INTRAMOLECULAR ENERGY TRANSFER BETWEEN TRIPLET LEVELS

V. L. ERMOLAEV and A. N. TERENIN

IN previous papers, we have demonstrated and studied the phenomenon of sensitized phosphorescence associated with intermolecular energy transfer from the triplet state of aromatic aldehydes and ketones to molecules of naphthalene, its halogenated derivatives, biphenyl, etc., with the direct transition of the latter molecules to the triplet state, by-passing the singlet state.[1-7] The question arises: if such an energy transfer between triplet levels is possible under the conditions of the weak intermolecular interactions due to the overlap of the peripheral parts of the electron clouds of the two molecules, then this process may take place even better, in principle, between two groups in the same molecule. The difficulty lies in the fact that the finding of autonomous groups in conjugated aromatic molecules and ascribing to them of separate systems of electronic levels is very involved. Nevertheless, with all these reservations, we have examined experimentally the possibility of such an intramolecular transfer between different groups in the same molecule.

With this goal, we chose the carbonyl derivatives of naphthalene and biphenyl, since we had observed <u>intermolecular</u> energy transfer between the triplet levels of, namely, molecules containing the carbonyl group and those of naphthalene and biphenyl. The absorption spectra of these derivatives which we measured showed, in fact, the localization of the primary excitation within the carbonyl group, while the phosphorescence spectra gave evidence of emission from the triplet level of the naphthalene or biphenyl group. We obtained the most distinct results with phenyl-4-biphenylylketone (4-phenylbenzophenone). The absorption spectrum of this compound in an ethanol-ether mixture (2:1) at −196°C is given in Fig. 1, where it is compared with the absorption spectrum of benzophenone under the same conditions (concentration ~ 10^{-2} moles/liter). The absorption spectrum of phenylbiphenylylketone shows two bands: the first is in the long-wavelength region $26000 - 30000$ cm^{-1} ($\epsilon = 100 - 400$), and the second starts at 30000 cm^{-1} and continues toward shorter wavelengths ($\epsilon = 10000 - 20000$). The first band is very similar in its position and intensity to the first band of benzophenone. In frozen solutions, a structure is visible which is very similar to that observed for benzophenone (Fig. 1). This similarity in spectral distribution and structure of the first band is further supported by their identical behavior on going from an inert solvent (petroleum ether) to a hydrogen-bonding solvent (ethanol-
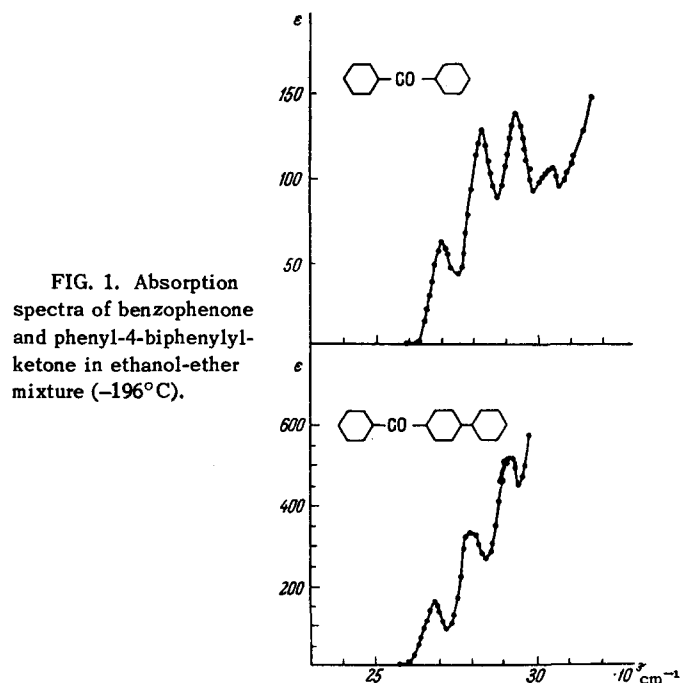

FIG. 1. Absorption spectra of benzophenone and phenyl-4-biphenylyl-ketone in ethanol-ether mixture (−196°C).

ether mixture). When the former solvent is replaced by the latter, a shift toward shorter wavelengths is observed in the spectral band under discussion. This is an indication that the electronic transition belongs to the n-π* type, localized in the carbonyl group. We have shown previously for benzaldehyde and benzophenone[8-9] that this transition is actually localized in the carbonyl group, and does not involve the remainder of the electronic system of the molecule. This interpretation remains valid also for 4-phenylbenzophenone, the substance under discussion, since in the structure of the absorption region, as reproduced in Fig. 1, a series is shown with the single spacing of 1200 cm^{-1}, just as in benzophenone. This series belongs to the valence-bond oscillation of the C=O bond in the excited singlet state. We also encounter analogous peculiarities in the study of the absorption spectra of other carbonyl derivatives of biphenyl and naphthalene discussed below.

All that has been stated thus far permits us to consider that the first excited singlet state of the compounds being studied is highly similar in position and properties to the state of the excited carbonyl group in benzene derivatives. The fluorescence and phosphorescence spectra of the latter have already been studied in references 8 and 9. It was shown there that the fluorescent (S*) and phosphorescent triplet (T)
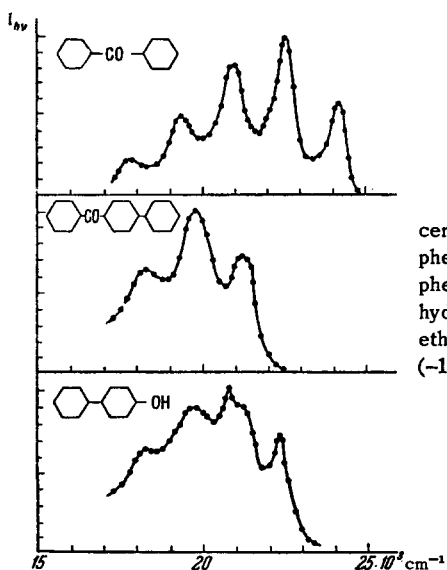
FIG. 2. Phosphorescence spectra of benzophenone, phenyl-4-biphenylylketone, and p-hydroxybiphenyl in ethanol-ether mixture (−196°).

FIG. 3. Diagram of electronic levels of phenyl-4-biphenylylketone.

levels are separated only by the small interval of $2000 - 3000$ cm^{-1}. In addition, the probability of internal conversion from the fluorescent to the phosphorescent level is 2 or 3 orders of magnitude greater than the value of the probability of transition from the fluorescent to the ground level ($S^* - S_0$) with emission. This explains the fact that phosphorescence alone (T → S_0 transition) takes place in carbonyl derivatives of benzene, and fluorescence with a lifetime shorter than $10^{-6} - 10^{-7}$ sec is totally absent.

The luminescence which we have studied in solutions of phenyl-4-biphenylylketone (with excitation by 366 mμ) has shown that this compound also exhibits no emission other than phosphorescence. That is, the solutions luminesce only at low temperatures, and the spectra of total emission and phosphorescence coincide.

However, this phosphorescence spectrum of phenylbiphenylylketone is completely different in position and structure from the spectrum of benzophenone, and is rather similar to the phosphorescence spectrum of para-substituted biphenyl (see Fig. 2), although it is appreciably more diffuse and shifted toward longer wavelengths in comparison with the latter.

In addition, the lifetime of phosphorescence of phenylbiphenylylketone, (0.3 sec) is two orders of magnitude greater than that of benzophenone (4.7 × 10^{-3} sec), and is close to that of p-hydroxybiphenyl (2.5 sec). All of this compels us to ascribe the emission to the biphenylyl group in phenylbiphenylylketone. Inasmuch as the light absorption, as we have stated above, is initially localized in the carbonyl group, we arrive at the inevitable conclusion that the absorbed excitation energy has migrated from the latter to the biphenylyl group within the molecule. The solution was sufficiently dilute to exclude an intermolecular transfer mechanism, and the quantum yield of phosphorescence was high (about 0.5). In order to depict
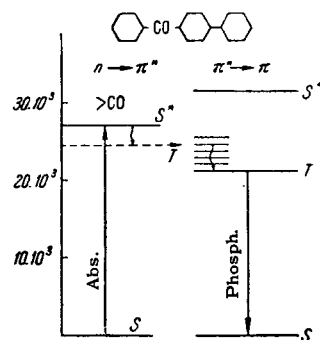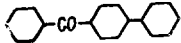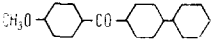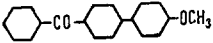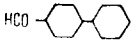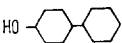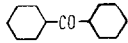
this process of intramolecular transfer, we shall make use of the following scheme of electronic levels in phenyl-4-biphenylylketone. We shall assume that the molecule retains the electronic levels which we indicated for the n → π* transition of the carbonyl group, as well as the levels of the biphenylyl group. In addition, of course, higher electronic levels may exist, corresponding to the entire conjugated system, including all the parts discussed here. The diagram of levels based on this assumption is given in Fig. 3. At the left we see the electronic levels of the carbonyl group, as they are shown by the absorption and luminescence spectra of benzophenone. At the right are drawn the lower singlet and triplet levels of a para-substituted biphenyl, in particular, p-hydroxybiphenyl. These levels are near those of phenylbiphenylylketone, as is shown by experiment.

Upon excitation in the first absorption band, the molecule enters the upper singlet level S^*_{CO} of the carbonyl group. This transition corresponds to the excitation of an unshared 2p electron of the oxygen atom to the excited π* orbital of the C=O bond of the carbonyl group. As has been shown for simple carbonyl derivatives of benzene, the molecule goes from this S^*_{CO} state without emission to the triplet level T with a probability 10^2 to 10^3 times greater than that for transition to the ground state with emission of fluorescence. Analogously, fluorescence is also absent in phenyl-4-biphenylylketone. That is, a fast radiationless transition must also take place here from the fluorescent state to the triplet state of the carbonyl group, from which the corresponding phosphorescence spectrum would normally be emitted. However, in the case of phenylbiphenylylketone, we do not observe such a spectrum at all, but only a phosphorescence spectrum arising from the triplet level of the biphenylyl group. This compels us to assume that the molecule goes over radiationlessly in a period of $10^{-13} - 10^{-14}$ sec from the triplet state of the carbonyl group to the lower triplet state of the biphenylyl group, corresponding to π* → π transitions of this electronic system. The entire conjugated system, including the ketone and biphenylyl groups, has a singlet excited level situation above the n → π* level. This corresponds to the second absorption band of the given compound. Another explanation of the observed phenomenon

TABLE I. Height of the lowest excited singlet level ($\nu_{0\,abs}$),
height of the lowest triplet level ($\nu_{0\,phos}$), decay time
(τ_{phos}), and quantum yield of phosphorescence (η_{phos})
of certain carbonyl derivatives of biphenyl in
ethanol-ether mixture at $-196°$ C

Compound*	ν_0 abs. cm^{-1}	ν_0 phos cm^{-1}	τ_{phos} sec.	η_{phos}
⬡-CO-⬡-⬡	26 800	21 225	0.30±0.02	0.47±0.05
CH₃O-⬡-CO-⬡-⬡	—	21 350	0.28±0.02	0.65±0.06
⬡-CO-⬡-⬡-OCH₃	—	20 600	0.48±0.02	0.50±0.10
HCO-⬡-⬡	—	21 050	—	—
HO-⬡-⬡	32 000	22 350	2.5±0.5	—
⬡-CO-⬡	27 000	24 250	4.7·10⁻³	0.74 **)

*The first three compounds were given to us by I. Ya. Postovskiĭ.
**According to the data of McClure.
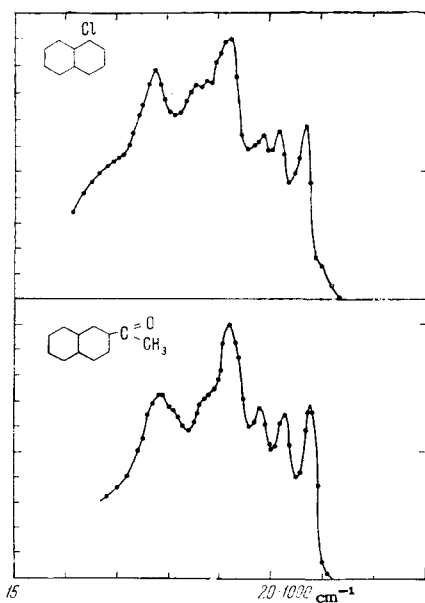
FIG. 4. Phosphorescence spectra of 1-chloronaphthalene and 2-naphthylmethylketone in ethanol-ether mixture (–196°C).

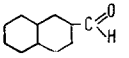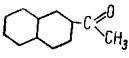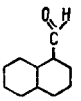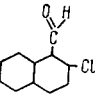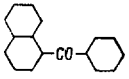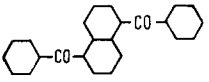consists in the assumption of a radiationless transition from the singlet level S^*_{CO} of the carbonyl group by an ordinary vibrational deactivation to the lowest triplet level of the conjugated electronic system of the mole-cule as a whole. This explanation is less plausible, since complete conjugation between the carbonyl group $>C = O$ and the biphenylyl group does not exist be-cause of the non-coplanarity of these parts of the mole-cule, as has been shown by study of the infrared spec-tra of such compounds by I. Ya. Postovskiĭ and his associates.[10]

We have observed analogous phenomena also in other carbonyl derivatives of biphenyl and naphthalene (Tables I and II). When excited by a wavelength of 366 mμ in the first absorption band, these compounds show no fluorescence, but only a phosphorescence spectrum similar to that of biphenyl or napththalene.

In Table II are given data on the luminescence and absorption of certain carbonyl derivatives of naphtha-lene. It is noteworthy that none of them show fluores-cence. Also, the positions, and in part the structures, of the phosphorescence spectra are very similar to the phosphorescence spectrum of naphthalene and its halogenated derivatives (see Fig. 4). On the other hand, the absorption spectra of these compounds dif-fer greatly in position and structure from that of naphthalene (as well as its halogenated derivatives). In distinction from phenyl-4-biphenylylketone, the n-π* transition in the carbonyl derivatives of naph-thalene may be detected only in the form of a slight shoulder on the long-wave side of the second intense absorption band.

TABLE II. Height of the lowest excited singlet level (ν_0 abs), height of the lowest triplet level (ν_0 phos), decay time (τ_{phos}), and quantum yield of phosphorescence (η_{phos}) of certain carbonyl derivatives of naphthalene in ethanol-ether mixture at $-196°$ C

Compound*	ν_0 abs cm^{-1}	ν_0 phos cm^{-1}	τ_{phos} sec.	η_{phos}
[structure: naphthalene–CHO]	(26 800)	20 800	0.35±0.02	0.03±0.01
[structure: naphthalene–COCH$_3$]	(27 200)	20 775	0.97±0.03	0.05±0.01
[structure: naphthalene with COH]	—	19 750	0.08±0.01	0.03±0.01
[structure: naphthalene with COH and Cl]	—	19 250	—	0.06±0.02
[structure: naphthalene–CO–phenyl]	(26 700)	20 100	0.74±0.03	0.25±0.03
[structure: phenyl–CO–naphthalene–CO–phenyl]	—	19 925	0.56±0.02	0.29±0.03
[structure: naphthalene]	31 740	21 250	2.3±0.1	0.05±0.005

*The cited naphthalene derivatives were given us by A. I. Shattenshteĭn, V. K. Matveev, and A. T. Troshchenko.

It follows from our studies that the luminescence of carbonyl derivatives of biphenyl and naphthalene may be ascribed to intramolecular transfer of excitation energy. This explains the absence in these compounds of a fluorescence spectrum adjacent to the first absorption maximum, with the presence alone of a phosphorescence spectrum characteristic of the biphenylyl or naphthyl group. In the structure of these spectra, we do not encounter the frequency $1600 - 1700$ cm^{-1} of the $C=O$ group, but only the 1400 cm^{-1} frequency of aromatic rings for phenyl-biphenylylketone, and the naphthalene frequency in acetylnaphthalenes.

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