[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

Molecular Complexes of the Biphenylenes. π-Complexes with Tetracyanoethylene

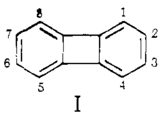
DONALD G. FARNUM,[1] EDWARD R. ATKINSON, AND WARREN C. LOTHROP

Received February 1, 1961

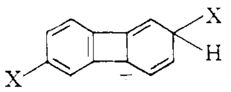
Spectroscopic and thermodynamic properties for charge-transfer complexes of biphenylene and three of its substituted derivatives with tetracyanoethylene have been compared with these properties for similar complexes of fluorene and the alkylated benzenes. The significance of the greater stability of the biphenylene complexes and a difference in the observed isokinetic relationship for the two types of complexes is discussed in terms of the cross-ring interactions in biphenylene and the geometry of the complexes.

INTRODUCTION

The theory and chemistry of biphenylene (I) have been the subjects of a number of recent reviews.[2] Thus far, evidence for "cyclobutadienoid character" of the central ring has been adduced either from the ultraviolet spectrum, which exhibits abnormally long wave-length absorption, or from the results of disubstitution reactions, which indicate resonance interaction between the rings.[2a] In either case little can be said about the *ground* state of biphenylene, as the ultraviolet spectrum is intimately concerned with the nature of the ground and the electronically excited states, while the rates of aromatic substitution reactions are dependent upon the stability of a highly distorted intermediate such as II relative to the ground state.



I



II

The present communication on the spectroscopic and thermodynamic properties of biphenylene-tetracyanoethylene (TCNE) charge-transfer complexes describes a part of a more extensive program designed to determine the effects of both minor and major perturbations of the π-electron system of biphenylene.

EXPERIMENTAL

The method used was similar to that of Andrews and Keefer[3] and Merrifield and Phillips,[4] except that tetracyanoethylene was used in excess rather than the hydrocarbon, and all spectra were taken in dichloromethane solution.

Materials. Tetracyanoethylene and the biphenylenes were prepared by literature methods[5] and purified to constant melting points by recrystallization and sublimation. Fluorene was a commercial sample similarly purified. The properties of the prepared biphenylenes were as follows: biphenylene, m.p. 110–110° (rec. 110°), $\lambda_{\max}^{C_2H_5OH}$ 360 (log ϵ 3.80), 345 (3.59)), 340 (3.63), 250 (4.90), 241 mμ (4.60); 1,8-dimethylbiphenylene, m.p. 80–81° (rec. 79–80°), $\lambda_{\max}^{C_2H_5OH}$ 367 (4.08), 348 (3.95), 254 (5.15), 245 mμ (4.88); 2,7-dimethylbiphenylene, m.p. 111–112° (rec. 110–111°), $\lambda_{\max}^{C_2H_5OH}$ 360 (3.68), 345 (3.58), 340 (3.58), 257 (5.10), 248 mμ (4.78); 2.7-dimethoxybiphenylene, m.p. 108–108.5° (rec. 107–108°), $\lambda_{\max}^{C_2H_5OH}$ 362 (4.15), 342 (4.08), 256 (5.10), 246 mμ (4.91).

Standard solutions of the reagents (*ca.* 0.1M for tetracyanoethylene and *ca.* 0.001M for the biphenylenes) were prepared in reagent grade dichloromethane at 22° and aliquots of these solutions were mixed and made up to volume at 22° for the determination of spectra. The concentrations at the temperatures at which the spectra were taken were corrected for the thermal coefficient of cubical expansion of dichloromethane (+0.12% per degree at 0°[6]).

Determination of spectra. Visible spectra were obtained on a Beckmann Model DK Automatic recording ultraviolet spectrophotometer equipped with a thermostated cell holder. The reference cell was filled with a solution of the appropriate concentration of tetracyanoethylene in dichloromethane. Thermal equilibration of the sample was ensured by retracing the spectrum periodically until the absorption remained constant. In no case was there evidence of further reaction, as indicated by the constancy of the absorption with time.

ANALYSIS OF THE DATA

The determination of association constants for π-complexes from the concentration dependence of their electronic absorption spectra has received detailed treatment elsewhere.[3,4] It is only necessary to note in connection with this work that the usual roles of the π-base as the excess reagent and the π-acid as the controlling reagent were inverted. This modification was advisable because of the

---

(1) To whom correspondence concerning this paper should be addressed. Present Address: Department of Chemistry, Cornell University, Ithaca, N. Y.

(2)(a) W. Baker and J. F. W. McOmie in *Non-benzenoid Aromatic Compounds*, D. Ginsburg, ed., Interscience, New York, 1959, p. 43. (b) Chemical Society Symposia, Bristol. 1958, London, 1958. (c) W. Baker and J. F. W. McOmie in *Progress in Organic Chemistry*, Vol. 3, J. W. Cook, ed., Butterworths, London (1955).

(3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73**, 462 (1951).

(4) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(5) W. C. Lothrop, *J. Am. Chem. Soc.*, **63**, 1187 (1941); **64**, 1698 (1942).

(6) V. Griffing, M. A. Cargyle, L. Corvese, and D. Eby, *J. Phys. Chem.*, **58**, 1054 (1954).

TABLE I

SPECTROSCOPIC AND THERMODYNAMIC PROPERTIES OF SOME TCNE-π-COMPLEXES

T = 22°; Solvent = CH_2Cl_2

π-Base	λ_{max} (mμ)	$\epsilon_{max} \pm 10\%$	$K_x \pm 10\%$	$-\Delta H$, Kcal./Mole ± 0.3	$-\Delta S$, Cal./Deg. ± 1
2,7-Dimethylbiphenylene	765	1160	132	7.4	15.6
1,8-Dimethylbiphenylene	715	1670	100	6.4	12.2
2,7-Dimethoxybiphenylene	840	1720	102	5.2	8.6
Biphenylene	680	500	80	2.8	1.0
Fluorene	570	2000 (lit.[4] = 1430)	19[a] (lit.[4] = 18)	4.0	7.8

[a] Determined from Merrifield and Phillips[4] more accurate value of ϵ_{max}.

small amounts of the biphenylenes available for study, and led to the final expression[7]

$$y = \frac{(B)\,l}{\log I_0/I} = \frac{1}{K_c\epsilon(\mathrm{TCNE})} + \frac{1}{\epsilon} \qquad (1)$$

where (B) is the *molar* concentration of the π-base, l is the cell length, $\log I_0/I$ is the optical density, ϵ is the molar extinction coefficient of the π-complex, (TCNE) is the *molar* concentration of tetracyanoethylene, and K_c is the association constant for formation of the complex *expressed in liters per mole.* For all 1:1 complexes, then, a plot of y *vs.* 1/(TCNE) should be linear and yield ϵ as the reciprocal of the y intercept and the product $K_c\epsilon$ as the reciprocal of the slope. Such plots of the results from spectroscopic data on four biphenylenes and fluorene are given in Fig. 1.

It is necessary to consider possible errors introduced by this modified analysis of the π-complex spectra. First, it is quite possible that the presence of a large excess of the π-acid, tetracyanoethylene, would favor the formation of 2:1 complexes. This source of error is, however, ruled out by the linearity of the plots in Fig. 1. Second, the values of 1/(TCNE) are limited by the solubility of tetracyanoethylene in dichloromethane (*ca.* 5 g./*l.* at 22°), thus a long extrapolation is necessary in order to obtain the intercept, $1/\epsilon$. It can be seen that the magnitude of the error thus introduced in the value of $1/\epsilon$ will depend upon the stability of the complex; those complexes with a large value of K—*i.e.* a gentle slope in the plot of Fig. 1—will give more accurate values for $1/\epsilon$. An estimate of the magnitude of this error can be obtained by a consideration of the fluorene-tetracyanoethylene complex. Analysis of this complex by the present method gave a value of $\epsilon = 2000$, while Merrifield and Phillips,[4] by the more usual analysis, obtained a value for $\epsilon = 1430$. These values are in quite good agreement when the sharp slope of the plot for the fluorene-tetracyanoethylene complex—a result of the comparative instability of the complex—is considered. As is evident from the other, more gently sloping plots of Fig. 1, the biphenylene-tetracyanoethylene complexes are considerably more stable than the fluorene-tetracyanoethylene complex, hence the probable error in ϵ from these data is of the order of 10%.

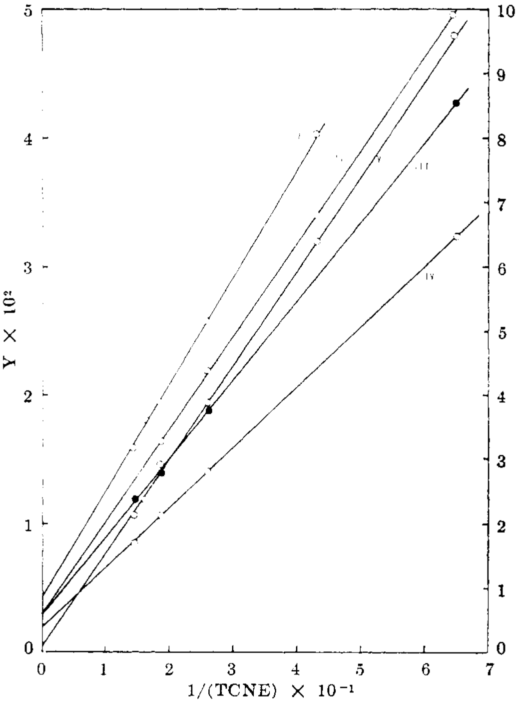


Fig. 1. Analysis of the concentration dependence of the visible absorption maxima for some tetracyanoethylene-π-complexes: I, 2,7-dimethylbiphenylene (right-hand coordinate); II, 1,8-dimethylbiphenylene (right-hand coordinate): III, 2,7-dimethoxybiphenylene (right-hand coordinate); IV biphenylene (left-hand coordinate); V, fluorene (left-hand coordinate)

In order to obtain similar plots at different temperatures only one observation is necessary, if it is assumed that ϵ is temperature independent.[4] In this way, the temperature dependence of K_c for the several complexes was determined. K_c was then converted to the equilibrium constant, K_x, expressed in *mole fractions*, by multiplication by the molarity of dichloromethane at the temperature in question and ΔH and ΔS for the complexes were determined by plotting log K_x *vs.* $1/T$ as shown in Fig. 2.

The spectroscopic and thermodynamic properties thus obtained for the tetracyanoethylene π-complexes studied in this work are shown in Table I.

---

(7) *Cf.* Equation 3 in ref. 4 (the sign of the term $1/\epsilon$ should be positive rather than negative).

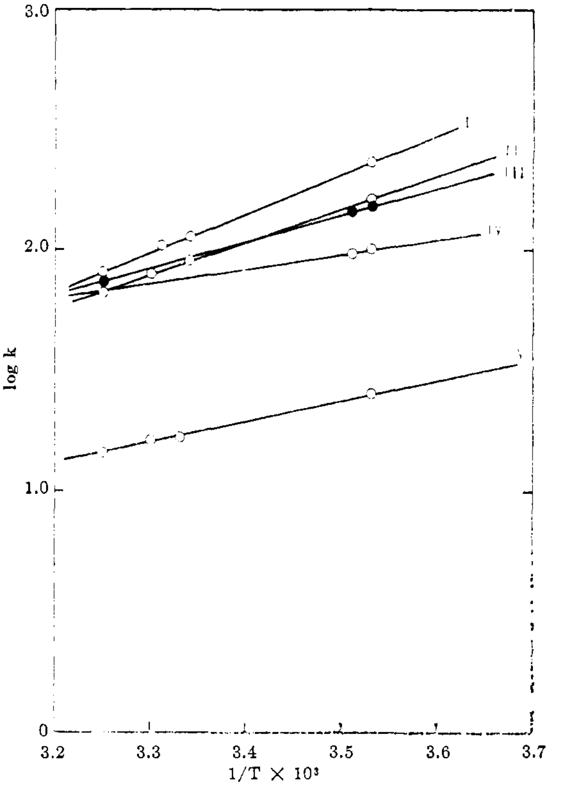


Fig. 2. Temperature dependence of K for some tetracyanoethylene-π-complexes: I, 2,7-dimethylbiphenylene; II, 1,8-dimethylbiphenylene; III, 2,7-dimethoxybiphenylene; IV, biphenylene; V, fluorene

Equilibrium constants in this table are given in terms of *mole fractions* (*i.e.*, K_x) in order that they may be directly comparable with earlier work.

DISCUSSION OF RESULTS

The plots in Fig. 2 emphasize the fruitlessness of attempting to discern any simple trend in the relative values of the equilibrium constants for the biphenylene-tetracyanoethylene complexes. The value of the constant for 1,8-dimethylbiphenylene, for instance, can be taken as greater than, equal to or less than that for 2,7-dimethoxybiphenylene, dependent upon the temperature chosen, within the 35° temperature range investigated. Nevertheless, it is also apparent from Fig. 2 that the biphenylene-tetracyanoethylene complexes are considerably more stable than the fluorene-tetracyanoethylene complex. The motivation toward the choice of fluorene as a model compound was, in part, derived from the fact that the conjugated phenyl rings in this substance are held copolanar, as is the case with biphenylene. Thus, any increase in stability of the biphenylene-tetracyanoethylene complexes could reasonably be ascribed to increased electronic interaction between the benzene rings in the complex as compared with fluorene. The more favorable equilibrium (by a factor of five or more) for the biphenylene-tetracyanoethylene complexes as compared with the fluorene-tetracyanoethylene complex thus constitutes the first demonstration of delocalization between the rings of a biphenylene system which is derived neither from a consideration of excited states (as in the "abnormal" ultraviolet spectrum of biphenylene[2a]), nor from a consideration of a highly distorted "activated complex" (as in the aromatic substitution reactions of biphenylene and its derivatives[2a]), but from a stable entity, the charge-transfer complex, which may represent a less violet perturbation[8] of the electronic system of biphenylene. If "complete" delocalization of biphenylene is assumed, a crude estimate of the expected stability of the biphenylene-tetracyanoethylene complex can be reached by considering biphenylene as a *planar* "diphenylbenzene". The effect of the introduction of one conjugated planar phenyl group on the benzene nucleus can be estimated by a comparison of fluorene ($K_{22^\circ} = 18.0$, statistically corrected $K = 9.0$) with benzene ($K_{22^\circ} = 2.0$).[4] Assuming that this stabilization energy is additive, a hypothetically fully conjugated, planar "diphenylbenzene" would have $K_{22^\circ} = 40.5$, thus suggesting a predicted $K_{22^\circ} = 81$ for biphenylene. A similar analysis based upon literature values[4] for the equilibrium constants of biphenyl, *p*-terphenyl, and fluorene leads to a predicted $K_{22^\circ} = 100$ for biphenylene. It can therefore be seen that, within the context of the expected effect of phenyl conjugation on the stability of charge-transfer complexes with tetracyanoethylene, the observed equilibrium constants of 80 or greater of such complexes with biphenylenes evidence a very real stabilization.

Previous articles[4,10] concerned with charge-transfer spectra have generally applied the results to a determination of ionization potentials of the hydrocarbons from either ultraviolet spectra or free energies of formation of their complexes. The correlations suggested by Merrifield and Phillips[4] for tetracyanoethylene complexes, though validated neither theoretically nor empirically, have been utilized to calculate the ionization potentials given in Table II. These authors suggested that the empirical relationship

$$\bar{\nu}_{\max} = 0.487\, I_p - 1.30 \text{ (e.v.)} \qquad (2)$$

yielded a fair description of the data for the methylated benzenes, though the application to naphthalene (and, hence, very probably, to the biphenylenes) was very poor. A better linear correlation of ΔF° for the complexes with the ionization poten-

---

[8] This conclusion is suggested by the fact that both the activation energies and free energy changes accompanying π-complex formation are generally quite small as compared with electronic excitation energies and activation energies of aromatic substitution reactions.[9]

(9) S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958); L. E. Orgel, *Quart. Revs.*, **8**, 422 (1954).

(10) G. Briegleb and J. Czekalla, *Angewandte Chemie*, **72**, 401 (1960).

TABLE II

PREDICTED VALUES FOR THE IONIZATION POTENTIALS OF SOME BIPHENYLENES

Compound	$-\Delta F^\circ_{298}$, Kcal./Mole	$I_P{}^a$ E. V.	$\bar{\nu}_{\max}$, Cm.$^{-1}$	$I_P{}^b$ E. V.
Fluorene	1.71	8.13	17,550	7.15
Biphenylene	2.59	7.37	14,700	6.40
1,8-Dimethylbiphenylene	2.69	7.28	14,000	6.22
2,7-Dimethoxybiphenylene	2.72	7.26	11,900	5.71
2,7-Dimethylbiphenylene	2.85	7.15	13,100	6.00

[a] As determined from Equation 3. [b] As determined from Equation 2.

tials of the hydrocarbons was found by these authors as expressed in the empirical relationship.

$$\Delta F^\circ = 0.0510\, I_p - 11{,}230 \text{ cal.} \qquad (3)$$

It is unlikely that either of these expressions will adequately predict the ionization potentials of the biphenylenes, as has been shown by the original authors, Equation 2 is no longer satisfactory when applied to the fused ring aromatic, naphthalene. It may be noted that ionization potentials for the biphenylenes as determined from Equation 2 are extraordinarily low. Furthermore, the already noted variations in relative equilibrium constants of the biphenylenes near room temperature renders any correlation of ionization potential with standard free energy change, as in Equation 3, suspect. Correlations of the ionization potential with $\bar{\nu}_{\max}$, or with the free energy change at some temperature far removed from room temperature may well exist in the biphenylene-tetracyanoethylene complexes, but discovery of their nature awaits the determination of the ionization potentials of the biphenylenes by some independent method.

Although the apparently random fluctuations of the equilibrum constants of tetracyanoethylene complexes with the substituted biphenylenes near room temperature effectively prohibit the application of even the crudest of linear free energy correlations, they suggest the possibility of a linear enthalpy-entropy[11] relationship, and, indeed, the clear linearity of that relationship in the present case is illustrated in Fig. 3. Although the physical meaning of this phenomenon in this and other cases remains somewhat obscure, it has been stated by Leffler[11] that "the existence of the [isokinetic] relationship is evidence favoring a constant mechanism." This consideration, of course applies to equilibria as well as to reaction rates. For this reason, the data obtained previously by Merrifield and Phillips[4] for tetracyanoethylene complexes with a number of substituted aromatics were reinterpreted in order to obtain ΔS values and provide an opportunity for the revelation of any functional connection with the ΔH values. The plot thus obtained is also reproduced in Figure 3. There is, clearly, a near-linear correlation of ΔH-ΔS for the investigated hydrocarbons. *This correlation, however, leads to a line of entirely different slope from that obtained from the biphenylenes.* The utility of this result is further amplified by the fact that fluorene (again corrected statistically) falls in line with the *alkylated benzenes* as indicated in Fig. 3. Thus, simply the introduction of a planar phenyl group in conjugation with the benzene ring or fusion of a planar ring is not sufficient to displace a π-base from the line. The displacement of the biphenylenes to give an entirely new series is, therefore, the result of a common, and quite probably, a unique characteristic.

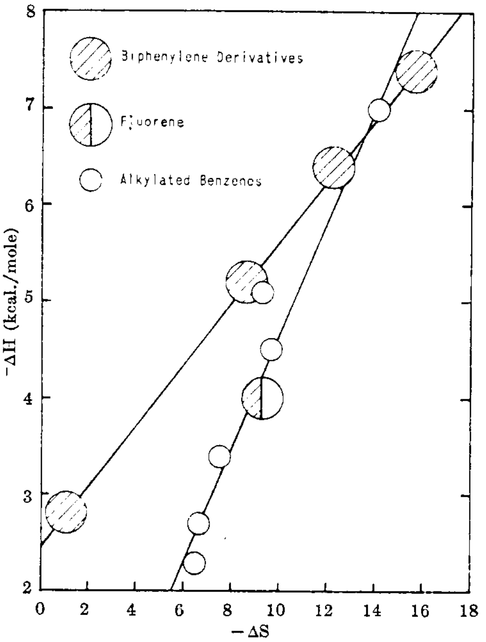
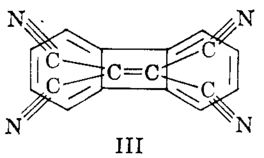


Fig. 3. Plots of enthalpy *vs.* entropy for a number of tetracyanoethylene-π complexes

Throughout the discussion thus far, some restriction, however vague, on the geometry of the biphenylene-tetracyanoethylene complexes has been tacitly assumed. Thus, in comparing benzene and biphenylene systems, tetracyanoethylene has been implicitly visualized as being closer to one of the benzene rings of biphenylene. In a potentially peripherally conjugated system like biphenylene this arrangement is certainly not a necessary one and perhaps not even a desirable one. We suggest that a more attractive explanation of our results is embodied in a pictorial representation as in III, with tetracyanoethylene lying in a plane parallel to that of the biphenylene and *symmetrically placed over the potential cyclobutadiene ring* (rotational



III

---

[11] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

isomer not implied). The concept of stabilization of a cyclobutadiene system through complex formation is not new,[12] although significant stabilization in such a loosely bound state as that in a charge-transfer or π-complex would be a novel and intriguing circumstance. The inordinate stabilities of the biphenylene complexes and, more pertinently, the requirement of a geometry somewhat different from that of the substituted benzene complexes as imposed by the different isokinetic relationship, are easily reconciled to the new geometry. We do not advocate this dibenzocyclobutadiene-tetracyanoethylene π-complex more vigorously because a clear physical interpretation and a definition of the limits of applicability of the enthalpy-entropy correlation have not yet been described.

We hope that work in progress will establish the geometry of other more firmly associated complexes of the biphenylenes.

CAMBRIDGE 40, MASS.

---

[12] R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

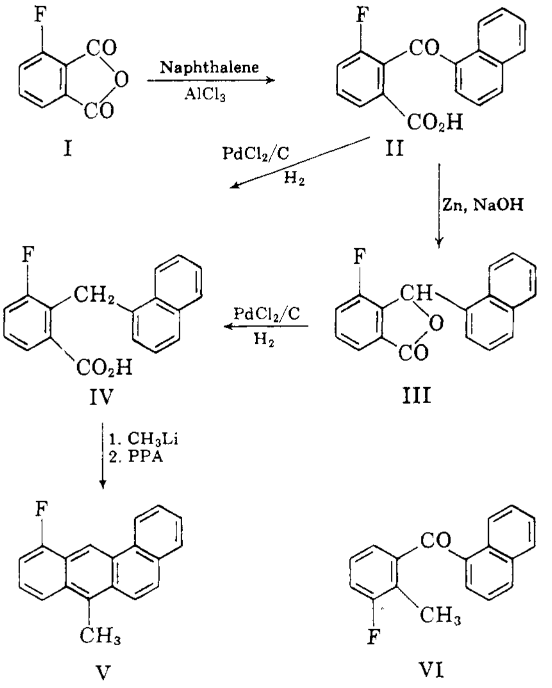
Synthesis of 8-Fluoro-10-methyl-1,2-benzanthracene[1]

MELVIN S. NEWMAN AND EDWARD H. WISEMAN[2]

Received January 5, 1961

The synthesis of 8-fluoro-10-methyl-1,2-benzanthracene is described. The elimination of a fluorine atom during the Elbs pyrolysis of 1-(3-fluoro-2-methylbenzoyl)naphthalene (VI) is noted.

In this paper we report the synthesis of 8-fluoro-10-methyl-1,2-benzanthracene (V), in continuation of a previously described program[3] to provide all of the monofluoro-10-methyl-1,2-benzanthracenes for carcinogenic studies.



The 3-fluorophthalic anhydride needed for the synthesis was prepared by oxidation of 2,3-dimethylfluorobenzene, obtained by decomposition of 2,3-dimethylbenzenediazonium hexafluorophosphate.[4] As a byproduct in this reaction, 2,2'-3,3'-tetramethylbiphenyl was isolated, the identity of which was established by synthesis from the known[5] 2,3-dimethyliodobenzene.

2,3-Dimethylfluorobenzene was oxidized to 3-fluorophthalic acid in high yield by potassium permanganate in aqueous pyridine solution. Distillation of the acid gave the required 3-fluorophthalic anhydride (I). The anhydride (I) was also prepared by heating 3-chlorophthalic anhydride with potassium fluoride, a method described[6] while our work was in progress. In our hands,[7] however, the yields obtained with small quantities could not be reproduced on a larger scale.

Attempts to oxidize 2,3-dimethylfluorobenzene with nitric acid led to the formation of 2-methyl-3-fluorobenzoic acid, the structure of which was established by decarboxylation to *o*-fluorotoluene and by conversion to 3-fluoro-2-methylaniline[8] by the Schmidt Reaction.[9]

Condensation of the anhydride (I) with naphthalene under Friedel-Crafts conditions gave 2-(1-naphthoyl)-3-fluorobenzoic acid (II) exclusively. This parallels the reaction[10] of 3-chlorophthalic anhydride, in that condensation occurs at the

---

[1] This work was supported by Grant C-4395 from the National Institutes of Health.

[2] One of us (E.H.W.) gratefully acknowledges the receipt of a Travel Grant from the Wellcome Trust, London W. 1, England.

[3] M. S. Newman, D. MacDowell, and S. Swaminathan, *J. Org. Chem.*, **24**, 509 (1959).

[4] K. Rutherford, paper to be published in *Canadian Journal of Research.*

[5] A. Klages and C. Liecke, *J. prakt. Chem.*, (2) **61**, 323 (1900).

[6] A. Heller, *J. Org. Chem.*, **25**, 834 (1960).

[7] This work was carried out by Mr. V. DeVries.

[8] G. Lock, *Ber.*, **69**, 2253 (1936).

[9] K. F. Schmidt, *Z. angew. Chem.*, **36**, 511 (1923).