Mohraz, J.Electron Spectr.and Related Phenom., 1980, **19**, 11.
110. V.E.Bondybey, T.A.Miller and J.H.English, J.Chem., Phys., 1979, **71**, 1088.
111. J.H.Miller and L.Andrews, Chem.Phys.Letters, 1980, **72**, 90.
112. V.E.Bondybey, T.A.Miller, and J.H.English, J.Amer.Chem.Soc., 1979, **101**, 1248.
113. T.A.Miller and V.E.Bondybey, J.Chim.Phys., 1980, **77**, 695.
114. V.E.Bondybey, J.Photochem., 1982, **18**, 97.
115. V.E.Bondybey and T.A.Miller, Phys.Rev.Letters, 1980, **44**, 1344.
116. J.P.Maier, O.Marthaler, M.Mohraz, and R.H.Shiby, Chem.Phys., 1980, **47**, 307.
117. C.Cossart-Magos, D.Cossart, and S.Leach, J.Chem. Phys., 1978, **69**, 4313.
118. T.Sears, T.A.Miller, and V.E.Bondybey, J.Chem. Phys., 1980, **72**, 6070.
119. V.E.Bondybey, T.J.Sears, J.H.English, and T.A.Miller, J.Chem.Phys., 1980, **73**, 2063.
120. C.J.M.Brugman, R.P.H.Rettschnick, and G.J.Hojtink, Chem.Phys.Letters, 1971, **8**, 263.
121. C.J.M.Brugman, R.P.N.Rettschnick, and G.J.Hojtink, Chem.Phys.Letters, 1971, **8**, 574.
122. V.Ya.Oginets and V.L.Rapoport, Zhur.Fiz.Khim., 1974, **48**, 729 [Russ.J.Phys.Chem., 1974(3)].
123. G.K.Oster and N.-L.Yang, J.Phys.Chem., 1973, **77**, 2159.
124. V.E.Bondybey, C.Vaughn, T.A.Miller, J.H.English, and R.H.Shiley, J.Amer.Chem.Soc., 1981, **103**, 6303.
125. J.P.Maier, O.Marthaler, M.Mohraz, and R.H.Shiley, Chem.Phys., 1980, **47**, 295.
126. V.E.Bondybey, J.Chem.Phys., 1979, **71**, 3586.
127. T.J.Sears, T.A.Miller, and V.E.Bondybey, J.Amer. Chem.Soc., 1980, **102**, 4864.
128. T.A.Miller, B.R.Zegarski, T.J.Sears, and V.E.Bondybey, J.Phys.Chem., 1980, **84**, 3154.
129. V.E.Bondybey and T.A.Miller, J.Chem.Phys., 1979, **70**, 138.
130. V.E.Bondybey, J.H.English, T.A.Miller, and C.B.Vaughn, J.Phys.Chem., 1981, **85**, 1667.
131. J.P.Maier and F.Thommen, J.Chem.Phys., 1982, **77**, 4427.
132. V.E.Bondybey, J.H.English, and R.H.Shiley, J.Chem.Phys., 1982, **77**, 4826.
133. V.E.Bondybey, G.H.English, T.A.Miller, and R.H.Shiley, J.Chem.Phys., 1983, **78**, 2227.
134. W.A.Gibbons and A.M.Trozzolo, J.Amer.Chem. Soc., 1966, **88**, 172.
135. A.M.Trozzolo and W.A.Gibbons, J.Amer.Chem. Soc., 1967, **89**, 239.
136. E.Wasserman, A.M.Trozzolo, and W.A.Yager, J.Chem.Phys., 1964, **40**, 2408.
137. A.M.Trozzolo, R.W.Murray, and E.Wasserman, J.Amer.Chem.Soc., 1962, **84**, 4990.
138. L.Maritani, S.-I.Murahashi, M.Mishino, K.Kimura, and H.Tsubomura, Tetrahedron Letters, 1966, 373.
139. G.Closs, C.A.Hutchison, and B.E.Kohler, J.Chem.Phys., 1966, **44**, 413.
140. A.M.Trozzolo, W.A.Gibbons, and S.R.Farenholtz, in "Svobodnoradikal'nye Sostoyaniya v Khimii" (Free Radical States in Chemistry) (Edited by L.A.Blyumfel'd and O.N.Molin), Izd.Nauka, Novosibirsk, 1972, p.154.

141. K.B.Eisenthal, N.J.Turro, M.Aikawa, J.A.Bucther, J.C.Dubuy, G.Hefferom, W.H.Hetherington, G.M.Korenowski, and M.J.McAuliffe, J.Amer.Chem. Soc., 1980, **102**, 6563.
142. G.L.Closs and B.E.Rabinow, J.Amer.Chem.Soc., 1976, **98**, 8190.
143. C.Dupuy, G.M.Korenowski, M.McAuliffe, W.M.Hetherington III, and K.B.Eisenthal, Chem. Phys.Letters, 1981, **77**, 272.
144. R.Noyori, M.Yomakawa, and W.Ando, Bull.Chem. Soc.Japan, 1978, **51**, 811.
145. W.R.Ware and P.J.Sullivan, J.Chem.Phys., 1968, **49**, 1445.
146. V.I.Derkach and G.N.Lyalin, Vestnik Leningrad. Gos.Univ., Fiz.-Khim., 1979(4), 48.
147. S.Patai (Editor), "The Chemistry of the Azido Group", Intersci.Publ., New York, 1971.
148. A.V.El'tsov (Editor), "Fotokhimicheskie Protsessy v Sloyakh" (Photochemical Processes in Layers), Izd.Khimiya, Leningrad, 1978, p.114.
149. V.A.Smirnov and S.B.Brichkin, Chem.Phys. Letters, 1982, **87**, 548.
150. H.Kashiwagi, S.Iwata, T.Yamaoka, and S.Nagakura, Bull.Chem.Soc.Japan, 1973, **46**, 417.
151. M.Sumitani, S.Nagakura, and K.Yoshihara, Bull. Chem.Soc.Japan, 1976, **49**, 2995.
152. V.A.Sazhnikov, O.M.Andreev, M.V.Alfimov, and Yu.A.Kruglyak, Dokl.Akad.Nauk SSSR, 1973, **210**, 1375.
153. V.A.Smirnov, S.B.Brichkin, M.V.Alfimov, L.I.Tyltina, and L.F.Avramenko, Khim.Vys. Energii, 1981, **15**, 526.
154. E.Migirdicyan and C.R.Held, Seances Acad.Sci., 1968, **266**, 756.
155. E.Migirdicyan and J.Baudet, J.Amer.Chem.Soc., 1975, **97**, 7400.
156. J.Boudet, J.Chim.Phys., 1971, **68**, 191.
157. S.B.Brichkin, V.A.Smirnov, M.V.Alfimov, T.P.Naydenova, and L.F.Avramenko, J.Photochem., 1980, **12**, 25.
158. Y.Ono and W.R.Ware, J.Phys.Chem., 1983, **87**, 4426.
159. P.M.Johnson, J.Chem.Phys., 1970, 52, 5745.
160. C.A.Backes, B.Bruklehurst, S.Plimbey, J.Stevenson, and D.N.Town, Spectrochim.Acta, 1983, **39A**, 917.
161. G.J.Snyder and D.A.Dougherty, J.Amer.Chem. Soc., 1986, **108**, 299.

State Research and Design Institute for the Paint and Varnish Industry, Moscow

Branch of the Karpov Physicochemical Institute, Obninsk, Kaluga Region