that it is probably somewhat more nephelauxetic than Cl^- or Br^-. The present data on $[MnI_4]^{2-}$ are too limited and inaccurate to offer any definite evidence on this point.

There is a notable discrepancy between our Δ value of $\sim$3600 cm.$^{-1}$ and Buffagni and Dunn's value[14] of 2650 cm.$^{-1}$ for the $[MnCl_4]^{2-}$ ion. So large a discrepancy obviously requires comment. First, it should be emphasized that the difference in Δ values is due entirely to a difference in interpretation of data; there are no significant differences between Dunn's data and ours. It also should be noted that the exact numerical value of Δ is of somewhat limited significance, since it is impossible, within the theoretical framework of the Tanabe and Sugano treatment, to obtain perfect agreement between calculated and observed energies of the lower six transitions for any reasonable Δ value. This is because the ratio of the separations $^4T_2(^4G)$–$^4T_1(^4G)$ and $^4E,{}^4A_1(^4G)$–$^4T_2(^4G)$ is theoretically of the order of $\sim$3 throughout the range of Δ from 1000 to 4000 cm.$^{-1}$ (see Fig. 1), whereas, experimentally, this ratio is $\sim$1. Finally, it also must be recognized that the slopes of the energy lines for all of the lower states, on which the evaluation of Δ depends, are not great, so that the sum of squares of deviations has no pronounced minimum in the range of reasonable Δ values. The center of the broad shallow minimum is, however, at $\sim$3600 cm.$^{-1}$. The sum of squares of deviations at Δ = 2650 cm.$^{-1}$ is about two times greater than at Δ = 3600 cm.$^{-1}$.

As a form of independent support for a Δ value of $\sim$3600 cm.$^{-1}$ in preference to one of $\sim$2600 cm.$^{-1}$, we have made a comparison of Δ values for $[MnCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[NiCl_4]^{2-}$ with those for the corresponding hexa-aquo ions, which Buffagni and Dunn regarded as offering support for their results. Their results and ours for the $[CoCl_4]^{2-}$ and $[NiCl_4]^{2-}$ systems have previously been shown to be in satisfactory agreement.[16,17] Δ values for the aquo ions have been taken from the sources noted in Table III. It can be seen that, with Δ equal to $\sim$3600 cm.$^{-1}$ for $[MnCl_4]^{2-}$, the Δ_t/Δ_0 ratio for Mn(II) is within 4% of the average value of this ratio for Co(II) and Ni(II) while with Δ equal to 2650 cm.$^{-1}$, the ratio is 25% lower.

TABLE III

COMPARISON OF Δ VALUES IN $[MCl_4]^{2-}$ AND $[M(H_2O)_6]^{2+}$ SPECIES FOR M = Mn, Co AND Ni

Metal	Δ_0 in $[M(H_2O)_6]^{2+}$	Δ_t in $[MCl_4]^{2-}$	Δ_0/Δ_t
Mn	8500[a]	2650[d]	0.312
		3600[e]	.423
Co	8300[b]	3200[f]	.386
Ni	8500[c]	3625[g]	.427

[a] From ref. 6. [b] Obtained from the results of C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, 9, 397 (1955), using an energy level diagram computed by A. D. Liehr from the complete matrices of J. C. Eisenstein, *J. Chem. Phys.*, 34, 1628 (1961); A. D. Liehr, private communication, presented in part at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June 12–16, 1961 (to be submitted to *J. Phys. Chem.*). [c] From A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (*N. Y.*), 6, 134 (1959). [d] From ref. 14. [e] Present work. [f] Average of values in ref. 14 and 17. [g] Average of values in ref. 14 and 16.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL]

Intramolecular Energy Transfer in a Naphthalene–Anthracene System

BY O. SCHNEPP AND M. LEVY

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Intramolecular energy transfer has been demonstrated in three homologous 9-anthryl-1′-naphthyl-alkanes in which the anthracene and naphthalene units were joined by saturated chains of 1, 2 and 3 carbon atoms. The absorption spectra of these compounds bear evidence that the two aromatic π-electron systems do not overlap appreciably. The naphthalene group of the compound molecule was excited by appropriately filtered radiation and the resulting fluorescence was characteristic of the anthracene group. From the comparative fluorescence intensity measurements relative as well as absolute values of the quantum efficiencies of the energy transfer process were calculated. The relative fluorescence quantum yields were also obtained.

Introduction

The absorption spectrum of naphthalene[1] begins at 3100 Å. with a very weak absorption system (ϵ = 200) which fuses into a much stronger system with maximum at 2770 Å. (ϵ = 5000) and a very intense absorption band appears at 2200 Å. (ϵ = 10^5). The absorption spectrum of anthracene[1] begins with a medium absorption at 3750 Å. (ϵ = 8000) and has a very intense peak at 2530 Å. (ϵ = 1.6×10^5). It is clear from these data that the intense peaks of these two compounds do not overlap and it should therefore be possible to excite one of the substances by irradiation in the presence of the other. This is only approximately true, however, since the absorption coefficient of anthracene at 2800 Å. still has a finite value, even though it is much smaller than that of naphthalene at this wave length.

It was believed that in view of the discussion of the last paragraph a molecule consisting of nonconjugated anthracene and naphthalene units would be very suitable for a study of intramolecular energy transfer. Such molecules were synthe-

(1) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

sized upon our request in Professor Ginsburg's laboratory.[2] The compounds were homologous 9-anthryl-1′-napthyl-alkanes in which the anthracene and naphthalene units were joined by saturated chains of one, two and three carbon atoms. The absorption spectra of these substances are given in reference 2 and clearly represent superpositions of naphthalene and anthracene spectra. As a matter of fact they were found to agree within very close limits with the spectrum of a solution containing a mixture of 1-methyl-naphthalene and 9-methylanthracene. Such a solution could therefore be used for calibration in the course of this work.

Intramolecular energy transfer resulting in sensitized fluorescence has been previously investigated in rare earth chelates[3] and in complex organic molecules.[4] The mechanism of radiationless energy transfers between two molecular systems, the sensitiser and the acceptor, has been treated in detail by Foerster[5] who also recently reviewed the experimental results in this field.[6] The Foerster mechanism undoubtedly also applies to molecules with two independent absorbing systems[6] such as those investigated in the present work.

It was possible here to demonstrate, both by qualitative experiments, as well as by quantitative measurements, the occurrence of intramolecular energy transfer from the naphthalene to the anthracene unit of the compound molecules (9-anthryl-1′-naphthyl-alkanes). The relative intramolecular energy transfer quantum efficiencies of the three compounds investigated were measured and also the measurement of the absolute magnitudes of these efficiencies was attempted with reasonable results. In the course of these measurements, the relative fluorescence quantum yields of the compounds were determined.

Materials

The compounds $1\text{-}C_{10}H_7\cdot(CH_2)_n\cdot C_{14}H_9\text{-}9$ (9-anthryl-1′-naphthyl-alkanes) with n being 1, 2 and 3 (referred to as I, II and III respectively from here on) were obtained through the kindness of Professor Ginsburg of this department.[2] They had been chromatographed and recrystallized and were used without further purification. Their absorption spectra in solution were reproduced in reference 2. 1-Methylnaphthalene was an Eastman-Kodak sample which was, however, colored before purification. It was vacuum distilled and chromatographed and was then a colorless liquid whose solution spectrum agreed well with that found in the literature.[1] 9-Methyl-anthracene was prepared from 9-anthrone and methyl bromide by a Grignard reaction. The compound was purified by chromatography and by recrystallization. Its solution spectrum agreed with that found in the literature.[1] Isopentane and methylcyclohexane were used as solvents and were purified by passage through a silica gel column. They were then transparent to 2200 Å.

Experimental

Stock solutions of concentrations close to $4 \times 10^{-4}M$ in a methylcyclohexane–isopentane 4:1 by volume solvent mixture were prepared of methyl-anthracene, and compounds I, II and III. A near-equimolar mixture of 9-methyl-anthracene and 1-methyl-naphthalene in the same solvent was prepared and the concentrations of the solutes so adjusted as to match the optical densities of the solutions of compounds I, II and III as closely as possible over the entire spectral range of interest here. The exact concentrations of the stock solutions are listed in Table I. The absorption spectra of the solutions of the three compounds and of the mixture containing methyl-anthracene and methyl-naphthalene all were in very close agreement with each other, the spectra of the solutions of I, II and III being almost identical while that of the mixture agreed with the former within 10% of optical density at all wave lengths of interest, and all absorption peaks were within 10 Å. of those of the three compounds. Experiments were performed with the stock solutions and with solutions obtained by dilution by a factor of 11.

TABLE I

STOCK SOLUTION CONCENTRATIONS

Solution	Concentration (M)
(1) Compound I	3.4×10^{-4}
(2) Compound II	3.3×10^{-4}
(3) Compound III	3.4×10^{-4}
(4) Mixture:	
9-Methyl-anthracene	4.2×10^{-4}
1-Methyl-naphthalene	4.8×10^{-4}
(5) 9-Methyl-anthracene	4.2×10^{-4}

All solutions were placed in quartz or Vycor test tubes which were connected to a glass vacuum system by means of graded seals, degassed and sealed off under vacuum. These samples were then used for room temperature experiments as liquid solutions or they were inserted in a quartz Dewar flask containing liquid nitrogen or liquid air. At the temperature of liquid nitrogen or liquid air the solutions froze to form transparent glasses.

The fluorescence of the samples was excited by irradiation with a General Electric high pressure mercury arc (A-H6) filtered by filter combinations "B" and "D" described by Kasha.[7] The first of these isolates light suitable for exciting the anthracene molecule in its first absorption band while the second filter isolates light which excited the naphthalene molecule in the region of its strong absorption in the neighborhood of 2800 Å. Filter "D" was used as described by Kasha in part of the experiments and the other part of the experiments were performed using a modified filter "D" where the carbon tetrachloride component was replaced by a solution of benzene in *iso*-octane (10 g. in 150 ml., 1 cm. cell). The benzene solution absorbs strongly at wave lengths[8] shorter than 2700 Å. whereas the carbon tetrachloride filter component transmits to about 2600 Å.

The fluorescence spectra were photographed on a medium Hilger spectrograph. The fluorescence intensity was measured by means of a 931A RCA photomultiplier, the current being measured by a galvanometer. The anode currents measured were kept below 50 μ amp. Corning glass filter number 7380 was found to be most suitable for filtering out the stray exciting light while transmitting all of the anthracene fluorescence. This filter was therefore placed in front of the photomultiplier tube. It also absorbs all naphthalene fluorescence.

In a typical series of measurements the following solutions were irradiated and the photocurrent recorded in rapid succession: (1) compound I, (2) compound II, (3) compound

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(2) P. Rona and U. Feldman, *J. Chem. Soc.*, 1737 (1958).

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(5) T. Foerster, "Fluoreszenz organischer Verbindungen," Vandenhoek and Ruprecht, Goettingen 1951, Chapter IV, and references therein.

(6) T. Foerster, *Discussions Faraday Soc.*, **27**, 7 (1959).

(7) M. Kasha, *J. Optical Soc. Am.*, **38**, 929 (1948).

(8) A. M. Bass, *ibid.*, **38**, 977 (1948).

TABLE II

VALUES OF B

Temperature	Concn., M	B_{15}	B_{25}	B_{35}	B_{13}	B_{23}	B_{45}
Room	3 × 10⁻⁴	1.1 ± 0.1	2.1 ± 0.2	1.6 ± 0.15	0.69 ± 0.07	1.3 ± 0.13	1.0 ± 0.1
Liquid air or liquid nitrogen	3 × 10⁻⁴	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
Room	2.6 × 10⁻⁵	1.1 ± 0.1	1.9 ± 0.1	1.4 ± 0.1	0.8 ± 0.1	1.3 ± 0.1	1.0 ± 0.1
Liquid air	2.6 × 10⁻⁵	0.95 ± 0.1	0.95 ± 0.1	0.90 ± 0.1	1.05 ± 0.1	1.05 ± 0.1	1.0 ± 0.1

III, (4) mixture of 9-methyl-anthracene and 1-methyl-naphthalene, (5) 9-methyl-anthracene, (6) solvent.

Experimental Results

When the stock solution 4 containing a near-equimolar mixture of 9-methyl-anthracene and 1-methyl-naphthalene was irradiated through Kasha's filter "D," two sets of fluorescence spectra were obtained on the spectrographic plates. The shorter wave length fluorescence consisted of broad bands which lay between 3160 and 3400 A. The longer wave length fluorescence was similarly banded and lay between 3880 and 4740 A. These spectra are easily identified to be the fluorescence spectra of naphthalene and anthracene respectively. When, on the other hand, solutions of the compounds I, II and III are irradiated through the same filter, only the anthracene fluorescence could be photographed and all attempts to obtain the naphthalene emission were unsuccessful. The same results were obtained both at room temperature and for the rigid glass solutions at liquid nitrogen temperature.

Tables II and III list the values of certain ratios which are calculated from the experimental measurements. The ratio B_{xy} represents the relative quantum yields of the solutions on direct excitation of the anthracene part of the molecule in the case of solutions 1, 2 and 3 of the methyl-anthracene molecule itself in the case of solutions 4 and 5. (x) and (y) are the fluorescence intensities as measured by

$$B_{xy} = \frac{[(x) - (6)]_B}{[(y) - (6)]_B}$$

the photocurrent obtained when any of these solutions are irradiated through filter "B" (subscript B). (6) represents the photocurrent obtained under the same conditions when a sample tube containing the pure solvent is substituted in the sample holder. D_{xy} expresses the ratio of the anthracene fluorescence intensities of two solutions when the naphthalene group is excited. Here the solutions are irradiated

$$D_{xy} = \frac{[(x) - (6)]_D - [(5) - (6)]_D \cdot B_{x5}}{[(y) - (6)]_D - [(5) - (6)]_D \cdot B_{y5}}$$

through filter "D" (subscript D) and (x) and (y) may, in practice, be (1), (2), (3) or (4) or in other words the solutions of compounds I, II and III or the solutions of the mixture of methyl-anthracene and methyl-naphthalene. In order for the desired ratio to be obtained, the measured fluorescence intensity $[(x) - (6)]_D$ must be corrected for the anthracene fluorescence resulting from direct excitation of the anthracene group by light transmitted by filter "D." This correction is the fluorescence intensity of solution 5 or the value $[(5) - (6)]_D$ corrected for relative quantum yield of the solution studied (x) and (5) or B_{x5}. Implicit in this calculation is the assumption that the quantum yields for the anthracene group remain constant for exciting light wave lengths[4] between 4000 and 2600 Å.

Analysis of Results

If the intensity of the anthracene fluorescence excited by irradiation with filter "B" (expressed as number of quanta) is I_B and the number of quanta absorbed by the anthracene compound under these conditions be N_B, then the quantum yield k_Q is defined by the equation

$$I_B = k_Q \cdot N_B$$

On the other hand if the anthracene fluorescence intensity on excitation of the naphthalene group be I_D and the number of quanta absorbed by the naphthalene group be N_D, then we define a transfer coefficient k_T by the equation

$$I_D = k_Q \cdot k_T \cdot N_D$$

The product $k_T \cdot N_D$ gives the number of quanta which come to reside on the anthracene group after transfer from the naphthalene group. If two solutions of very closely similar optical density are irradiated, we can assume that the number of quanta absorbed is the same. As a result, we can calculate ratios of the k_Q's and the k_T's for the different compounds and the mixture investigated here from the fluorescence intensity measurements.

TABLE III

VALUES OF D

Temperature	Concn., M	D_{13}	D_{23}	D_{43}
Room	3 × 10⁻⁴	0.70 ± 0.05	1.25 ± 0.15	0.0 ± 0.1
Liquid air or liquid nitrogen	3 × 10⁻⁴	1.0 ± .1	1.1 ± .1	.0 ± .1
Room	2.6 × 10⁻⁵	0.8 ± .15	1.25 ± .1	.0 ± .1
Liquid air	2.6 × 10⁻⁵	1.05 ± .1	1.0 ± .1	.0 ± .1

If the subscripts x and y denote different compounds, we have

$$B_{xy} = \frac{I_{Bx}}{I_{By}} = \frac{k_{Qx} \cdot N_{Bx}}{k_{Qy} \cdot N_{By}} = \frac{k_{Qx}}{k_{Qy}}$$

or, as pointed out before, the ratios B_{xy} represent the quantum yield ratios of the anthracene groups. Similarly

$$D_{xy} = \frac{I_{Dx}}{I_{Dy}} = \frac{k_{Qx} \cdot k_{Tx} \cdot N_{Dx}}{k_{Qy} \cdot k_{Ty} \cdot N_{Dy}} = \frac{k_{Qx} \cdot k_{Tx}}{k_{Qy} \cdot k_{Ty}}$$

It is clear that we can now obtain the ratios of the transfer coefficients from the two ratios B and D

$$T_{xy} = \frac{D_{xy}}{B_{xy}} = \frac{k_{Tx}}{k_{Ty}}$$

The values of the ratios T_{xy} are given in Table IV.

It has also been attempted to calculate the absolute values of the k_T's from the results obtained here. For this purpose consider the ratio of the fluorescence intensities resulting from the irradiation of the naphthalene part of the molecule

TABLE IV

VALUES OF T

Temperature	Concn., M	T_{13}	T_{23}	T_{43}
Room	3×10^{-4}	1.0 ± 0.1	1.0 ± 0.15	0.0 ± 1.0
Liquid air or liquid nitrogen	3×10^{-4}	$1.0 \pm .1$	$1.1 \pm .1$	$.0 \pm .1$
Room	2.6×10^{-5}	$1.0 \pm .1$	$1.0 \pm .1$	$.0 \pm .1$
Liquid air	2.6×10^{-5}	$1.05 \pm .1$	$1.0 \pm .1$	$.0 \pm .1$

(I_{Nx}) to those resulting from the irradiation of the anthracene part (I_{Ax}), all using filter "D." We have the following relations which are self-explanatory in the light of the earlier paragraphs of this section

$$I_{\mathrm{Nx}} = k_{\mathrm{Qx}} \cdot k_{\mathrm{Tx}} \cdot N_{\mathrm{Nx}}$$

$$I_{\mathrm{Ax}} = k_{\mathrm{Qx}} \cdot N_{\mathrm{Ax}}$$

where N_{Nx} and N_{Ax} are the number of quanta absorbed by the naphthalene and anthracene group of the molecule, respectively, when solution (x) is irradiated through filter "D." Consider further the ratio

$$\frac{I_{\mathrm{Nx}}}{I_{\mathrm{Ax}}} = \frac{k_{\mathrm{Qx}} \cdot k_{\mathrm{Tx}} \cdot N_{\mathrm{Nx}}}{k_{\mathrm{Qx}} \cdot N_{\mathrm{Ax}}} = \frac{k_{\mathrm{Tx}} \cdot N_{\mathrm{Nx}}}{N_{\mathrm{Ax}}}$$

From this we obtain

$$k_{\mathrm{Tx}} = \frac{I_{\mathrm{Nx}}}{I_{\mathrm{Ax}}} \cdot \frac{N_{\mathrm{Ax}}}{N_{\mathrm{Nx}}}$$

or in terms of measured quantities

$$k_{\mathrm{Tx}} = \frac{[(x) - (6)]_{\mathrm{D}} - [(5) - (6)]_{\mathrm{D}} B_{\mathrm{x5}}}{[(5) - (6)]_{\mathrm{D}} B_{\mathrm{x5}}} \cdot \frac{N_{\mathrm{Ax}}}{N_{\mathrm{Nx}}}$$

In order to be able to evaluate the ratio $N_{\mathrm{Ax}}/N_{\mathrm{Nx}}$, the following assumptions have to be made: (1) we assume that the quantum yield of 9-methylanthracene is constant with wave length of exciting radiation between 3600 and 2600 Å.; (2) we assume that the ratio of quanta absorbed by the naphthalene group to quanta absorbed by the anthracene group for compounds I, II and III is the same as for a near-equimolar mixture of 1-methyl-naphthalene and 9-methyl-anthracene such that the absorption intensities match (see section III). The relative emission intensities of the A-H6 high pressure mercury arc as function of wave length published by the General Electric Corp. were used and corrected for the filter transmission. Absorption coefficients of 1-methyl-naphthalene and 1-methylanthracene were taken from reference 1. For the concentration of the stock solutions the optical density is greater than 2 for a path length of 1 cm. throughout most of the wave length region transmitted by filter "D," *i.e.* between 2900 and 2600 Å. or by the modified filter "D" between 2900 and 2700 Å. For this concentration it can therefore be assumed that all available light was absorbed. This assumption is not valid for lower concentrations and for these the ratio is concentration dependent. In order to evaluate $N_{\mathrm{Ax}}/N_{\mathrm{Nx}}$ for these lower concentrations, the optical path must be accurately known. This was not possible in the experiments described here and therefore the calculation was only made for the stock solution concentration for two filter combinations, filter "D" and modified filter "D" in which a benzene solution was used instead of carbon tetrachloride to provide the short wave length cut-off. The wave length region was divided into 40 Å. wide sections and the relative number of quanta absorbed by the different parts of the molecules calculated for each section. The addition of the contributions of these wave length sections gave the final results from which the ratio was evaluated. The value calculated for the ratio $N_{\mathrm{Ax}}/N_{\mathrm{Nx}}$ was 0.18 for filter "D" (using the carbon tetrachloride component) and 0.08 for the modified filter "D" (using the benzene solution). These values were used to calculate k_{T} and the results so obtained are tabulated in Table V. It was found that the absorption intensities of the filter solutions used as parts of the filter combinations "B" and "D" changed measurably in the course of time and the solutions had to be renewed frequently. The values of the above ratios were calculated using absorption intensities of fresh filter solutions as measured after they had been used in one experiment.

TABLE V

(A) Values of k_{T}, room temperature

(1) Filter "D" including carbon tetrachloride component

0.40
0.43
0.17

(2) Filter "D" using benzene component

0.22
0.19

(B) Values of k_{T}, liquid nitrogen temperature

(1) Filter "D" including carbon tetrachloride component

0.60
0.20

(2) Filter "D" using benzene component

0.25

Discussion of Results

The phenomenon of intramolecular energy transfer is conclusively demonstrated by the results of this work. The fluorescence spectra obtained on excitation of the naphthalene group demonstrate qualitatively that, at most, only a small fraction of the excitation energy remains on the naphthalene part of the compound molecules I, II or III a time interval of about 10^{-7} seconds after excitation. This can be concluded from the observation that no naphthalene emission was observed in these experiments and only the anthracene fluorescence spectrum was recorded. On the other hand, the fluorescence spectra of both anthracene and naphthalene were observed when the solution of a mixture of 1-methyl-naphthalene and 9-methylanthracene was irradiated under identical experimental conditions. In this case the anthracene fluorescence is due to direct excitation of the anthracene group which absorbs weakly in the wave length region of filter "D." The above observations and conclusions hold for the liquid solutions at room temperature as well as for the rigid glasses at liquid air and liquid nitrogen temperatures.

The quantitative results obtained in this work prove that the intramolecular energy transfer efficiency between the two parts of the compound molecules is at least ten times greater than the intermolecular energy transfer efficiency between 1-methyl-naphthalene and 9-methylanthracene molecules in the stock solution of the equimolar mixture of these two compounds. The ratio of the energy transfer efficiencies T_{43} is given in Table IV as 0.0 ± 0.1. It is therefore clear that the lower limit of 10 for the ratio between intramolecular and intermolecular energy transfer is determined by the experimental error of 10% and the actual ratio is probably even greater. It is not considered likely that the efficiency of intermolecular transfer is appreciably different for the compound molecules from that for the pair 1-methyl-naphthalene, 9-methyl-anthracene at the concentrations used here. It is further to be noted that the ratio T_{43} remained 0 ± 0.1 for both concentrations for which measurements were made and for the liquid solution at room temperature as well as for the rigid glass solution at liquid nitrogen temperature. If intermolecular energy transfer contributed significantly in the experiment, it might be expected that the value of T_{43} would be sensitive to changes in concentration as well as viscosity of the solution. It is therefore concluded that the lower limit of 10 for the ratio of intramolecular to intermolecular energy transfer efficiency holds for the solutions of the compounds I, II and III used in the present measurements.

The values of the energy transfer efficiency ratios T show that the transfer efficiency is identical within the limits of experimental error for all three compounds I, II and III, both at room temperature and at liquid nitrogen temperature. This result shows that no information concerning the variation of energy transfer efficiency with distance between the naphthalene and anthracene groups was obtained here. The main reason for this is believed to lie in the fact that the molecular systems investigated are not rigid and in compounds II and III relative motion of the aromatic groups is comparatively unrestricted. As a result, these groups can approach to within van der Waals distance of each other many times during the life time of an excited electronic state. It is quite possible that such freedom to local motion also exists in the disordered rigid glass.

The values of k_T are listed in Table V. These values are obviously subject to large experimental error and vary from 0.17 to 0.43 except for one high value of 0.60. It is believed that this one large value is in error due to an exceptionally great experimental error inherent in the liquid nitrogen experiments. The value of k_T can then be quoted as 0.3 ± 0.13. The limits of error, it should be noted, are such as to include the values obtained for k_T for two different filters which differ primarily in their short wave length transmission characteristics. The value of k_T is much more sensitive than those of the other magnitudes listed in the tables since it is an absolute value rather than a ratio. The principal errors are believed to be due to changes in intensity and wave length characteristics of the source and due to lack of accurate information on the dependence if fluorescence quantum efficiency of anthracene on the wave length of exciting light.[4,9]

It seems somewhat difficult to explain the relatively low value of the absolute quantum efficiency for intramolecular energy transfer as measured by k_T. Gilmore, Gibson and McClure report[10] a value of 0.32 to 0.39 for the absolute quantum yield for fluorescence of naphthalene in a rigid glass at liquid nitrogen temperature. As outlined in the following paragraph, the value for anthracene under similar conditions is believed to be close to unity. It may then be suggested on the basis of the results of this work and in view of the results of reference 10 that the absolute quantum yield for intramolecular energy transfer in compounds I, II and III agrees with the fluorescence quantum efficiency of naphthalene. This agreement requires the conclusion that the non-radiative quenching processes which compete with the fluorescence of naphthalene compete with similar success with the process of intramolecular energy transfer from the naphthalene group to the anthracene group of the compound molecules. It can then be concluded that the intramolecular energy transfer process is faster than the fluorescence of the naphthalene unit but slower than the radiationless deactivation processes. It should be added that no phosphorescence characteristic of naphthalene was observable in the rigid glass solutions at liquid nitrogen temperature for the solutions of compounds I, II and III. The phosphorescence quantum yield for naphthalene under similar conditions is, however, very low.[10]

Table II lists the values of the quantum efficiency ratios B. At room temperature the fluorescence quantum efficiencies of the different compounds on direct anthracene excitation (filter "B") vary greatly. In particular the variation of the fluorescence quantum efficiencies of compounds I, II and III over a factor of two is somewhat surprising. No explanation can be offered for this variation. It has been previously reported, however, that the fluorescence quantum efficiency of anthracene varies greatly with substituents.[11] In rigid glass solutions at low temperature on the other hand, the values of the ratios B become unity within experimental error. This result probably indicates that under these conditions the absolute fluorescence quantum yields all approach the maximum value of unity.

It should be emphasized that throughout this

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(9) J. Bowen and A. H. Williams, *Trans. Faraday Soc.*, **35**, 765 (1939).

(10) E. H. Gilmore, G. E. Gibson and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952).

(11) F. I. Polovikov, *Doklady Akad. Nauk, S.S.S.R.*, **71**, 453 (1950).

discussion it was assumed that all intramolecular energy transfer occurs by radiationless resonance mechanism.[5] The absorption spectra of the molecules studied represent superpositions of anthracene and naphthalene spectra, and this fact proves that there is no overlap between the two π-electron systems. No energy transfer is, therefore, expected by way of the hydrocarbon chain.

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Infrared Spectra of Some Substituted *p*-Benzoquinones

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The infrared spectra of a number of halogenated *p*-benzoquinones are examined between 1800–800 cm.$^{-1}$. The influence of an α-halogen atom on the perturbation of the carbonyl stretching mode is discussed. The out-of-plane deformation of the hydrogen atoms attached to a substituted *p*-benzoquinone nucleus observed by earlier workers is confirmed and extended over a wider range of compounds. An attempt is made to characterize frequencies in the 1400–1000 cm.$^{-1}$ region of the spectra and to deduce a relationship between the characteristic bands and the structure of the isomeric disubstituted (2,3, 2,5 and 2,6) *p*-benzoquinones having one or both substituents as halogen atoms.

The study of the infrared spectra of substituted *p*-benzoquinones represents only a small portion of the spectroscopic studies of quinones. Most of these studies[2] were directed only towards the examination of the carbonyl stretching mode of the quinone molecule. More recently, two publications[3,4] have appeared wherein all the major bands in the infrared spectra of the substituted *p*-benzoquinones are mentioned. Whereas the study of the German group[4] is restricted to the alkyl, hydroxy and methoxy substituted *p*-benzoquinones, that of the American workers[3] includes a few halogenated derivatives.

Over the last few years, several aryl- and haloaryl-*p*-benzoquinones have been synthesized[5,6] in this Laboratory. We have examined the spectra of some of these compounds, and in the present paper report some correlations that result from the investigation.

Results and Discussion

C═O Stretching Frequencies.—The carbonyl stretching frequencies of the *p*-benzoquinones examined are listed in Table I. The data shows that of the twenty eight compounds listed, ten exhibit a doublet in the carbonyl region. Some evidence has already been put forth[7] on the nature of the splitting of the C═O band of *p*-benzoquinone (no. 1).

Splitting of the bands in the carbonyl region of an infrared spectrum of a compound possessing two C═O groups can be caused by (1) vibrational coupling between suitably located vibrations of the same frequency within a molecule, as that demonstrated for diacyl peroxides and anhydrides,[8] (2) intramolecular vibrational effect of the type recently reported by Jones and co-workers[9] or (3) separation of the unperturbed frequencies of the stretching mode of two carbonyls caused by steric, electronic or electrical influences prevailing in a molecule. These factors may operate singly or jointly to influence the C═O stretching vibrations. Thus with increased separation of the unperturbed frequencies, the vibrational coupling would be expected to diminish. It has been suggested[7] that the two carbonyl bands in chloro-*p*-benzoquinone (no. 2) do not result from an intramolecular vibrational effect of the type postulated for *p*-benzoquinone. That the two bands in the carbonyl region of benzoquinones No. 2, 5, 6, 11 and 12 are indeed caused by the separation of the unperturbed vibrations of the two carbonyls is readily seen from an analysis of the data in Table I.

Introduction of a chlorine atom in *p*-benzoquinone produces two carbonyl bands (Fig. 1), the relative intensities of which are independent of the polarity of solvent.[7] The $\Delta\nu$ value between these bands is 20 cm.$^{-1}$. This value is in excellent agreement with those recorded for a positive shift of the carbonyl band due to the dipolar field effect in α-halo (equatorial)-cyclohexanone[10] and in α-halo-α,β-unsaturated ketones.[11] Thus the band at 1680 cm.$^{-1}$ (Band A) in no. 2 may be assigned to the carbonyl group with the halogen atom α to it, whereas the one at 1660 cm.$^{-1}$ (Band B) is attributable to the carbonyl flanked by two hydrogens. The following facts strongly support the above postulate. The introduction of another chlorine atom α to the second carbonyl as in nos. 3 and 4 produces a single intense band at 1692 and 1686 cm.$^{-1}$, respectively (Fig. 1). On the other

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[2] For references to these studies see ref. 3.

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