hydrogenated products) τ 8.5 (complex broad multiplet with side peaks) and 9.15 (multiplet).

The absorption at τ 9.15 is consistent with a cyclopropyl CH_2 grouping in both the original and the hydrogenated reaction products.[21] Thus in the original reaction mixture to the extent of 32% can be assigned structure **5** on the basis of the infrared and n.m.r. data. No attempt was made to identify the component originally present in a 3% yield.

Acknowledgment.—The partial financial assistance of National Science Foundation Grant 19490 is gratefully acknowledged. The authors wish to thank Dr. Lillya of the Chemistry Department of the University of Massachusetts for running the n.m.r. spectra.

(21) (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) J. P. Chesick [*J. Am. Chem. Soc.*, **84**, 3250 (1962)] reported the cyclopropyl CH_2 grouping at τ 9.5 in bicyclo[2.1.0]pentane. (c) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

9-Dicyanomethylene-2,4,7-trinitrofluorene, A New Electron Acceptor

Tapan K. Mukherjee[1] and Leonard A. Levasseur

Energetics Branch, Air Force Cambridge Research Laboratories, Bedford, Massachusetts, and Tyco Laboratories, Inc., Waltham 54, Massachusetts

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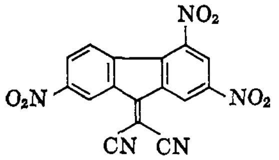
We wish to report the preparation of 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF), an acceptor which has superior complexing properties to its precursor, 2,4,7-trinitrofluorenone (TNF). In addition DTF forms stable anion-radical salts of lithium and triethylammonium cations. Although the ammonium acetate–acetic acid catalyzed condensation of fluorenone and malononitrile proceeds smoothly in benzene, this procedure, when applied to TNF, led to the recovery of starting material. This failure can be attributed to the donor activity of the solvent, which evidently converts TNF completely to its benzene complex. The alternative procedure of piperidine-catalyzed condensation in methyl alcohol gave an excellent yield of DTF.



The structure of DTF has been assigned on the basis of elemental analysis and infrared spectrum. Hydrolysis in concentrated sulfuric acid led to 9-biscarboxamidomethylene-2,4,7-trinitrofluorene. Alkaline hydrolysis with sodium hydroxide in dilute tetrahydrofuran failed to regenerate 2,4,7-trinitrofluorenone.

Solid charge-transfer complexes of DTF with aromatic hydrocarbons and amines are easily prepared by mixing chloroform or dichloromethane solutions of the components. In comparison with the TNF–hydrocarbon complexes, it was generally observed that the extent of dissociation into components on crystallization is markedly less with the corresponding DTF–hydrocarbon complexes. In Table I some of the donor–acceptor complexes of DTF are listed.

Table I

Charge-Transfer Complexes of DTF

Donor	Decompn. range, °C.	Calcd. for 1:1 complex C	H	N	Found C	H	N
Anthracene	258–261	66.54	2.78	12.93	66.69	2.80	12.79
Coronene	400	72.39	2.58	7.00	72.73	2.70	8.72
Fluorene	212–215	65.78	2.86	13.22	65.73	2.93	13.27
Perylene	365	70.23	2.78	11.38	70.08	2.90	11.11
Pyrene	330–340	67.95	2.67	12.38	67.69	2.79	12.27
Diaminodurene	195–198	59.20	4.00	18.59	58.92	4.20	18.30
N,N-Dimethyl-2-naphthylamine	215	62.91	3.39	15.72	62.81	3.33	15.48
4-Iodoaniline	203–204	45.37	1.90	14.30	45.53	2.17	14.45
2-Naphthylamine	210–212	61.67	2.78	16.59	61.59	2.76	16.48
Phenothiazine	235–238	59.60	2.51	14.92	59.89	2.93	14.21

The advantage of DTF as a complexing agent is evident from spectral studies of the charge-transfer transition bands, the results of which are presented in Table II.

Table II

Charge-Transfer Spectra for Hydrocrbon–DTF and Hydrocarbon–TNF Complexes and Energies of Highest Occupied MO's of the Hydrocarbons

Symbol	Donor	DTF^a	TNF^b	x_i^{c}
1	Acenaphthylene	550	415 ± 15	0.637
2	Anthracene	662	541 ± 4	0.414
3	1,2-Benzanthracene	640	522 ± 5	0.452
4	1,12-Benzoperylene	675	570 ± 5	0.439
5	1,2-Benzopyrene	600	510 ± 5	0.497
6	3,4-Benzopyrene	726	590 ± 5	0.371
7	3,4-Benzoteraphene	686	561 ± 5	0.405
8	Chrysene	576	482 ± 10	0.520
9	Coronene	650	512 ± 5	0.539
10	1,2,3,4-Dibenzanthracene	610	505 ± 5	0.499
11	1,2,3,4-Dibenzopyrene	647	548 ± 7	0.398
12	1,2,4,5-Dibenzopyrene	689	562 ± 2	0.442
13	Fluoranthene	500	430 ± 15	0.618
14	Perylene	745	620 ± 5	0.347
15	Phenanthrene	500	435 ± 15	0.605
16	Picene	561	470 ± 10	0.501
17	Pyrene	650	520 ± 5	0.445
18	Triphenylene	508	425 ± 15	0.684
19	Benzo[*ghi*]fluoranthene	510	430 ± 15	0.63^b
20	3,4-Benzofluorene	615	495 ± 5	0.505^b
21	2,3-Benzofluorene	570	485 ± 5	0.52^b
22	1,2-Benzofluorene	588	492 ± 5	0.51^b
23	Decacyclene	625	518 ± 10	0.47^b
24	Fluorene	523	425 ± 10	0.635^b

^{a} Spectra taken in CH_2Cl_2 solution. ^{b} See ref. 2. ^{c} C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," 2nd Ed., Mathematical Institute, Oxford, England, and the Centre de Mecanique Ondulatoire Applique, Paris, France, 1959.

The second column lists the donors, while the third and fourth columns show charge-transfer band maxima of DTF and TNF complexes, respectively. A few of the DTF–hydrocarbon spectra were measured in KBr disks and the absorption maxima were found to be within the same range with those obtained in solution. Since no sharp peaks could be obtained in the measurement of the spectra of TNF–hydrocarbon solutions, Lepley's[2] data on the spectra of solid TNF–hydrocarbon complexes is used for comparison. The fifth column

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[1] To whom inquiries regarding this article should be sent at the Air Force Cambridge Research Laboratories, Bedford, Mass.

[2] A. R. Lepley, *J. Am. Chem. Soc.*, **84**, 3577 (1962).

records the Hückel coefficients of the highest occupied molecular orbital (χ_i) of the donor. The charge-transfer bands of DTF complexes occur at considerably longer wave lengths, and are well separated from those of the components. In comparison, most of the observed charge-transfer regions of the TNF complexes are overlapped by donor absorption. The linear relationship[3] between the charge-transfer transition energy (E_π) and the donor orbital coefficient according to eq. 1 has been found to apply to the DTF–hydrocarbon

$$E_\pi = \text{constant} - \chi_i\beta \tag{1}$$

complexes (see Figure 1). In this equation, β is the carbon–carbon resonance integral; the constant is related to the energy of the lowest unfilled orbital of the acceptor, E'.

The straight line of Figure 1 was obtained by the method of least squares. The slope of Figure 1 gives -3.13 e.v. as the value of the carbon–carbon resonance integral which is in good agreement with previous values. From the intercept of the straight line with the x-axis, the energy level of the lowest unoccupied molecular orbital of DTF is found to be $E' = \alpha - 0.21\beta$. If we accept the generalization that for complexes of the same bond type (*e.g.*, π–π, n–π, etc.) a decrease in the transition energy is associated with the increase in the formation constant,[4] then DTF is intermediate in π-acid strength between tetracyanoethylene[5] ($E' = \alpha - 0.11\beta$) and TNF[2] ($E' = \alpha - 0.30\beta$).

The association constant (K) of the DTF–pyrene complex was determined by the Benesi–Hildebrand procedure.[6] The observed value of K (23.0) is higher than that for the TNF–pyrene complex (20.9). However, this evidence must be viewed with caution since the Benesi–Hildebrand procedure is subject to considerable error.[7] Further, it was shown by Melby and coworkers[8] that, unless appropriate consideration of the geometry of the π-complexes is made, the K-value as a sole measure of relative π-acid strength may lead to erroneous conclusions.

The lithium salt of the anion radical of DTF has been obtained as stable blue-black microcrystals from hot solutions of DTF and lithium iodide in acetonitrile. Similar experiments with sodium, potassium, and copper iodides gave highly colored but analytically impure paramagnetic ion-radical salts. Under similar conditions, TNF does not form any ion radicals. Electron spin resonance spectroscopy showed a single sharp line for the solid $DTF^{\cdot -}$–Li^+ anion-radical salt. Thus far, we have been unsuccessful in obtaining the fine structure of the anion radical in solution and, consequently, a detailed structural assignment cannot yet be made.

The electrical and photoelectrical properties of the DTF charge-transfer complexes and ion-radical salts will be described elsewhere.

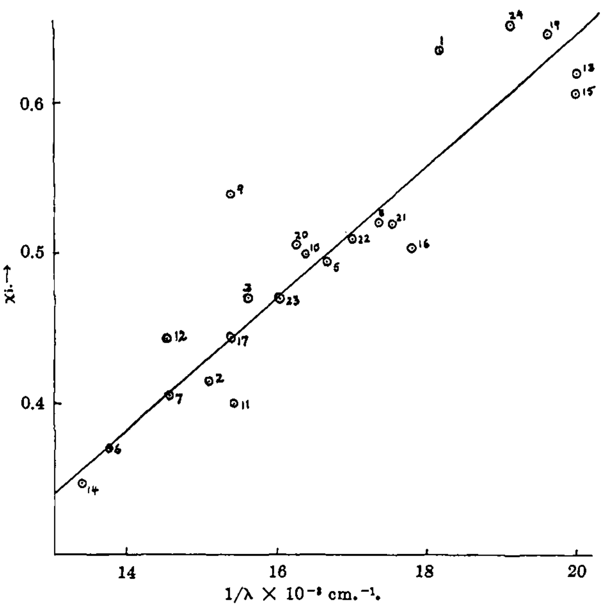

Figure 1.—Plot of the frequencies, $1/\lambda$, of the charge-transfer bands of DTF complexes against the molecular orbital coefficient, χ_i, for the highest filled orbital of the hydrocarbon.

Experimental[9]

Materials.—2,4,7-Trinitrofluorenone (TNF) was recrystallized from a 3:1 nitric acid–water mixture, washed with water, and dried under vacuum over silica gel. Anthracene, dibromoanthracene, pyrene, chrysene, and fluorene were purified by chromatography. Synthetic coronene was purified by repeated crystallization which was followed by sublimation and chromatography.[10] All the other hydrocarbons were used in the form obtained from Rutgerswerke-Aktiengesellschaft, Frankfurt-am-Main, West Germany. The purity of these materials was checked by melting point, absorption spectra, and thin layer chromatography. In several cases, further purification by chromatography was necessary.

Spectra.—Measurements were made with a Cary-14 spectrophotometer. Solution spectra were measured from 300 to 800 mμ with equal volume mixtures of 0.01 M acceptor and 0.02 M donor in Spectrograde dichloromethane. In cases of poor donor solubility, saturated solutions were used. Potassium bromide discs containing weighed amounts of pure complexes were prepared by standard techniques.[11] The disks were dipped in Nujol to prevent light scatter and moisture absorption. The electron spin resonance spectra were measured with a Varian e.s.r. spectrometer using 100-kc. field modulation.

Charge-Transfer Complexes.—Solid π-complexes were prepared by the following general procedures. A 1.5×10^{-3} M solution of the aromatic hydrocarbon in chloroform or dichloromethane was mixed with a 1.6–1.7×10^{-3} M solutions of DTF in the same solvent. Most of the reported π-complexes precipitated immediately. These were collected, washed with cold solvent, and dried under vacuum. In some instances, however, insolubility of the hydrocarbon in the nonpolar solvent necessitated mixing hot dilute solutions of the ingredients. On gradual cooling the π-complexes separated out as fine needles or microcrystals.

9-Dicyanomethylene-2,4,7-trinitrofluorene (DTF).—To a suspension of 3.15 g. (1×10^{-1} mole) of powdered TNF in 250 ml. of boiling methyl alcohol, 2.0 g. (3×10^{-1} mole) of malononitrile and 2 drops of piperidine were added. After 10 min. the mixture was allowed to cool to room temperature. The precipitate was filtered, washed with methyl alcohol, and recrystallized from acetonitrile to furnish 3.4 g. (93%) of large (1–1.5 cm.^{2}), yellow crystals of DTF, m.p. 266–268°.

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(3) M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

(4) R. E. Merrifild and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

(5) M. J S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962).

(6) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(7) For a discussion, see P. R. Hammond, *J. Chem. Soc.*, 479 (1964).

(8) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benons, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

(9) All melting points are uncorrected. Microanalysis were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn.

(10) The preparation and purification of coronene were carried out by Monsanto Research Corporation, Dayton, Ohio, under Contract AF19-(604)-8497.

(11) G. M. Wyman, *J. Opt. Soc. Am.*, **45**, 965 (1955).

Anal. Calcd. for $C_{16}H_5N_5O_6$: C, 52.89; H, 1.38; N, 19.25. Found: C, 52.49; H, 1.56; N, 19.33.

Ultraviolet absorption spectra in dichloromethane show maxima at 365 mμ (log ε 4.38). Infrared spectra in acetonitrile and in a KBr disk showed no absorption for the cyano group.

Acid Hydrolysis of DTF.—DTF (300 mg., 0.8×10^{-3} mole) was suspended in 25 ml. of concentrated sulphuric acid and warmed for 20 min.; then the mixture was poured on crushed ice. The precipitate was washed free from acid and dried to give 330 mg. of white solid, m.p. 355–360° dec. A sample recrystallized from acetonitrile had m.p. 359–360° dec. and analyzed for biscarboxamidomethylene-2,4,7-trinitrofluorene.

Anal. Calcd. for $C_{16}H_9N_5O_8$: C 48.12; H, 2.27; N, 17.54. Found: C, 47.96; H, 2.28; N, 17.30.

Lithium-DTF Anion-Radical Salt.—Lithium iodide (1.8 g., 4×10^{-3} mole) and DTF (1.5 g., 1×10^{-2} mole) were each separately dissolved in 25 ml. of hot Spectrograde acetonitrile and the solutions were mixed under a nitrogen atmosphere. On cooling, the anion-radical salt separated as blue-black microcrystals (1.24 g., 75%), m.p. 290° (explodes).

Anal. Calcd. for $C_{16}H_5LiN_5O_6$: C, 51.87; H, 1.36; Li, 1.88; N, 19.92. Found: C, 51.57; H, 1.60; Li, 1.62; N, 18.57.

Electronic absorption spectra taken in acetonitrile show maxima at 740 mμ (log ε 3.21); 562 mμ (log ε 3.29); 525 mμ (log ε 324); and 425 mμ (log ε 3.20). In the infrared, relatively strong absorption at 2200 cm.$^{-1}$ for the CN group was observed. The e.s.r. signal intensities of the microcrystals corresponded to about 5×10^{20} spins/mole.[12]

Attempted Preparation of Et_3NH^+-$(DTF)_2^{\cdot-}$.—In a boiling solution of 0.716 g. (1.9×10^{-3} mole) of DTF in 40 ml. of dichloromethane was dissolved a solution of 0.10 g. (1.0×10^{-3} mole) of TEA in 10 ml. of the same solvent. The mixture was cooled; the solid (50 mg.) was filtered and washed with cold solvent, m.p. 185–190° dec. The analysis gave values close to 1:1 composition.

Anal. Calcd. for $C_{22}H_{20}N_6O_6$: C, 56.89; H, 4.34; N, 18.10. Found: C, 56.67; H, 4.37; N, 16.13.

The above preparation was repeated using acetonitrile and THF as solvent. The ion-radical salt was obtained after evaporation of the solvent to a small volume. The resulting paramagnetic solid did not analyze for either the 1:1 or the 1:2 complex; in every case a low nitrogen value was obtained.[13]

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[12] The e.s.r. measurements were carried out by Dr. Kedma Bar-Eli. The absorption of weighed solid samples was compared with that of solid diphenylpicryl-hydrazyl. The accuracy of the measurements is estimated to be ±25%.

[13] NOTE ADDED IN PROOF.—We have now prepared a number of salts of DTF anion radical by the metathetical reaction between the onium iodides and lithium DTF. Typical examples of the cations are triethyl methyl ammonium, N-methyl quinolinium, triphenyl methyl phosphonium, and triphenyl methyl arsonium ions. These salts have the composition $(\text{cation})^+(\text{DTF})^{\cdot-}$.

α-Myrcene (2-Methyl-6-methylene-1,7-octadiene)

B. M. MITZNER, E. T. THEIMER, L. STEINBACH, AND J. WOLT

Research and Development Department, International Flavors and Fragrances, Inc., Union Beach, New Jersey

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α-Myrcene (2-methyl-6-methylene-1,7-octadiene) (I) has neither been reported as found in nature nor unequivocally prepared synthetically. The only mention of I in the literature is that of G. V. Pigulevskii, *et al.*,[1] who deduced its formation in the iodine-catalyzed dehydration of linalool (II) based upon Raman spectral data. Other apparent references[2] are not pertinent, since the corresponding abstracts do not mention α-myrcene.

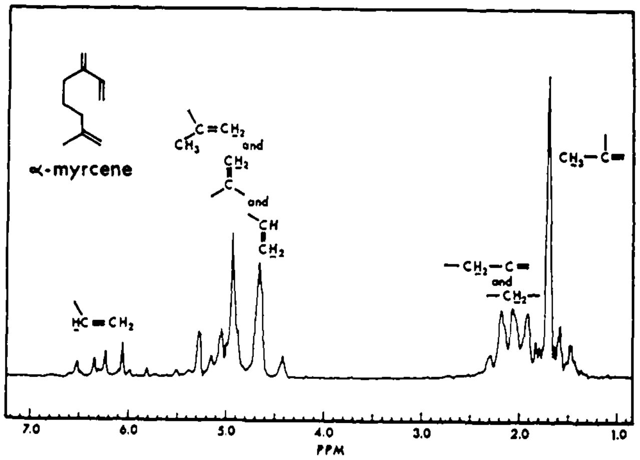


Figure 1.—N.m.r. spectrum of α-myrcene.

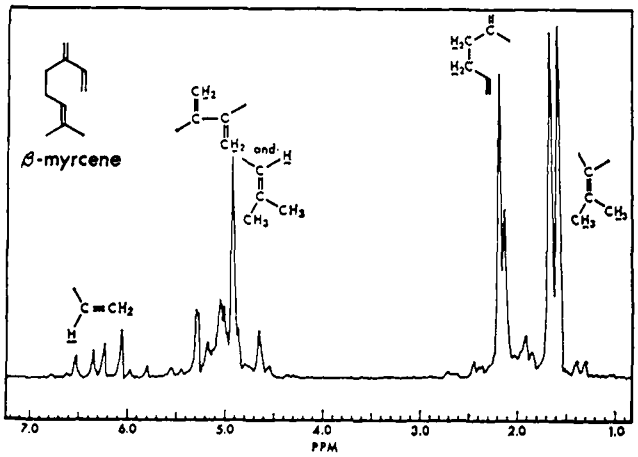
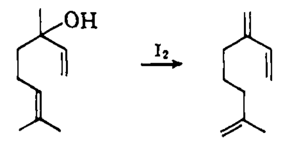
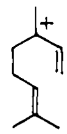


Figure 2.—N.m.r. spectrum of β-myrcene.



II I

The formation of I would not be predicted *via* a dehydration through carbonium ion III, and has not been reported as a product of such dehydration by other workers.[3,4]



III

On the other hand, *cis*- and *trans*-ocimene, β-myrcene (7-methyl-3-methylene-1,6-octadiene), and dipentene can be predicted as products and have, in fact, been so reported when using acid-type catalysts.[5,6]

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[1] G. V. Pigulevskii and N. L. Prokudina, *Dokl. Akad. Nauk SSSR*, **67**, 283 (1949).

[2] F. K. Beilstein, "Handbuch der Organischen Chemie," Vol. I, 4th Ed., 3rd Supplement, 1958, p. 1053.

[3] B. A. Arbusov and W. S. Ambramov, *Chem. Ber.*, **67**, 1942 (1934), and older references cited therein.

[4] F. Ascoli and V. Crescenzi, *Chim. Ind.* (Milan), **40**, 724 (1958).

[5] M. Günzl-Schumacher and U. Wicker, *Chem. Ber.*, **93**, 974 (1960).

[6] International Flavors and Fragrances, Inc., unpublished work.