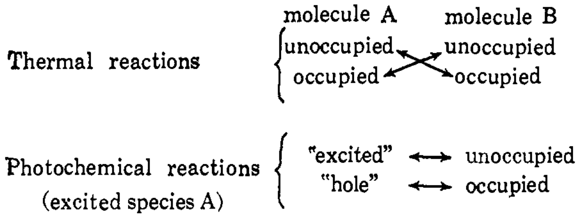
intermediate. The reaction path may then be useful only in determining the *first* step.

Another reason is the achievement of a certain degree of physical insight into the electronic mechanism of the reaction. Just as molecular orbitals have become important in understanding the stability of a given conjugated molecule, the specific interaction of molecular orbitals in a reaction, and their combination to form intermolecular orbitals are crucial factors in determining the readiness of a reaction. There have been many pioneers in this field.[15,16,20,34] The purpose of these papers has been to establish more rigorously the role of each molecular orbital interaction. The important orbital interactions may be summarized in the scheme shown where "excited" and "hole" refer to the orbital of the excited electron and the orbital with the hole, respectively. This scheme emphasizes which orbital interactions must be favorable for a given reaction to be allowed. The relevant orbitals are generally the top occupied and lowest unoccupied on each molecule. This scheme is strictly valid only for closed-shell molecules.



Acknowledgments. The author thanks Dr. J. Dannenberg and Professor Paul De Mayo for stimulating discussions relating to the experimental aspects of the subject, and Dr. Jean Durup for a critical discussion on reaction surfaces. He wishes to acknowledge some private communications from Professor Roald Hoffmann and a referee's useful comment on the interaction between neutral molecules and ionic species. He thanks Professor George S. Hammond for his kind and stimulating hospitality at the California Institute of Technology, where this work was completed.

Finally, he is particularly grateful to Professor Michel Magat for having aroused his interest in photochemical reactions.

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(34) See also H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, 87, 2045 (1965); H. E. Zimmerman, *Science*, 153, 837 (1966).

Anomalous Fluorescence Characteristics of Fluoranthene and Some of Its Derivatives[1]

I. B. Berlman, H. O. Wirth, and O. J. Steingraber

Contribution from Argonne National Laboratory, Argonne, Illinois.
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Abstract: The fluorescence characteristics of fluoranthene and three of its derivatives, 3-phenylfluoranthene, 3,3′-bifluoranthenyl, and 3-aminofluoranthene, are reported. For fluoranthene in particular, the natural lifetime, Stokes shift, and relative immunity to concentration and oxygen quenching are found to be anomalous. The first two of these characteristics, long lifetime and large Stokes shift, are interpreted as supporting evidence that fluorescence takes place from a partially hidden level. For the most intense absorption band associated with this transition (^1L_b), ϵ_{max} is estimated to be 270 ± 40. The anomalous immunity to quenching has not been explained as yet. Depending on the type and position of the substituents, derivatives of fluoranthene also possess some or all of the above anomalies. The synthesis and purification of the above derivatives of fluoranthene are also reported.

Fluoranthene (II in Table I) is a nonalternate conjugated hydrocarbon and therefore has been of interest in theoretical and experimental studies.[2,3] We have studied the fluorescence characteristics of fluoranthene and several of its derivatives (III–V in Table I) in a dilute cyclohexane solution and have found that most of these compounds have many anomalous characteristics. In particular, II has four anomalous fluorescence characteristics: (1) the value of the fluorescence lifetime τ_{0m} obtained from measuring the decay time, τ, and the quantum yield, QY, is many times greater than a calculated value, τ_{0c} (Table I), obtained by integrating over its long-wavelength band; (2) its Stokes shift is very large; (3) it appears to be immune to concentration quenching and excimer formation; and (4) it is relatively resistant to oxygen quenching. It is our belief that the last two anomalies are unrelated to the first two.

Fluorescence measurements were made with equipment and according to procedures described elsewhere.[4] All measurements were made on dilute cyclohexane solutions in the concentration region of about 0.2 g/l., and the solute was excited directly by monochromatic radiation. The following data were obtained: the absorption spectrum, the fluorescence spectrum, the fluorescence decay time, τ, and the relative intensities of the fluorescence spectra of a nitrogenated and an aerated solution, L_0/L. They are shown in Figure 1 in part. From the data, calculations were made of (1) the

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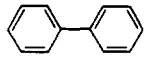
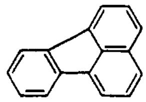
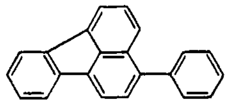
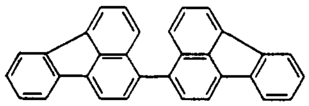
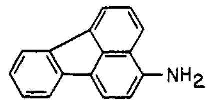
(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) J. Koutechy, P. Hockman, and J. Michl, *J. Chem. Phys.*, 40, 2439 (1964); (b) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradnik, *Theoret. Chim. Acta*, 6, 141 (1966).

(3) B. L. Van Duuran, *Anal. Chem.*, 32, 1436 (1960).

(4) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press Inc., New York, N. Y., 1965.

Table I. Structural Formula, Time Constants,[a] Quantum Yield (QY), Stokes Shift, Susceptibility to Oxygen Quenching (L_0/L), Solubility,[b] and Melting Point of Biphenyl, Fluoranthene, and Some Fluoranthene Derivatives

Structural formula	No.	τ, nsec	QY	τ_0 (τ_{0c}), nsec	L_0/L	Stokes shift, cm^{-1}	Sol, g/l.	Mp, °C
	I	16.0	0.18	(2.8)	1.95	3300	414	71
	II	53.0	0.30	(16.4)	1.47	3970	>100	111
	III	34.5	0.63	(11.0)	1.28	2950	>20	145
	IV	8.0		(4.0)	1.16	2700	0.2	331
	V	11.4	0.65	22.3	1.46	2700	10	117

[a] τ_0, natural lifetime; τ, decay time. [b] Solubility of toluene, 20°.

quantum yield, QY, computed by integrating over the emission spectrum, (2) the natural fluorescence lifetime, τ_0, computed[4] by integrating over the long-wavelength absorption bands, that are related to the transition leading to fluorescence, and (3) the Stokes shift. The results of these measurements and computation are given in Table I.

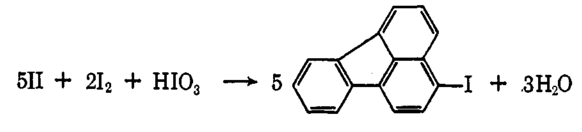
It is immediately seen from the results of Table I that the fundamental relationship $\tau_0 = \tau/\text{QY}$ is not satisfied. The discordance in this relationship requires for clarity that we distinguish between two τ_0 parameters, τ_{0c} and τ_{0m}, where τ_{0c} is obtained by integrating over the absorption bands and $\tau_{0m} = \tau/\text{QY}$. Our experience has been that, when $\tau_0 \neq \tau/\text{QY}$, the difficulty can usually be traced to an improper evaluation of τ_0, in which absorption bands not related to the fluorescence have been included in the integration.

L_0/L is a measure of the relative sensitivity of the first excited singlet state to quenching by oxygen. For aromatic molecules dissolved in cyclohexane, a direct correlation has been found between the value of L_0/L and the value of the fluorescence decay time.

In addition to those on II, measurements were also made on derivatives of II such as 3-phenylfluoranthene (III), 3,3′-bifluoranthenyl (IV), and 3-aminofluoranthene (V). The results of these investigations as well as the structural formulas of these compounds are also shown in Table I.

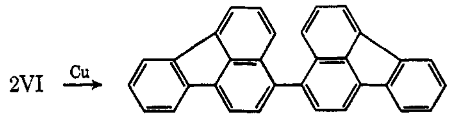
Synthesis and Purification of Fluoranthene Derivatives. Although both 3,3′-bifluoranthenyl (IV) and 3-phenylfluoranthene (III) were already known,[5] we were able to synthesize each of them in a different and (especially III) more efficient manner.

In both cases 3-iodofluoranthene (VI) was used as starting material. This compound was easily obtained by direct iodination[6] of fluoranthene (II) according to eq 1. The substitution of the iodine in the 3 position is according to expectation;[7] as far as electrophilic substitution is concerned, fluoranthene behaves as a biphenyl derivative. VI was also known previously[8] but was obtained by a procedure involving several steps.



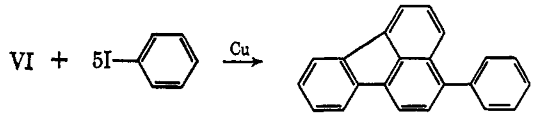
VI (1)

The Ullmann reaction with VI, according to eq 2, led to a fair yield of 52% of the bifluoranthenyl derivative IV. Table I shows physical properties of this compound.



IV (2)

The synthesis of 3-phenylfluoranthene (III) was achieved by a so-called mixed Ullmann reaction[9] with an excess of iodobenzene as indicated in eq 3. In this reaction, three compounds were actually formed, but by the application of excess iodobenzene, the formation of one of these compounds, bifluoranthenyl, was strongly reduced and there remained only the problem of separation of biphenyl from the desired 3-phenylfluoranthene. This problem was easily solved by tak-



III (3)

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(5) J. von Braun and G. Manz, *Ber.*, **70**, 1063 (1937).

(6) H. O. Wirth, O. Königstein, and W. Kern, *Ann. Chem.*, **634**, 84 (1960).

(7) E. Clar, "Polycyclic Compounds," Vol. 2, Academic Press Inc., New York, N.Y., 1964, p 295 ff.

(8) H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 2936 (1951).

(9) H. O. Wirth, G. Waese, and W. Kern, *Makromol. Chem.*, **86**, 139 (1965).

ing advantage of the steam volatility of biphenyl. In Table I physical properties of III are listed.

Several techniques were applied to achieve the desired high purity necessary for luminescence studies. A chromatographic column extractor, which is a simplified version of the adsorption–purification apparatus developed by Sangster and Irvine,[10] proved to be very efficient. We found the extraction technique to be especially useful in the purification of poorly soluble compounds like IV. The use of alumina saturated with dry hydrogen chloride, as previously reported,[11] was also very effective in connection with the column-extraction technique. More details concerning this purification technique will be presented elsewhere.[12]

Experimental Section

3-Iodofluoranthene (VI). A mixture of 11.2 g of fluoranthene, 5.0 g of iodine, 2.0 g of iodic acid (large crystals), 50 ml of acetic acid, 5 ml of water, 1 ml of concentrated sulfuric acid (the last two mixed beforehand), and 5 ml of carbon tetrachloride was heated and stirred at 80° until the iodine was completely consumed (about 7 hr). The crude iodine compound was isolated (16.2 g) by the addition of water. A chromatographic process using benzene as solvent and alumina as adsorbent, followed by crystallization from ethyl acetate–methanol (solution being cooled to −20°), gave pure VI, 13.6 g, mp 112° (lit.[8] 110°).

3 3′-Bifluoranthenyl (IV). In a reaction apparatus described previously,[13] a mixture of 6.3 g of 3-iodofluoranthene (VI), 5.8 g of copper powder,[14] about 100 mg of mercury, and 3 ml of 3,3′-dimethylbiphenyl was heated in a nitrogen atmosphere and stirred first for 2 hr at 200°, then 2 hr at 220°, and finally for 1 hr at 250°. After cooling to room temperature, the reaction mixture was mixed with about the same volume of alumina and then extracted with chloroform in a Soxhlet apparatus or in the chromatographic column extractor; 2.1 g (52% of the theoretical amount) of rather pure IV was isolated, mp 328–330°. The final purification was achieved by chromatographic column extraction with benzene as solvent and over alumina as adsorbent (half of it, the upper layer, saturated with dry hydrogen chloride gas), followed by crystallization from boiling triethylbenzene under conditions of slowly decreasing temperature (using a dewar vessel). By this method, it was possible to obtain IV with a sharp melting point of 331° (lit.[5] 327–329°).

3-Phenylfluoranthene (III). A mixture of 6.6 g of 3-iodofluoranthene (VI), 20.5 g of iodobenzene, 30.6 g of copper powder, 0.5 g of mercury, and 3 g of biphenyl was allowed to react as described for IV. After the extraction, a steam distillation was performed to remove the biphenyl. The remainder was dissolved in benzene and the insoluble side-product, IV, was filtered off. The dried benzene solution ($CaCl_2$) was then poured over an alumina column, the upper layer of which had been saturated with dry hydrogen chloride gas. After crystallization from ethyl acetate–methanol (cooling at −20°) 2.5 g of III was obtained, mp 141–143°. The final purification was effected by a chromatographic column extraction technique as described for IV but using petroleum ether (bp 30–60°) as solvent; 1.9 g of pure III, mp 145° (lit.[5] 144°), was obtained.

Discussion

Testing for Artifacts. To make certain that our results were not governed by ubiquitous impurities, much effort was expended in purifying and testing our compounds, especially fluoranthene. II was bought from several different suppliers, and various techniques of purification were employed, such as zone refining, recrystallization from various solvents, and column chromatography.

An additional test for detecting an impurity consisted of exciting the solution with radiation of different wavelengths in succession, recording the fluorescence spectrum each time, and then looking for any major changes as a function of the exciting wavelength. This procedure is very sensitive in highlighting the presence of an impurity which has a different fluorescence spectrum. Except for minor variations, the fluorescence spectrum of II was independent of the wavelength of the exciting wavelength.

Excimer fluorescence has also been investigated by us as a source of the fluorescence anomalies of II, and concentration studies were therefore made over a concentration range from 0.01 to 14 g/l. The fluorescence spectrum, decay time, quantum yield, and degree of quenching by oxygen were found to be invariant to the concentration of the solute.

Fluorescence decay time measurements provided us with more information than just values of the decay time. The technique of exciting the solute directly by pulsed monochromatic radiation established the decay time as being single valued and exponential. It can be demonstrated that, when the decay curve has more than one component, either a secondary process such as excimer formation has been initiated or an impurity is present. All of our measurements yielded decay curves which were exponential and single valued.

Further tests on II gave negative results. For example, varying the temperature of the solution over a temperature range of about 30° produced no significant change in the shape of the fluorescence spectrum. Also, measurements with either ethanol or benzene as solvent yielded only minor modifications in the position and shape of the absorption and fluorescence spectra. Because of these negative results, the presence of impurities or excimer formation can be discounted.

A Partially Hidden Transition. In studies[2] on fluoranthene, it has been suggested that a weak band at about 3900 Å represents a transition from a level below that represented by the intense bands at 3590 and 3240 Å. Our findings, including the apparent large Stokes shift of about 4000 cm^{-1}, provide confirming evidence for the existence of a partially hidden level. Furthermore, a long-wavelength band at approximately 4040 Å (Figure 1) corresponds to the band from which fluorescence takes place. On the basis of a natural fluorescence lifetime τ_{0m} of 177 nsec and an assumed electronic level width equal to that for most molecules, we estimate the maximum value of the molar extinction coefficient of the most intense band associated with this transition to be $\epsilon_{max} = 270 \pm 40$. This low value of ϵ_{max} is consistent with the designation of the transition ${}^1L_b - {}^1A$.

Anomalous fluorescence characteristics have been encountered and reported before[15] in biphenyl (I in Table I). The fluorescence decay time of I is abnormally long, its apparent Stokes shift is large, and it is immune to concentration quenching and excimer formation. Since biphenyl (I) is structurally related to fluoranthene (II) as shown in Table I, it is not surprising that both have similar anomalies. The long decay time

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(10) R. C. Sangster and J. W. Irvine, Jr., *J. Chem. Phys.*, **24**, 672 (1956); for further details, see Annual Report, Radiological Division, Argonne National Laboratory, July 1966–June 1967, ANL-7360.

(11) H. O. Wirth, W. Kern, and E. Schmitz, *Makromol. Chem.*, **68**, 69 (1963).

(12) H. O. Wirth and E. B. White, First International Congress on Heterocyclic Chemistry, University of New Mexico, Albuquerque, N. M., June 12–15, 1967.

(13) H. O. Wirth, K. H. Gönner, R. Stück, and W. Kern, *Makromol. Chem.*, **63**, 30 (1963).

(14) Purchased from the firm of Venus, Nuremberg, Germany.

(15) I. B. Berlman and O. J. Steingraber, *J. Chem. Phys.*, 43, 2140 (1965).

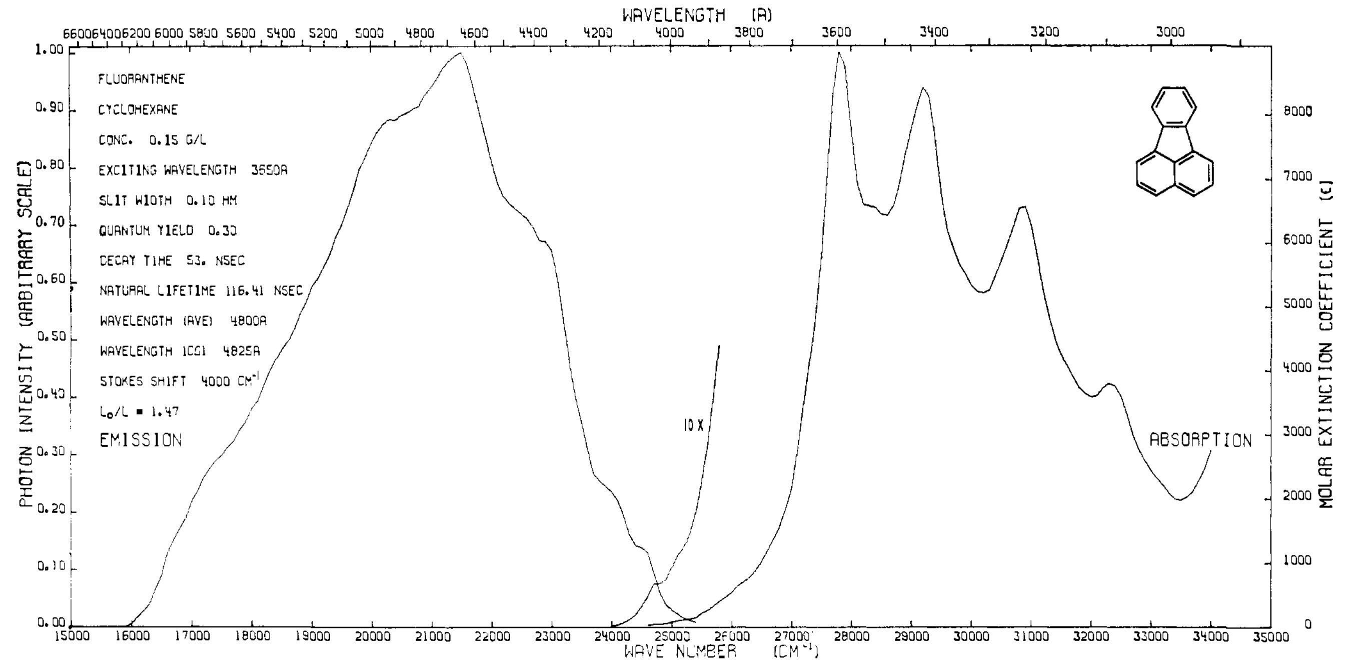

Figure 1. Absorption and fluorescence spectra of fluoranthene. Technique and symbols are given in ref 4. Limits of integration to compute τ_{0c} cover a wave-number range from 24,000 to 34,000 cm^{-1}.

of I has already been explained[15] by postulating a hidden but weak transition as just described for II. The fluorescence spectrum of I possesses an apparent Stokes shift of 3300 cm^{-1}, and such a large shift is consistent with the proposal of a hidden level. Steric hindrance in both the excited state and ground state is probably responsible for the lack of concentration quenching or excimer formation.

As shown in Table I compounds III and IV also exhibit anomalous characteristics but to a lesser degree. Concentration studies were not made with these materials. The fluorescence characteristics of V appear to be normal in that $\tau_{0m} \approx \tau_{0c}$. Also $L_0/L = 1.46$ is approximately the value that would be expected for a decay time value of 11.4 nsec. The reason that this latter compound conforms to the general rules of behavior may be found in its absorption spectrum wherein the band at 4040 Å is more intense than its adjacent absorption band at about 3700 Å.

Oxygen Quenching. It has been shown[4,16] that in the case of aromatic compounds, including biphenyl and its derivatives, the first excited singlet state is quenched by oxygen in proportion to the decay time of that state. This result is interpreted to mean that oxygen quenching is a diffusion-controlled process and that every encounter between an oxygen molecule and a molecule in an excited state leads to quenching of that state.

Fluoranthene is singularly different. It has a fluorescence decay time, τ, of 53 nsec, yet its ratio of L_0/L is only 1.47 (Table I), whereas, for example, τ and L_0/L of 2-methylnaphthalene are 59 nsec and 4.1, respectively.

The answer to the obvious question of why fluoranthene is relatively immune to oxygen quenching has not as yet been resolved. Part of the uncertainty stems from our lack of knowledge concerning the mechanisms by which the first excited singlet state is quenched so effectively by oxygen. One possibility is that oxygen quenching in certain cases can be explained by an electron-transfer reaction. We have not investigated this possibility. A second mechanism proposed for oxygen quenching is given by the expression

$$M^* + O_t \rightarrow M_t + O^*$$

where M* is a molecule in its first excited singlet state, O_t is an oxygen molecule in its ground state (triplet), M_t is a molecule in its lowest triplet state, and O* is an oxygen molecule in its first excited singlet state. Since the energy difference between the states M_t and M is about 0.8 ev,[17] and this is less than the energy required to produce a transition between the states O* and O_t which is about 1.0 ev, one may conclude that every encounter between an oxygen molecule and an excited fluoranthene molecule does not necessarily lead to quencing. Other factors may also contribute to a reduced sensitivity to oxygen quenching, *e.g.*, steric hindrance. Further investigations are intended to clarify this problem.

Acknowledgments. We thank Mr. J. Ostapowicz, Jr., for his skillful and generous assistance in constructing the chromatographic column extractor. Also our sincere thanks go to Mr. W. R. Anderson for his many suggestions concerning the presentation of this paper.

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(16) I. B. Berlman and T. A. Walter, *J. Chem. Phys.*, 37, 1888 (1962).

(17) A. Weller, private communication.