isomer was cut out and extracted with 120 ml of ether. The residue obtained by evaporation of the ether solution was recrystallized twice from petroleum ether (bp 30-60°) to give yellow crystals, mp 148-149° (lit.[10] mp 150-151°). The mixture melting point of this substance with an equal quantity of authentic p-nitro-N-methylaniline was 149-150°. The chromatographic behavior of the reaction product was also identical with that of p-nitro-N-methylaniline.

Determination of Nitrogen-15 Content.—Kjeldahl digestion of the sample converted it into ammonia which was oxidized to nitrogen by hypobromite. The nitrogen was analyzed by mass spectrometry.[11] In the Kjeldahl procedure, excess glucose was added to the potassium sulfate-sulfuric acid digestion mixture, and it was cooled to 0° before addition of the sample to avoid the loss of nitrogen oxides. Titration of an aliquot of the distillate indicated that conversion of organically bound nitrogen to ammonia was complete in each case. Methylamine was shown to be absent by gas chromatography.

The ammonium ion in the distillate was converted into nitrogen by oxidation with sodium hypobromite which contained 0.1% sodium iodide. The nitrogen was then analyzed by mass spectrometry.

Spectrophotometric Analysis of the Rearrangement Products of N-Nitro-N-methylaniline and p-Fluoro-N-nitro-N-methylaniline.—The previously described procedure[1a,e] was utilized. However, the reaction mixtures were made up somewhat differently: 25.0 ml of 1.022 M perchloric acid, 3.061 g (0.025 mol) of sodium perchlorate, 0.25 g of sulfamic acid, and about 20 ml of water was thermostated at 40.0 ± 0.2° before the addition of 2.0 ml of a dioxane solution of the sample and enough water to bring the volume to 50.0 ml. The presence of sulfamic acid in the reaction mixture obviated the necessity of heating aliquots of the latter with sulfamic acid solution before diluting with buffer.

Kinetic Measurements.—Rate constants for rearrangement of the two nitramines were determined spectrophotometrically.[1b,e] The reaction mixtures were made up as described in the previous paragraph.

Chromatographic Analysis of Rearrangement Product of p-Fluoro-N-nitro-methylaniline.—The concurrent rearrangement

procedure described above was utilized with p-fluoro-N-nitro-N-methylaniline alone being added to the reaction mixture. The chromatographic eluate containing the ortho isomer was evaporated, and the residue was diluted with 95% ethanol to a concentration convenient to measure. The column was extruded and the central portion which should contain any p-nitro-N-methylaniline formed was cut out and extracted with ether. The residue from evaporation of the ether solution was also dissolved in a convenient amount of 95% ethanol. The absorbances of these two ethanol solutions at 370, 390, 410, and 430 mμ were determined. By comparing these with the absorbances of standard solutions of 2-nitro-4-fluoro-N-methylaniline and p-nitro-N-methylaniline in 95% ethanol, it was possible to compute the yields of these two compounds from the rearrangement: 77.2 ± 0.7% of the former and 0.16 ± 0.10% of the latter.

A synthetic mixture containing 1.31% p-nitro-N-methylaniline and 98.69% 2-nitro-4-fluoro-N-methylaniline was subjected to the same rearrangement conditions, separated chromatographically, and analyzed spectrophotometrically. The assay indicated that the mixture consisted of 1.37 ± 0.1% p-nitro-N-methylaniline and 94.3 ± 0.4% of 2-nitro-4-fluoro-N-methylaniline.

Reaction of N-Methylaniline with Nitrous Acid and Nitric Acid.—A 1.00-ml aliquot of 0.10 M sodium nitrite solution was added to a thermostated (40.0 ± 0.2°) solution of 25.0 ml of 1.022 M perchloric acid, 3.061 g (0.025 mol) of sodium perchlorated, 2.00 ml of 0.025 M N-methylaniline, and about 20 ml of water. Enough water at 40° was added to bring the volume to 50.0 ml, and the mixture was shaken and then kept at 40.0 ± 0.2° for 90 min. The solution was cooled and a 5.0-ml aliquot was heated with 5.0 ml of 5% ammonium sulfamate solution and then analyzed for o- and p-nitro-N-methylaniline as previously described.[1a] Not more than 0.21 ± 0.11% of the ortho isomer and 0.14 ± 0.09% of the para isomer were detected.

Substitution of 0.10 M sodium nitrate solution for the sodium nitrite resulted in not more than 0.16 ± 0.08% of the ortho isomer and 0.08 ± 0.10% of the para isomer.

(11) D. Rittenberg in D. W. Wilson, A. O. C. Nier, and S. P. Riemann, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Mich., 1948, p 31.

Electron Acceptors Derived from Fluorenecarboxylic Acids and Their Charge-Transfer Complexes

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Fluorenone-2,7-dicarboxylic acid (XII) and fluorenone-2-carboxylic acid (XVI) and -4-carboxylic acid (XIX) have been nitrated to give 4,5-dinitrofluorenone-2,7-dicarboxylic acid (Va), 4,5,7-trinitrofluorenone-2-carboxylic acid (XVII), and 2,5,7-trinitrofluorenone-4-carboxylic acid (XX), respectively. Reaction of these acids, or the corresponding methyl esters, with malononitrile in the presence of piperidine gave the 9-dicyanomethylene derivatives. These compounds, which represent a new class of functionalized electron acceptors, readily formed charge-transfer complexes with aromatic hydrocarbons and aromatic monoamines. With N,N,N',N'-tetramethyl-p-phenylenediamine, the radical anions and cations were formed exclusively. By use of simple molecular orbital theory, it was shown that these compounds have acceptor strengths similar to chloranil.

Charge-transfer complexes have been studied by many workers from various viewpoints. Their research has been described in several reviews.[1] Until recently, this work was limited to the interactions of monomeric electron donors and electron acceptors. Because of active interest in preparing practical organic semiconductors, these studies were extended to include

donor polymer–acceptor monomer complexes.[2] Interactions between polymers containing donor substituents with polymers containing acceptor groups were recently reported for the first time.[3] The donor polymers were prepared from aryliminodiethanols and the acceptor polymers from nitrated isophthalic and terephthalic acids. We found, however, that, while the donors

(1) (a) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964. (b) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965). (c) F. E. Gutmann and L. E. Lyons, "Organic Semiconductors" John Wiley & Sons, Inc., New York, N. Y., 1967.

(2) (a) W. Slough, *Trans. Faraday Soc.*, **158**, 2360 (1962); British Patent 1,009,361 (Nov 10, 1965). (b) J. H. Lupinski and K. D. Kopple, *Science*, **146**, 1038 (1964); U. S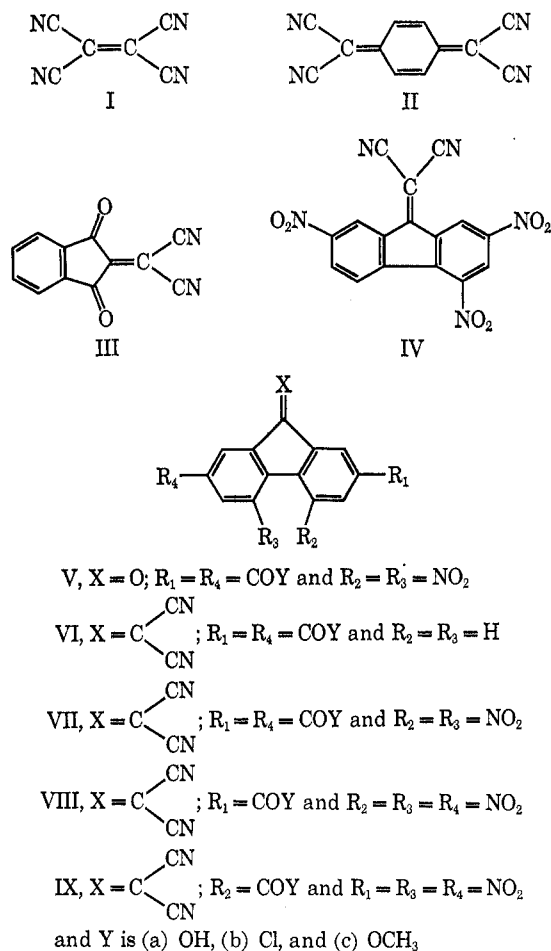. Patent 3,346,444 (Oct 10, 1967). (3) (a) T. Sulzberg and R. J. Cotter, *Macromolecules*, **1**, 554 (1968). (b) *ibid.*, **2**, 146 (1969). (c) *Chem. Eng. News*, **46** (54), 28 (1968).

were electron rich and readily formed strong charge transfer complexes, the acceptor polymers only formed weak complexes.

In order to prepare more powerful acceptor polymers, a species of much higher electron affinity than the nitrated phthalic acids should be constructed. Further, since one goal was the synthesis of tough, soluble, and well-defined polymers, research was concentrated on condensation polymers.[3]

A functional group that has been studied extensively to prepare acceptors of high electron affinity is the dicyanomethylene group.[4] Some compounds, such as tetracyanoethylene (I),[4a] tetracyanoquinodimethane (II),[4b] 2-dicyanomethylene 1,3-indanedione (III),[4c] and 9-dicyanomethylene-2,4,7-trinitrofluorene (IV),[4d,e] are readily prepared and have been characterized as being excellent electron acceptors. Therefore, we chose IV as a model on which to base our synthetic studies of new, functionalized electron acceptors.

This paper reports the synthesis and study of a series of functionalized fluorene acceptors (V–IX) for use in the synthesis of condensation polymers.

V, X = O; $R_1 = R_4 = $ COY and $R_2 = R_3 = $ NO$_2$

VI, X = C(CN)(CN); $R_1 = R_4 = $ COY and $R_2 = R_3 = $ H

VII, X = C(CN)(CN); $R_1 = R_4 = $ COY and $R_2 = R_3 = $ NO$_2$

VIII, X = C(CN)(CN); $R_1 = $ COY and $R_2 = R_3 = R_4 = $ NO$_2$

IX, X = C(CN)(CN); $R_2 = $ COY and $R_1 = R_3 = R_4 = $ NO$_2$

and Y is (a) OH, (b) Cl, and (c) OCH$_3$

Results and Discussion

Synthesis.—The synthesis of acceptors based on fluorenone-2,7-dicarboxylic acid (XII) as a key inter-

mediate is presented in Scheme I. Several methods were evaluated to diacetylate fluorene to XI. Adding acetyl chloride to a solution of fluorene and aluminum chloride in either carbon disulfide[5] or in methylene chloride was one variation. The reverse method of adding aluminum chloride to the other reactants was also tried. The purest product was obtained by adding a 1,2-dichlorethane solution of the acetic anhydride–aluminum chloride complex to a solution of fluorene in 1,2-dichloroethane.[6] Subsequent heating and work-up gave 60% yields of pure XI.

The use of sodium dichromate to oxidize XI to XII was attempted but it gave poor yields (<30%) because of the difficulty in separating XII from the resulting chromium salts.[7] While sodium hypochlorite prepared *in situ* gave <20% yields of XII, commercially available "Clorox" solutions gave 95% yields.

Conversion of XII to the diacid chloride (XIII) was performed routinely using an excess of thionyl chloride and N,N-dimethylformamide as catalyst.[7] While the keto diester (XIV) was prepared from either XII or XIII, reaction of XII with methanol and sulfuric acid was preferred.[7] The infrared spectra of compounds XII–XIV are discussed below.

The nitration of XII to yield Va was accomplished with a combination of fuming nitric acid and fuming sulfuric acid. A similar procedure was used to convert fluorenone to 2,4,5,7-tetranitrofluorenone.[8] Since the yields of Va were as high as 70%, alternate methods were not tried. Esterification of acid Va to Vc was done routinely with methanol–sulfuric acid.

The conversion of the various substituted 9-fluorenones (Va, Vc, XII, and XIV) to the corresponding 9-dicyanomethylene derivatives was carried out by two procedures. First, the compounds were slurried in methanol and malononitrile, piperidine was added, and then the reaction mixture was heated under reflux.[4a] Even though the reaction appears to occur heterogeneously, the reactants and products must possess slight solubility in methanol.

The second method for converting fluorenones to their dicyanomethylene derivatives used dimethyl sulfoxide as the reaction medium. The starting materials were dissolved in this solvent and the solution was heated to 120–130°. Since the products were very soluble in dimethyl sulfoxide, cooling in an ice bath was needed to precipitate them.

Finally, VIIa was converted to VIIc with thionyl chloride without the use of DMF. The latter complexes with VIIa and VIIc and was difficult to remove.

The procedures used to synthesize the two series of fluorene monocarboxylic acids are presented in Scheme II. Since these methods are very similar to those described above for the preparation of the fluorene-2,7-dicarboxylic acid acceptors, only the procedural differences will be discussed in detail. The use of crude XV for conversion to XVI probably accounts for the low yield (21%) that was attained. The synthesis of XVI was previously reported by the sodium dichromate oxi-

(4) (a) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958). (b) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *ibid.*, **84**, 3374 (1962). (c) S. Chatterjee, *Science*, **157**, 314 (1967). (d) H. D. Hartzler, U. S. Patent 3,226,388 (Dec 28, 1965) to Du Pont. (e) T. K. Mukherjee and L. A. Levasseur, *J. Org. Chem.*, **30**, 644 (1965).

(5) K. Dziewonski and J. Schnayder, *Bull. Int. Acad. Pol. Sci. Lett. Cl. Math. Natur.*, 529 (1930).

(6) M. M. Dashenskii and E. M. Shamis, *Ukr. Khim Zh.*, **30** (9), 938 (1964).

(7) (a) K. Dziewonski, St. Kuzdrol, and J. Mayer, *Bull. Int. Acad. Pol. Sci. Lett. Cl. Math. Natur.*, 348 (1934). (b) N. Ishikowa and T. Ozawa, *Yûki Gôsei Kogaku Kyokai Shi*, **17**, 553 (1959); *Chem. Abstr.*, **54**, 540f (1960).

(8) M. S. Newman and H. Boden, *Org. Syn.*, **42**, 95 (1962).

SCHEME I
FLUORENE-2,7-DICARBOXYLIC ACID ACCEPTORS

dation of XV.[9] Nitration of XVI to XVII proceeded in high yield (85%) because of the solubility of XVI in sulfuric acid. The subsequent conversions to XVIII and VIIIc and to VIIIa and VIIIb were performed as discussed above. Again, the nitration, esterification, dicyanomethylations and acid chloride formations were carried out in a similar manner to those discussed above.
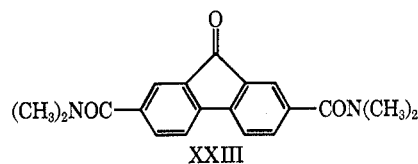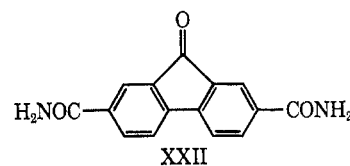
Infrared Spectra.—In the initial synthesis of the keto diester XIV, a single very strong carbonyl absorption band was observed at 5.81 μ (see Table I).

TABLE I
CARBONYL STRETCHING BANDS OF DISUBSTITUTED
FLUORENONE DERIVATIVES

Compd	Carbonyl bands and comments, μ
XII	5.79, 5.85, 5.90, and 5.95 (equal intensities)
XIII	5.73 (sharp)
	5.82 (shoulder)
XIV	5.81 (very sharp)
XXII	5.90 (6.05, very broad)
XXIII	5.82 (sharp, ketone band)
	6.14 (tertiary amide band)

Though XIV is a known compound some questions arose as to its structure.[7a] The infrared spectra of two precursors (XII and XIII) seemed consistent with their structures, but for confirmatory evidence fluorenone-2,-7-dicarboxamide (XXII) was prepared from XIII and ammonia.[7a] Unfortunately, the keto group was completely masked by being hydrogen bonded and one very broad carbonyl band appeared at 5.90-6.05 μ. Finally, the reaction of dimethylamine and XIII gave

the crude N,N,N',N'-tetramethylfluorenone-2,7-dicarboxamide (XXIII). This compound had a sharp

ketone band at 5.82 μ and a tertiary amide carbonyl band at 6.14 μ. This provided the conclusive proof of the position of the ketone carbonyl band in XIV.

Charge-Transfer Complexes and Spectra. A. With Aromatic Hydrocarbons.—As a means of determining the electron acceptor characteristics of the various fluorene compounds, a study of their complexes with aromatic hydrocarbons, aromatic monoamines, and aromatic diamines was undertaken.
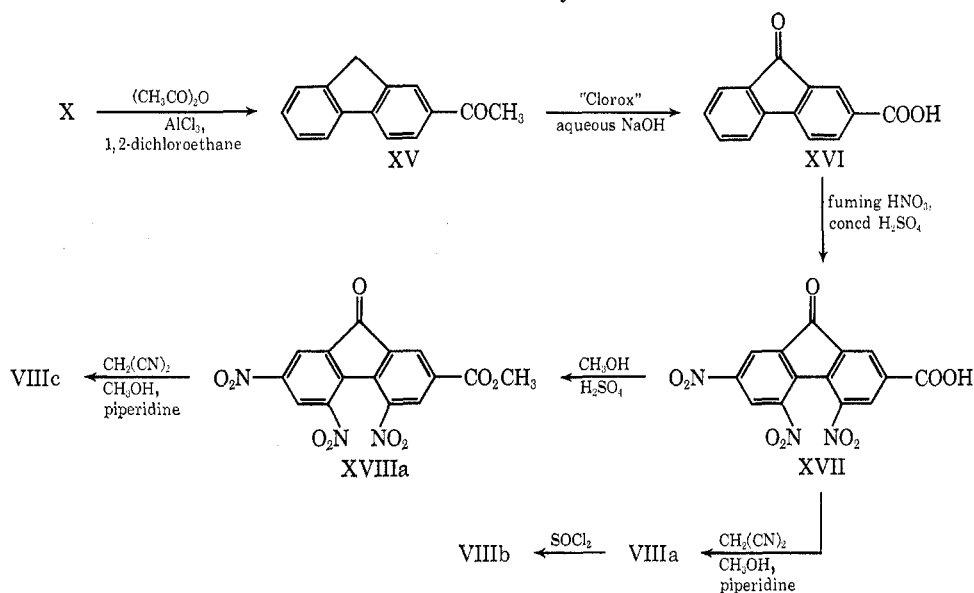
The acceptor strength of compounds can be determined by a method described by Dewar and co-workers.[10] The method is based on simple molecular orbital theory which states that the spectrum of a charge-transfer complex arises from an electronic transition from the highest occupied molecular orbital of the donor to the lowest vacant molecular orbital of the acceptor. Simply, if the acceptor is kept constant in a

(9) G. Rieveschl, Jr., and F. E. Ray, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 420.
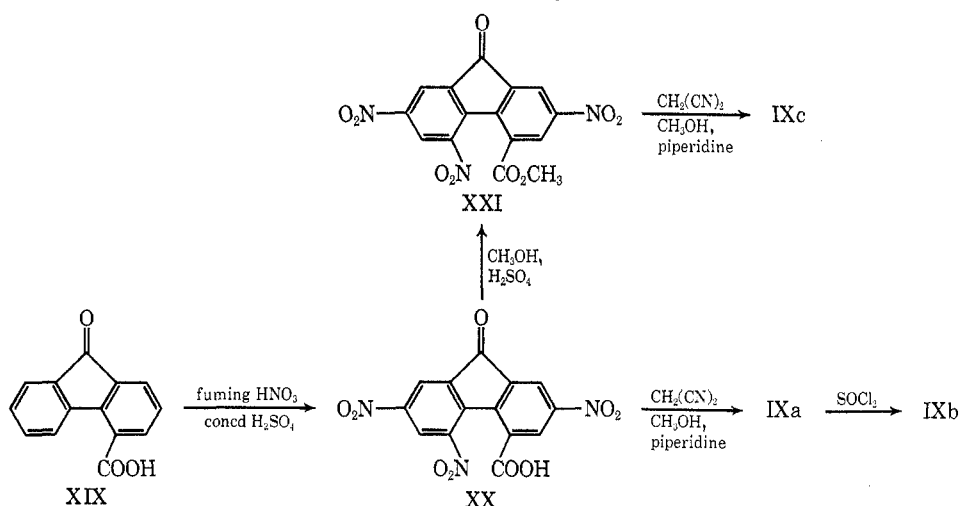
(10) (a) M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, **83**, 4560 (1961); (b) M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962).

SCHEME II
FLUORENE MONOCARBOXYLIC ACID ACCEPTORS

A. Fluorene-2-carboxylic Acid

$$X \xrightarrow[\substack{AlCl_3, \\ 1,2\text{-dichloroethane}}]{(CH_3CO)_2O} \quad XV \text{—}COCH_3 \xrightarrow[\text{aqueous NaOH}]{\text{"Clorox"}} \quad XVI \text{—}COOH$$

fuming HNO_3, concd H_2SO_4

VIIIc $\xleftarrow[\substack{CH_3OH, \\ piperidine}]{CH_2(CN)_2}$ XVIIIa (O_2N— —CO_2CH_3, O_2N NO_2) $\xleftarrow[H_2SO_4]{CH_3OH}$ XVII (O_2N— —COOH, O_2N NO_2)

VIIIb $\xleftarrow{SOCl_2}$ VIIIa $\xleftarrow[\substack{CH_3OH, \\ piperidine}]{CH_2(CN)_2}$

B. Fluorene-4-carboxylic Acid

XXI (O_2N— —NO_2, O_2N CO_2CH_3) $\xrightarrow[\substack{CH_3OH, \\ piperidine}]{CH_2(CN)_2}$ IXc

CH_3OH, H_2SO_4

XIX (—COOH) $\xrightarrow[\text{concd } H_2SO_4]{\text{fuming } HNO_3}$ XX (O_2N— —NO_2, O_2N COOH) $\xrightarrow[\substack{CH_3OH, \\ piperidine}]{CH_2(CN)_2}$ IXa $\xrightarrow{SOCl_2}$ IXb

series of complexes with different donors one derives the expression

$$\Delta E = \text{constant} - n\beta$$

where ΔE is the energy of the charge-transfer transition, β is the resonance integral, and n is the coefficient of β.
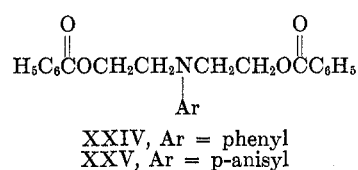
Since ΔE is proportional to spectral frequency, a plot of the observed charge transfer frequency against calculated n values[11] of the donors gives a straight line. Further, the y intercept of the line represents the energy level of the acceptor's lowest vacant molecular orbital (n value for acceptor) and a comparison of these values for various acceptors leads to a list of relative strengths.

The charge-transfer spectral absorption maxima of compounds Vc, VIc, VIIc, VIIIc, and IXc with a group of donor hydrocarbons are given in Table II. Also included are the published values for IV, 2,4,7-trinitro-fluorenone (TNF), and tetracyanoethylene (TCNE).

By plotting $1/\lambda$ (frequency of the charge-transfer absorption) against the molecular orbital coefficient (n) and determining the y intercepts for each compound, the relative acceptor abilities shown in Table III were obtained. The data indicates that the four dicyano-methylene fluorenes (IV, VIIc, VIIIc, and IXc) are of approximately equal acceptor strength, falling between TCNE and TNF. They appear to be quite similar in acceptor strength to chloranil.

B. **With Aromatic Monoamines.**—As model compounds for donor polymers,[3] dibenzoates XXIV and XXV were prepared. The charge transfer spectra

$$H_5C_6\overset{O}{\overset{\|}{C}}OCH_2CH_2NCH_2CH_2O\overset{O}{\overset{\|}{C}}C_6H_5$$
$$\overset{|}{Ar}$$

XXIV, Ar = phenyl
XXV, Ar = p-anisyl

(11) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," 2nd ed, Centre de Chemie Théoriqué de France, Paris, France, 1959.

of these amines with several acceptors were determined and are given in Table IV. These data confirm the

TABLE II

CHARGE-TRANSFER SPECTRA FOR HYDROCARBON–ACCEPTOR COMPLEXES[a]

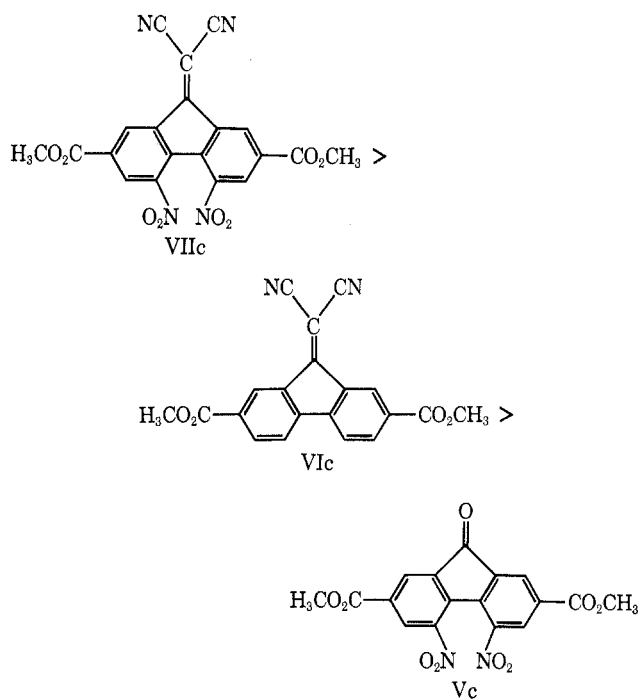| Donor	n^b	IV[c]	Vc	VIc	VIIc	VIIIc	IXc	TNF[d]	TCNE[e]
Fluorene	0.635	523	...[g]	450	517	537	525	425	...[h]
Anthracene	0.414	662	500	540	662	685	670	541	740
3,4-Benzopyrene	0.371	726	570	580	718	725	730	590	820
1,2,5,6-Dibenzanthracene	0.473	...[f]	500	515	...[f]	...[f]	590	...[f]	635
Perylene	0.347	745	600	610	790	790	785	620	920
Pyrene	0.445	650	500	535	644	670	645	520	720
Phenanthrene	0.605	500	...[g]	431	497	504	517	435	540
1,2-Benzanthracene	0.452	640	...[g]	...[g]	620	650	623	522	748
1,2-Benzoperylene	0.439	675	...[g]	...[g]	695	670	693	570	812
Triphenylene	0.684	508	...[g]	...[g]	508	535	533	425	570
Acenaphthylene	0.637	550	...[g]	...[g]	487	530	487	415	502

[a] Spectra of donors with acceptors run in 1,1,2,2-tetrachlorethane solution on a Cary 14 spectrophotometer. Data are presented in millimicrons (mμ). [b] The n values describe the donor ability of the aromatic hydrocarbons. These are calculated (lit.[11]) and the lower numbers indicate larger π electron availability. [c] See reference 4e. [d] Data for TNF from reference 4e. [e] Data for TCNE from reference 10b. [f] Several of the complexes of 1,2,5,6-dibenzanthracene were too insoluble and no spectral data was obtained. [g] Vc and VIc gave complexes which absorbed at low wavelengths with weak intensities and a further study was not made. [h] Not reported.

TABLE III

RELATIVE STRENGTHS OF CHARGE-TRANSFER ACCEPTORS

Compd	n^e
TCNE[a]	−0.11
VIIc	−0.20
IV	−0.21
Chloranil[b]	−0.22
IXc	−0.25
VIIIc	−0.26
TNF[c]	−0.30
VIc	−0.38
Vc	−0.40
1,3,5-Trinitrobenzene[d]	−0.46

[a] See M. J. S. Dewar and H. Rogers, *J. Amer. Chem. Soc.*, **84**, 395 (1962). [b] Calculated from data of G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin 1961. [c] See A. R. Lepley, *J. Amer. Chem. Soc.*, **84**, 3577 (1962). [d] See S. Chatterjee, *J. Chem. Soc. B*, 1170 (1967). [e] Just as n values represent donor abilities of electron rich systems, $-n$ values are a measure of ease of electron acceptor strength. The better the acceptor, the higher its n value.

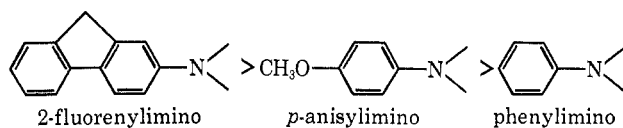previous evidence that the order of acceptor strength is as follows

VIIc

VIc

Vc

TABLE IV

CHARGE-TRANSFER SPECTRA OF
TERTIARY AMINE–ACCEPTOR COMPLEXES[a]

| Acceptor | Amine monomers | | Amine polymers | | |
	XXIV	XXV	...[b]	...[c]	...[d]
VIIc	662	800	640	760	800
VIc	530	620	530	600	630
Vc	<500	500			
DDQ	940	>1050			
Chloranil	670	795	535	735	740

[a] Spectra run in 1,1,2,2-tetrachloroethane on a Cary 14. Spectrophotometric data are presented in mμ. [b] Poly(phenyliminodiethanol-bisphenol A carbonate). [c] Poly(p-anisyliminodiethanol-bisphenol A carbonate). [d] Poly(2-fluorenyliminodiethanol-bisphenol A carbonate).

Further, it shows that VIIc is not so strong an acceptor as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) but, as previously shown, it is about equal to chloranil.

C. With Donor Polymers.—The charge-transfer spectra of several donor polymer–acceptor monomer mixtures are given in Table IV. The predicted order of donor ability is demonstrated, *i.e.*

2-fluorenylimino   p-anisylimino   phenylimino

Of further interest is the comparison of the data for the monomeric and polymeric amines. Using the same acceptor (VIIc), the monomeric phenylimino and p-anisylimino compounds absorb at higher wavelengths, 662 and 800 mμ, as compared with 640 and 760 mμ for the polymeric species. With chloranil, this effect is equally pronounced. The same is true, although to a lesser degree, with acceptor VIc. These data indicate that the acceptors form complexes of lower spectral transition energy with the monomeric donors than with less the mobile, donor polymer chains.
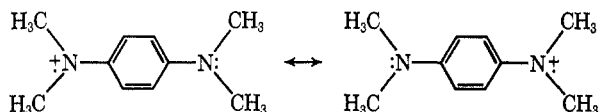
D. With Aromatic Diamines. Radical-Ion Formation.—It was shown above (Table IV) that the complex between VIIc and XXIV absorbed at 662 mμ. The addition of a p-methoxyl group in the donor caused the spectral maximum to shift to 800 mμ or a change of 138 mμ. If the more powerful dimethylamino group was used, an even longer wavelength absorption would be anticipated. In Table V is the data obtained from
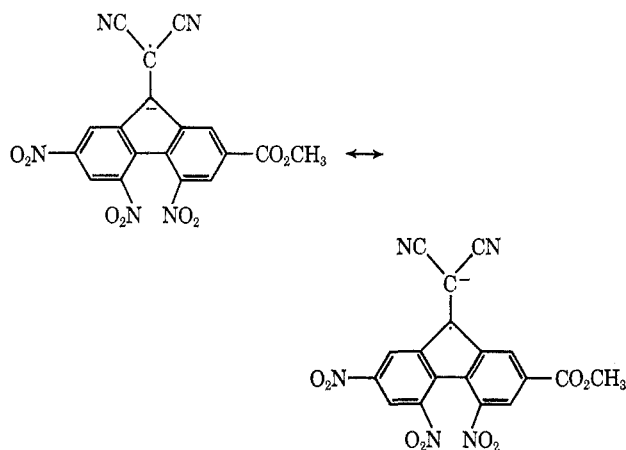
TABLE V

VISIBLE SPECTRA OF
TMPD WITH ACCEPTORS[a,b]

Acceptor	λ_{max}, mμ	Comments
	570	Purified TMPD
	620	Very weak owing to radical cation *via* air oxidation
VIIIc	567	Strong peaks (radical cation)
	620	
	745	Radical anion
IXc	570	Strong peaks (radical cation)
	620	
	750	Radical anion
IV[c]	740	No amine used; acceptor + LiI → radical anion

[a] Spectra run in 1,1,2,2-tetrachloroethane on a Cary 14 spectrophotometer. [b] The reported absorptions for the TMPD cation-radical are 570 and 620 mμ (see reference 12). [c] See reference 4e.

mixing VIIIc and IXc with N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD). The mixtures each have three absorption peaks at wavelengths below those previously discussed. The 570- and 620-mμ peaks are directly attributable to the radical cation of TMPD.[12]

The absorptions in the 740-750-mμ region are assigned to the radical anion of the α-dicyanomethylene fluorene species.[4e]

Experimental Section

2,7-Diacetylfluorene (XI).—To an ice-cooled mixture of 400 g (3 mol) of aluminum chloride and 500 ml of anhydrous 1,2-dichloroethane, acetic anhydride (153 g; 1.5 mol) was added dropwise with stirring. The addition time was 1.5 hr. The gray-green solution was added dropwise to 73 g (0.44 mol) of fluorene in 500 ml of 1,2-dichloroethane at 25°. After the addition, the reaction mixture was refluxed for 1.5 hr while 500 ml of 1,2-dichloroethane was distilled off. After pouring onto ice–HCl, the aqueous phase was decanted. The remainder was dissolved in 2 l. of hot acetone, cooled in the cold room and the solid collected. The 2,7-diacetylfluorene (77 g) which melted at 178–9° (lit.[5] mp 181–183°) was obtained in 62% yield.

Fluorenone-2,7-dicarboxylic Acid (XII).—A mixture of 76 g (0.3 mol) of 2,7-diacetylfluorene, 3 l. of "Clorox" (5.25% sodium hypochlorite), and 15 g of sodium hydroxide was heated slowly to about 65°. The reaction, which became exothermic, was kept below 80°. Periodic testing of the solution with pH

(12) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).

paper was done to keep it alkaline (pH >10). Adding small increments of sodium hydroxide ensured its basicity. After 4 hr, little solid was left floating in the solution and the reaction mixture was filtered to give 3.5 g of recovered 2,7-diacetylfluorene. After the excess sodium hypochlorite in the filtrate was destroyed with sodium hyposulfite, concentrated hydrochloric acid was added to obtain a pH of 3. The resulting yellow solid was collected, boiled in water for 0.5 hr, collected, and dried at 100° (1 mm). The yield of fluorenone-2,7-dicarboxylic acid was 77.2 g (94.7%) and the conversion was 99.4%. It appeared to melt with decomposition at 400° (reported 407°).[5]

Fluorenone-2,7-dicarboxylic Acid Chloride (XIII).—A mixture of 2.0 g (6.6 × 10⁻³ mol) of fluorenone-2,7-dicarboxylic acid, 25 ml of thionyl chloride and 1 ml of N,N-dimethylformamide was refluxed for 18 hr. After stripping the solvent, there was 1.5 g (70%) of solid. Recrystallization from toluene gave the acid chloride, mp 197–199° (lit.[7b] mp 198–200°).

Dimethyl Fluorenone-2,7-dicarboxylate (XIV).—A slurry of 10 g (3.8 × 10⁻² mol) of fluorenone-2,7-dicarboxylic acid in 200 ml of methanol and 20 ml of concentrated sulfuric acid was refluxed for 20 hr. The resulting yellow solid was collected, washed with water and dried. The dimethylfluorenone-2,7-dicarboxylate, which was recrystallized from acetic acid and melted at 217–218° (lit.[7a] mp 218°), was obtained in 85% yield (9.5 g): nmr (CF₃ COOH) δ 8.30 (doublet of doublet, 2, J = 1.4 and 8.2 Hz, aromatic protons in 3 and 6 positions), 8.09 (d, 2, J = 1.4 Hz, aromatic protons in 1 and 8 positions), 7.62 (d, 2, J = 8.2 Hz, aromatic protons in 4 and 5 positions), and 4.15 (s, 6, -OCH₃).

Anal. Calcd for $C_{17}H_{12}O_5$: C, 68.92; H, 4.08; O, 27.00. Found: C, 68.99; H, 4.00; N, 27.01.

The diester was also prepared from fluorenone-2,7-dicarboxylic acid chloride, methanol and pyridine. The infrared spectrum showed only a single sharp carbonyl band at 5.81 μ.

4,5-Dinitrofluorenone-2,7-dicarboxylic Acid (Va).—A heated solution of 5.4 g (2 × 10⁻² mol) of fluorenone-2,7-dicarboxylic acid in 40 ml of concentrated sulfuric acid, which was a deep red, was added dropwise over a 10-min period to a refluxing mixture (85°) of 65 ml of fuming nitric acid and 40 ml of concentrated sulfuric acid. A mixture of 45 ml of fuming nitric acid and 55 ml of concentrated sulfuric acid was added dropwise over a 4.5-hr period. The reaction, which was cooled to room temperature and stirred overnight, was poured onto 1 l. of ice water to give a pale yellow solid. It was collected, water washed and dried at 70° (1 mm). The 4,5-dinitrofluorenone-2,7-dicarboxylic acid (5.2 g, 72%) had a melting range of 285–294° dec.

Anal. Calcd for $C_{15}H_6N_2O_9$: C, 50.29; H, 1.69; N, 7.82; O, 40.20. Found: C, 48.44; H, 2.23; N, 8.77; O, 40.58.

Dimethyl 4,5-Dinitrofluorenone-2,7-dicarboxylate (Vc).—A mixture of 3.0 g (8.4 × 10⁻³ mol) of 4,5-dinitrofluorenone-2,7-dicarboxylic acid, 61 ml of concentrated sulfuric acid and 60 ml of methanol was heated at reflux for 18 hr. The solution was cooled, the solid filtered, washed with water and dried to give 2.1 g (66%) of Vc. After recrystallization from toluene-ethanol it melted at 252–255°: nmr (CF₃COOH) δ 9.92 (d, 2, J = 1.4 Hz, aromatic protons in 3 and 6 positions), 9.80 (d, 2, J = 1.4 Hz, aromatic protons in 1 and 8 positions) and 4.37 (s, 6, -OCH₃).

Anal. Calcd for $C_{17}H_{10}N_2O_9$: C, 52.86; H, 2.61; N, 7.25; O, 37.28. Found: C, 52.30; H, 2.54; N, 8.16; O, 37.20.

9-Dicyanomethylenefluorene-2,7-dicarboxylic Acid (VIa).—A mixture 2.7 g (1 × 10⁻² mol) of fluorenone-2,7-dicarboxylic acid and 250 ml of methanol was heated to reflux. Malononitrile (2.0 g, 3 × 10⁻² mol) and 2 drops of piperidine were added. The slurry turned from yellow to orange during 17 hr at reflux. The reaction mixture was cooled and the solid filtered. The product, which melted at 312–316°, was collected in 68% yield (2.15 g).

Anal. Calcd for $C_{18}H_8N_2O_4$: C, 68.36; H, 2.55; O, 8.86; O, 20.23. Found: C, 69.45; H, 2.88; N, 8.46; O, 17.25.

Dimethyl-9-dicyanomethylenefluorene-2,7-dicarboxylate (VIc).—Dimethylfluorenone-2,7-dicarboxylate (3.0 g, 1 × 10⁻² mol) and 250 ml of methanol were heated to reflux. Malononitrile (2.0 g, 3 × 10⁻² mol) and 2 drops of piperidine was added and heating continued for 1 hr. The reaction mixture was cooled, the orange solid collected and recrystallized from acetonitrile-dimethylformamide to give 2.5 g (74%) of product melting at 275–8°. An infrared spectrum had a cyano band at 4.48 μ.

Anal. Calcd for $C_{20}H_{12}N_2O_4$: C, 69.77; H, 3.51; N, 8.14; O, 18.58. Found: C, 69.59; H, 3.63; N, 8.05; O, 18.89.

Dimethyl 9-dicyanomethylenefluorene-2,7-dicarboxylate was also prepared in 76% yield by using dimethyl sulfoxide as solvent at 130° for 18 hr. Unlike the methanol procedure, the product was soluble in the solvent and ice bath cooling was required to obtain the product. This procedure was more useful for larger quantities than the above method.

4,5-Dinitro-9-dicyanomethylenefluorene-2,7-dicarboxylic Acid (VIIa).—After a mixture of 14.4 g (4 × 10⁻² mol) of 4,5-dinitrofluorenone-2,7-dicarboxylic acid and 400 ml of methanol was heated to reflux, 8.0 g (0.12 mol) of malononitrile and 8 drops of piperidine were added. After 1.5 hr at reflux, the solution was cooled in the cold room and 5.4 g (33%) of an orange solid was collected, mp 345°.

Anal. Calcd for $C_{18}H_6N_4O_8$: C, 53.22; H, 1.49; N, 13.79; O, 31.50. Found: C, 53.19; H, 1.55; N, 13.81; O, 31.38.

4,5-Dinitro-9-dicyanomethylenefluorene-2,7-dicarboxylic Acid Chloride (VIIb).—4,5-Dinitro-9-dicyanomethylenefluorene-2,7-dicarboxylic acid (1.6 g; 5 × 10⁻³ mol) and 25 ml of thionyl chloride were heated at reflux for 5 hr. The excess thionyl chloride was removed by distillation and the residue recrystallized from toluene to give 1.5 g (84%) of diacid chloride, mp 262–264°.

Anal. Calcd for $C_{18}H_4Cl_2N_4O_6$: C, 48.79; H, 0.91; Cl, 15.99; N, 12.64; O, 21.66. Found: C, 48.75; H, 1.22; Cl, 15.73; N, 12.48; O, 21.76.

Dimethyl 4,5-Dinitro-9-dicyanomethylenefluorene-2,7-dicarboxylate (VIIc).—Dimethyl 4,5-dinitrofluorenone-2,7-dicarboxylate (3.0 g; 7.8 × 10⁻³ mol) and 200 ml of methanol were heated to reflux. Malononitrile (1.4 g, 2.1 × 10⁻² mol) and 3 drops of piperidine were added and the solution changed from orange to red-purple. After refluxing for 2 days, the solution was cooled and the deep orange solid collected. The dimethyl 4,5-dinitro-9-dicyanomethylenefluorene-2,7-dicarboxylate (1.8 g, 53%) melted at 280–281° on recrystallization from acetonitrile.

Anal. Calcd for $C_{20}H_{10}N_4O_8$: C, 55.31; H, 2.32; N, 12.90; O, 29.47. Found: C, 55.19; H, 2.36; N, 12.89; O, 29.30.

2-Acetylfluorene (XV).—To an ice-cooled mixture of 135 g (1 mol) of aluminum chloride and 200 ml of anhydrous 1,2-dichloroethane, acetic anhydride (51 g, 0.5 mol) was added dropwise with stirring. The addition time was 1 hr. The gray-green solution was added dropwise to 83 g (0.5 mol) of fluorene in 150 ml of 1,2-dichloroethane at 25°. After the addition, the reaction mixture was refluxed for 1.5 hr while 200 ml of 1,2-dichloroethane was distilled off. The solution was poured onto ice-HCl and then warmed on the steam bath to remove the 1,2-dichloroethane. The resulting solid weighed 104 g (100% yield) and was oxidized without further purification to fluorenone-2-carboxylic acid.

Fluorenone-2-carboxylic Acid (XVI).—A mixture of 104 g (0.5 mol) of crude 2-acetylfluorene, 3 l. of "Clorox," and 15 g of sodium hydroxide were treated as described above for the preparation of fluorenone-2,7-dicarboxylic acid. There was obtained 24 g (21%) of fluorenone-2-carboxylic acid, mp ~335°C (lit.[7b] 340°).

4,5,7-Trinitrofluorenone-2-carboxylic Acid (XVII).—A solution of 10 g (4 × 10⁻² mol) of fluorenone-2-carboxylic acid in 80 ml of concentrated sulfuric acid, which was red in color, was added dropwise over a 10 minute period to a refluxing mixture (85°) of 130 ml of fuming nitric acid and 80 ml of concentrated sulfuric acid. A mixture of 90 ml of fuming nitric acid and 110 ml of concentrated sulfuric acid was added dropwise over a 4.5 hr period. After cooling to room temperature, the reaction mixture was stirred overnight, poured onto 1.5 l. of ice water and the yellow solid collected. After washing with a 5% sodium bicarbonate solution and water, the solid was dried overnight at 90° *in vacuo*. This afforded 12.2 g (85%) of 4,5,7-trinitrofluorenone-2-carboxylic acid melting at 267–275°.

Anal. Calcd for $C_{14}H_5N_3O_8$: C, 46.81; H, 1.40; N, 11.70; O, 40.09. Found: C, 46.79; H, 1.76; N, 11.61; O, 39.80.

Methyl 4,5,7-Trinitrofluorenone-2-carboxylate (XVIII).—A mixture of 4.0 g (1.1× 10⁻² mol) of 4,5,7-trinitrofluorenone-2-carboxylic acid, 200 ml of dry methanol and 5 ml of concentrated sulfuric acid was refluxed for 24 hr. The solution was cooled to afford 2.8 g (68%) of the yellow, crystalline methyl 4,5,7-trinitrofluorenone-2-carboxylate: mp 175–8°; nmr (DMSO-d_6) δ 8.97 (d, 1, J = 2.2 Hz, aromatic proton in 6 position), 8.72 (d, 1, J = 2.2 Hz, aromatic proton in 8 position), 8.67 (d, 1, J = 1.6 Hz, aromatic proton in 3 position), 8.51 (d, 1, J = 1.6 Hz, aromatic proton in 1 position), and 4.02 (s, 3, -OCH₃).

Anal. Calcd for $C_{15}H_7N_3O_9$: C, 48.27; H, 1.89; N, 11.26; O, 38.58. Found: C, 48.27; N, 1.83; N, 11.26; O, 38.73.

4,5,7-Trinitro-9-dicyanomethylenefluorene-2-carboxylic Acid (VIII).—To a refluxing mixture of 7.0 g (1.7 × 10⁻² mol) of 4,5,7-trinitrofluorenone-2-carboxylic acid and 200 ml of dry methanol, 2.2 g (3.4 × 10⁻² mol) of malononitrile and 3 drops of piperidine were added. After 24 hr, the solution was cooled to room temperature and filtered to afford 4.7 g (60%) of orange 4,5,7-trinitro-9-dicyanomethylenefluorene-2-carboxylic acid, mp 307–310°.

Anal. Calcd for $C_{17}H_5N_5O_8$: C, 50.14; H, 1.24; N, 17.19; O, 31.43. Found: C, 49.98; H, 1.58; N, 16.93; O, 31.51.

4,5,7-Trinitro-9-dicyanomethylenefluorene-2-carboxylic Acid Chloride (VIIIb).—A mixture of 1.0 g (2.4 × 10⁻³ mol) of 4,5,7-trinitro-9-dicyanomethylenefluorene-2-carboxylic acid and 25 ml of thionyl chloride was refluxed for 18 hr. The excess thionyl chloride was removed under reduced pressure and the residue was recrystallized from toluene to give 0.2 g (20%) of a solid melting at 292–300°.

Anal. Calcd for $C_{17}H_4ClN_5O_7$: C, 47.97; H, 0.95; Cl, 8.33; N, 16.45; O, 26.31. Found: C, 50.50; H, 1.47; Cl, 6.46; N, 16.40; O, 25.25.

Even though the analysis isn't too good, it is noted that at least 80% of the theroetical amount of chlorine is present. The high carbon and hydrogen values, as well as the other low values, can be explained on the basis of tightly complexed toluene in the final product.

Methyl 4,5,7-Trinitro-9-dicyanomethylenefluorene-2-carboxylate (VIIIc).—To a mixture of methyl 4,5,7-trinitrofluorenone-2-carboxylate (1.0 g; 2.7 × 10⁻³ mol) and 75 ml of methanol at reflux, 0.4 g (3 × 10⁻³ mol) of malononitrile and 1 drop of piperidine were added. After 4 hr, the solution was concentrated to 0.5 the volume and cooled overnight in the cold room. Filtration afforded 0.85 g (66%) of methyl 4,5,7-trinitro-9-dicyanomethylenefluorene-2-carboxylate melting at 269–273°.

Anal. Calcd for $C_{18}H_7N_5O_8$: C, 51.32; H, 1.68; N, 16.62; O, 30.38. Found: C, 51.04; H, 1.78; N, 16.54; O, 30.48.

2,5,7-Trinitrofluorenone-4-carboxylic Acid (XX).—By a procedure analogous to the preparation of 4,5,7-trinitrofluorenone-2-carboxylic acid, there was obtained 8.5 g (59%) of 2,5,7-trinitrofluorenone-4-carboxylic acid from fluorenone-4-carboxylic acid. The compound melted at 256–61°.

Anal. Calcd for $C_{14}H_5N_3O_9$: C, 46.81; H, 1.40; N, 11.70; O, 40.08. Found: C, 46.03; H, 1.90; N, 11.31; O, 40.80.

Methyl 2,5,7-Trinitrofluorenone-4-carboxylate (XXI).—This compound was prepared in the same way as methyl 4,5,7-trinitrofluorenone-2-carboxylate from 2,5,7-trinitrofluorenone-4-carboxylic acid. It melted at 183–184° and was obtained in 22% yield (0.9 g).

Anal. Calcd for $C_{15}H_7N_3O_9$: C, 48.27; H, 1.89; N, 11.26; O, 38.58. Found: C, 48.31; H, 2.20; N, 11.16; O, 38.58.

2,5,7-Trinitro-9-dicyanomethylenefluorene-4-carboxylic Acid (IXa).—To a refluxing mixture of 4.5 g (1.1 × 10⁻² mol) of 2,5,7-trinitrofluorenone-4-carboxylic acid and 200 ml of methanol, 1.5 g (2.2 × 10⁻² mol) of malononitrile and 3 drops of piperidine were added. After refluxing for 24 hr, the solution was cooled in an ice bath and the orange solid collected. The 2.0 g (40%) of 2,5,7-trinitro-9-dicyanomethylenefluorene-4-carboxylic acid melted at 313–5°.

Anal. Calcd for $C_{17}H_5N_5O_8$: C, 50.14; H, 1.24; N, 17.19; O, 31.43. Found: C, 50.02; H, 1.84; N, 17.09; O, 31.20.

2,5,7-Trinitro-9-dicyanomethylenefluorene-4-carboxylic Acid Chloride (IXb).—A mixture of 1.0 g (2.4 × 10⁻³ mol) of 2,5,7-trinitro-9-dicyanomethylenefluorene-4-carboxylic acid and 25 ml of thionyl chloride was refluxed for 18 hr. The excess thionyl chloride was removed under reduced pressure and the residue recrystallized from toluene to give a low yield (<10%) of a solid melting at 293–294°.

Anal. Calcd for $C_{17}H_4ClN_5O_7$: C, 49.97; H, 0.95; Cl, 8.33; N, 16.45; O, 26.31. Found: C, 48.50; H, 1.26; Cl, 7.84; N, 16.47; O, 25.32.

Methyl 2,5,7-Trinitro-9-dicyanomethylenefluorene-4-carboxylate (IXc).—Malononitrile (0.2 g, 3 × 10⁻³ mol) and 1 drop of piperidine were added to a refluxing mixture of 0.5 g (1.3 × 10⁻³ mol) of methyl 2,5,7-trinitrofluorene-4-carboxylate and 50 ml of dry methanol. After 4 hr, the mixture was concentrated to 0.5 the volume and cooled overnight in the cold room. Filtration gave 0.40 g (57%) of methyl 2,5,7-trinitro-9-dicyanomethylenefluorene-4-carboxylate melting at 285–7°.

Anal. Calcd for $C_{18}N_7N_5O_8$: C, 51.32; H, 1.68; N, 16.62; O, 30.38. Found: C, 51.25; H, 1.80; N, 16.22; O, 30.73.

Phenyliminodiethanol Dibenzoate (XXIV).—A mixture of 9.1 g (5 × 10⁻² mol) of phenyliminodiethanol (Matheson Coleman and Bell), 15.5 g (0.12 mol) of benzoyl chloride and 50 ml of pyridine was heated to 50° for 3 hr. The reaction mixture was poured onto ice water; the solid was collected and recrystallized from 400 ml of methanol to give 17.2 g (88%) of phenylimino-diethanol dibenzoate, mp 71.5° (lit.[13] 77°).

Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.59; O, 16.43. Found: C, 74.06; H, 6.09; N, 3.62; O, 16.18.

p-Anisyliminodiethanol Dibenzoate (XXV).—A mixture of *p*-anisyliminodiethanol (10.6 g, 5 × 10⁻² mol), benzoyl chloride (15.5 g; 0.12 mol) and 50 ml of pyridine gave *p*-anisylimino-diethanol dibenzoate by the same procedure used for XVII. One crystallization gave 10.6 g (50%) of XVIII, mp 62.4°.

Anal. Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34; O, 19.07. Found: C, 70.87; H, 6.04; N, 3.38; O, 19.65.

Charge-Transfer Complexes. Materials.—The aromatic hydrocarbons (Table II) were used as received from the Aldrich Chemical Company. The syntheses of the aromatic mono-amines are described above while the preparation of the phenyliminodiethanol polymers was previously described.[3b] TMPD was obtained from Matheson Coleman and Bell (MCB), converted to the dihydrochloride, recrystallized from 2-propanol,

(13) B. C. Mc Kusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.* **80**, 2806 (1958).

neutralized with sodium hydroxide and finally sublimed. It melted at 50°.[12]

The synthesis of the fluorene acceptors (Vc–IXc) are described above. Chloranil was obtained from MCB and recrystallized from benzene, mp 287°. DDQ was obtained from Aldrich Chemical Company and recrystallized from chloroform, mp 201°.

Spectra.—All measurements were made with a Cary 14 spectrophotometer using 1,1,2,2-tetrachloroethane of Spectro-grade quality as solvent.

Equilibrium in the Addition of Hydrogen Peroxide, Water, and Methanol to Acetone[1a]

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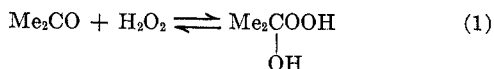
Equilibrium constants of 5.3 × 10⁻², 2.5 × 10⁻⁵, and 1.9 × 10⁻⁴ M^{-1} have been determined for the addition of hydrogen peroxide, water, and methanol to acetone. These equilibrium constants and values from the literature for hydroxylamine, hydrogen cyanide, and bisulfite ions give a satisfactory linear logarithmic plot against the γ of Sander and Jencks.

In connection with a study of the basicity of various nucleophilic reagents toward carbon,[2] equilibrium constants for the addition of hydrogen peroxide, water, and methanol to acetone were needed. These constants were determined by proton magnetic resonance (pmr) measurements.

Results

The addition of hydrogen peroxide to aqueous solutions of acetone gave rise to a new pmr peak at about τ 8.64 in addition to the acetone peak at about 7.84 ppm. The area of this new peak relative to that of the acetone peak grew over a period of hours, especially at high concentrations of hydrogen peroxide and acetone. This growth was more rapid when the solutions were made 0.001 M in perchloric acid but became unobservable in the presence of 0.1 M sodium acetate. By analogy to the fact that hemiacetal formation is both acid and base catalyzed and is fairly rapid in neutral solutions, whereas acetal formation is only acid catalyzed, we assumed that equilibrium in the addition of hydrogen peroxide to acetone had already been established by the

$$Me_2CO + H_2O_2 \rightleftharpoons Me_2COOH \qquad (1)$$
$$|$$
$$OH$$

time (about 1 hr) the first pmr measurements were made. The subsequent, slower, acid-catalyzed reaction is thought to consist of the formation of 2,2-bis-(hydroperoxy)propane, as shown in eq 2. In addition,

$$Me_2CO + 2H_2O_2 \rightleftharpoons Me_2C(OOH)_2 \qquad (2)$$

various other peroxide derivatives of acetone[3] were probably being formed to at least some extent. This interpretation of our results is consistent with the chemical shifts to be expected for the monohydroperoxy and bishydroperoxy products shown in eq 1 and 2. The new peak absorbs 0.80 ppm upfield from acetone. The methyl peaks for paraldehyde and acetaldehyde diethyl acetal appear 0.80 and 0.88 ppm, respectively, upfield from the methyl peak of acetaldehyde.[4] Since a hydroperoxy group has essentially the same effect as a hydroxy group on the chemical shift of a β proton,[5] the mono- and bishydroperoxy compounds would be expected to have about the same chemical shift. That this is the case is further supported by the observation to be described later in this paper that the pmr peaks

(2) J. Hine and R. D. Weimar, Jr. *J. Amer. Chem. Soc.*, **87**, 3387 (1965).

(3) *Cf.* N. A. Milas and A. Golubović, *ibid.*, **81**, 6461 (1959), and references listed therein.

(4) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Vol. 1, Varian Associates, Palo Alto, Calif., 1962, No. 6, 143; N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "High Resolution NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, no. 474.

(5) W. D. Wilk, A. L. Allred, B. A. Koven, and J. A. Marshall, *J. Chem. Soc. B*, 565 (1969).