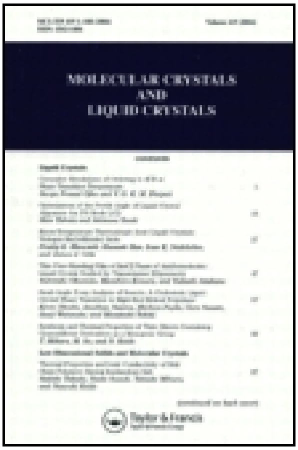

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Cyanocarbons—Their History From Conducting to Magnetic Organic Charge Transfer Salts

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Version of record first published: 06 Dec 2006.

To cite this article: W. R. Hertler , W. Mahler , L. R. Melby , J. S. Miller , R. E. Putscher & O. W. Webster (1989): Cyanocarbons—Their History From Conducting to Magnetic Organic Charge Transfer Salts, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 171:1, 205-216

To link to this article: http://dx.doi.org/10.1080/00268948908065796

Mol. Cryst. Liq. Cryst., 1989, Vol. 171, pp. 205–216
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Printed in the United States of America

Cyanocarbons—Their History From Conducting to Magnetic Organic Charge Transfer Salts†

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E. I. du Pont de Nemours and Co., Inc., Experimental Station E328, Wilmington, Delaware 19880-0328 U.S.A.

A generation ago scientists at Du Pont's Central Research and Development Department sought to prepare, understand, and exploit organic molecules lacking aliphatic hydrogens and possessing a large cyano group to carbon ratio. Like many other ambitious quests the anticipated goal (of commercializing a new family of polymers) was not realized. Nonetheless, the discoveries made during this pursuit have made a permanent mark on the evolution of science. Most notably, the discovery of tetracyanoethylene (TCNE), and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), and the remarkable stability of their radical anions led to an unusual series of charge transfer salts. Many of the TCNQ electron-transfer salts exhibit high, metal-like, dc electrical conductivity. These initial observations led to the evolutionary development of conducting polymers and the realization of molecular based ferromagnets.

INTRODUCTION

The year 1988 marked the Golden Jubilee celebration of the serendipitous discovery by Roy Plunkett of the scientifically fascinating and technologically exciting properties of poly(tetrafluoroethylene) (PTFE or Teflon®).[1] This invention spearheaded the development of fluoropolymers which find daily use in all segments of modern society. Teflon, along with nylon, which itself celebrates the Golden Jubilee anniversary of its commercialization, inaugurated the "Plastics Age." Cyanocarbons‡ were a deliberate outgrowth of these innovations. Based upon the importance of fluoropolymers and polyacrylonitrile, Orlon®, Theodore L. Cairns envisioned polymers with many highly electron-withdrawing, cyano groups might lead to another class of materials with intriguing and technologically important properties.

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†This manuscript is dedicated to the Du Pont scientists, Table I, who have made revolutionary and evolutionary contributions to the history of cyanocarbons chemistry and physics.

‡By analogy to fluorocarbons, cyanocarbons can be defined as compounds containing carbons with multiple nitrile groups without aliphatic hydrogens. A less restrictive definition cyanocarbons such as cyanoform and TCNQ.

Contribution No. 4833 from the Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station E328, Wilmington, Delaware 19880-0328 U.S.A.

TABLE I

DuPont scientists who contributed to the history of cyanocarbons

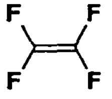
Scientist	Current Position
Donald S. Acker	Retired
Paul Arthur, Jr.	Retired
Paul Bierstedt	Central Research and Development Department
Richard E. Benson	Retired
Elwood P. Blanchard	Executive Vice President
Dale C. Blomstrom	Central Research and Development Department
Robert W. Begland	Petrochemicals Department
Richard H. Boyd	University of Utah
Morton Brown	Fibers Department
Allan Cairncross	Central Research and Development Department
Theodore L. Cairns	Retired
Joseph C. Calabrese	Central Research and Development Department
Rudolph A. Carboni	Electronics Department
Bruce A. Carlson	Polymer Products Department
Engelbert Ciganek	Medical Products Department
Donald D. Coffman	Deceased
Donald B. Chesnut	Duke University
Kenneth C. Dewhirst	
Jurgen Diekmann	Electronics Department
Clifford L. Dickinson	Retired
David A. Dixon	Central Research and Development Department
Dennis S. Donald	Central Research and Development Department
Joseph R. Downing	Retired
Vaughn A. Engelhardt	Retired
Joseph L. Gillson	Retired
Ronald P. Groff	Central Research and Development Department
James Gulley	Chevron Research
Bruce S. Fisher	
Harlan Foster	Retired
Charles J. Fritchie	Retired
Tadamichi Fukunaga	Central Research and Development Department
Robert J. Harder	Retired
Donald R. Hartter	Air Products, Inc.
Harris D. Hartzler	Central Research and Development Department
Richard E. Heckert	Chief Executive Officer
Walter R. Hertler	Central Research and Development Department
Edward G. Howard	Central Research and Development Department
Eric Jolley	Retired
Frank N. Jones	North Dakota State University
M. Thomas Jones	University of Missouri, St. Louis
Alden Josey	Retired
Glen Kepler	Sandia National Laboratories
Carl G. Krespan	Central Research and Development Department
Paul J. Krusic	Central Research and Development Department
Ernest L. Little	Deceased
William Linn	Agricultural Products Department
Catherine E. Looney	Imaging Systems Department
Walter Mahler	Central Research and Development Department
Elmore L. Martin	Retired
Blaine C. McKusick	Retired
Cameron C. McDonald	Retired
Edith Ann Graef McGeer	University of British Columbia
L. Russell Melby	Retired
Richard E. Merrifield	Central Research and Development Department
William J. Middleton	Ursinus College
Joel S. Miller	Central Research and Development Department

TABLE I (*continued*)

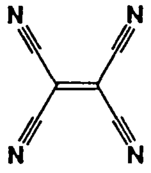
Scientist	Current Position
Walter E. Mochel	Retired
Howard F. Mower	University of Hawaii
William D. Phillips	Retired Senior Vice President, Mallinckrodt Corp.
William W. Prichard	Retired
Steven Proskow	Deceased
John C. Rowell	Retired
John R. Roland	Deceased
Donnie J. Sam	Polymer Products Department
George N. Sausen	Central Research and Development Department
Richard M. Scribner	Medical Products Department
W. Jan Siemons	Deceased
Howard E. Simmons, II	Vice President, Central Research and Development
Gilbert J. Sloan	Polymer Products Department
Andris Suna	Central Research and Development Department
William A. Sheppard	Deceased
Clem M. Theobald	Deceased
Swiatoslaw Trofimenko	Electronics Department
Susan Vladuchick	Fibers Department
Robert D. Vest	Retired
Owen W. Webster	Central Research and Development Department
Frank J. Weigert	Central Research and Development Department
Claus D. Weis	Retired
Robert C. Wheland	Central Research and Development Department
H. Ernest Winberg	Deceased
Douglas W. Wiley	Central Research and Development Department
Jack K. Williams	Deceased
David L. Woodward	Retired

EARLY HISTORY

In the early 1950's T. L. Cairns assembled a team of organic chemists to synthesize, characterize, study, and ultimately exploit the chemical reactivity and physical properties of cyanocarbons. Cyanogen, cyanoacetylene, dicyanoacetylene, and cyanoform were known compounds; however, more complex higher molecular weight compounds as well as polymers were unknown. The group of pioneers that developed the program included T. L. Cairns, Edith Ann Graef, Richard E. Heckert and William J. Middleton. The first of the cyanocarbons, tetracyanoethylene (TCNE), was synthesized in the laboratories of the Du Pont Company's Central Research and Development Department in 1952[2] by R. E. Heckert, the current Chief Executive Officer of the Du Pont Company.

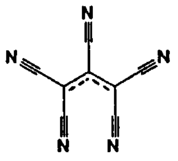


$F_2C{=}CF_2$

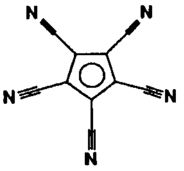


$[C(CN)_2]_2$ TCNE

Since the impetus for the synthesis of TCNE was the extraordinary properties of Teflon, the polymerization of TCNE was undertaken. TCNE, however, did not undergo polymerization like tetrafluoroethylene, but it did possess a rich chemistry which opened numerous synthetic routes to organic and organometallic compounds with unusual structures.[3] For example, TCNE forms a stable radical anion[4,5] and reacts with water to form pentacyanopropenide, $[C_3(CN)_5]^-$.[6] William Linn prepared tetracyanoethylene oxide, $[C(CN)_2]_2O$, which has the remarkable ability to add to aromatic rings via C—C bond cleavage,[7] and Owen W. Webster prepared pentacyanocyclopentadiene, $HC_5(CN)_5$, which is a stronger acid than perchloric acid.[8]



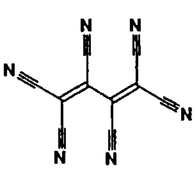
$[C_3(CN)_5]^-$



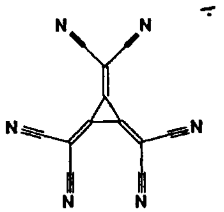
$[C_5(CN)_5]^-$

Two percyanoalkanes—tetracyanomethane[9] and hexacyanoethane[10]—have been reported by E. Meyer and S. Trofimenko, respectively. Both, however, are unstable and are of little chemical utility.

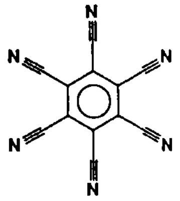
Cyanocarbons as well as their anions evolved to greater levels of complexity as Owen W. Webster prepared hexacyanobutadiene, $[n\text{-}C_4(CN)_6]^n$ (n = 0, 1-, 2-),[11] Tadamichi Fukunaga prepared hexacyanotrimethylenecyclopropane as its mono and dianions, $\{C_3[C(CN)_2]_3\}^n$ (n = 1-, 2-),[12] W. J. Middleton reported hexacyanoisobutylendiide, $\{C[C(CN)_2]_3\}^{2-}$,[6] Gunther Seitz and coworkers reported octacyanotetramethylenecyclobutadiendiide, $\{C_4[C(CN)_2]_4\}^{2-}$,[13] and K. Wallenfels and K. Friedrich described hexacyanobenzene, $C_6(CN)_6$.[14] Except for the poorly characterized poly(dicyanoacetylene)[15] these represent the highest molecular weight cyanocarbons reported to date.



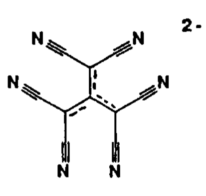
$n\text{-}C_4(CN)_6$



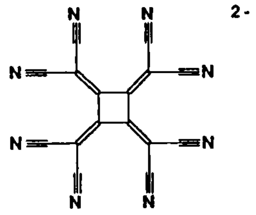
$\{C_3[C(CN)_2]_3\}^{\cdot -}$



$C_6(CN)_6$

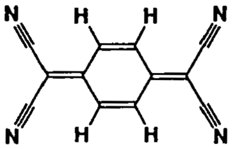


$\{C[C(CN)_2]_3\}^{2-}$

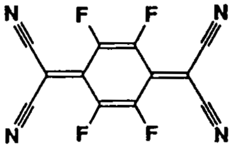


$\{C_4[C(CN)_2]_4\}^{2-}$

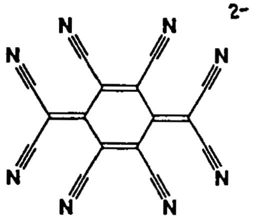
The rich and varied chemistry of TCNE led Donald S. Acker to consider the synthesis of the quinoid analog, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), and proposed a synthetic pathway. With collaboration of Dale S. Blomstrom, who suggested the use of bromine as an oxidant, Acker successfully executed the synthesis and obtained the now familiar orange crystals for the first time.[16] Subsequently, many substituted TCNQ derivatives including 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane, $TCNQF_4$[17] and 2,3,5,6-7,7,8,8-octacyano-*p*-quinodimethane as its dianion, $[TCNQ(CN)_4]^{2-}$, were also prepared.[18] Through the years a variety of more complex substituted TCNQ compounds including covalent polymers[19] have been reported. Langmuir-Blodgett films based on long chain-containing cation salts of radical anion of TCNQ[20] or substituted TCNQ's[21] have also been prepared.



TCNQ



$TCNQF_4$



$[TCNQ(CN)_4]^{2-}$

DONOR–ACCEPTOR CHARGE TRANSFER COMPOUNDS

Concomitant with the discovery of TCNE, donor–acceptor charge transfer complexes were discovered and the π acceptor strength of TCNE was reported by Richard E. Merrifield and William D. Phillips.[22] [Ferrocene][TCNE][5] is a prototypical example and in general these complexes exhibit a new charge transfer absorption that accounts for the observed color (*e.g.*, dark green for diamagnetic [ferrocene][TCNE]), however, electron transfer to form electron transfer ion-radical salts does not occur.[23]

DONOR–ACCEPTOR ELECTRON TRANSFER SALTS

The reaction of stronger donors and/or acceptors leads to the formation of electron transfer ion-radicals salts. Simple examples discovered early in the evolution of cyanocarbon chemistry included $K^+[TCNE]^{\cdot -}$.[4,5] The first of the TCNQ anion-radical salts, which were discovered by Walter R. Hertler[24] resulted from the reaction of triethylamine with TCNQ leading to the isolation of $[HNEt_3][TCNQ]_2$, was carried out by

CONDUCTING ELECTRON TRANSFER SALTS

Electrically conductive salts of the anion-radical of 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, provided a new class of organic semiconductors which, at the time of their discovery in the late 1950's, included all of the highly electrically conducting organic materials known.[24–26] Moreover, their conductivities and electron spin resonance (ESR) spectra were highly anisotropic with respect to crystal axis.[27] Subsequent studies at Du Pont and other laboratories worldwide led to discoveries of organic "metals," so called because of their unusual metal-like electrical properties.[28]

The most notable characteristic of both TCNQ and TCNE is the ease with which they accept an electron to form stable anion-radicals. However, the radical anion of TCNQ, $[\mathrm{TCNQ}]^{\cdot -}$, was substantially more stable than that of TCNE. The discovery of the anion-radical salts of TCNQ began an era of intense interest in the physics of organic solids, and a remarkably productive interplay of the disciplines of organic chemistry and physics characterized the quest for new materials having unconventional electronic properties. $[\mathrm{HNEt_3}][\mathrm{TCNQ}]_2$ was the first of the TCNQ anion-radical salts. Crystals of this black solid had a needle axis conductivity of 2 $\mathrm{Scm^{-1}}$ and the conductivity was highly anisotropic with respect to the other crystal axes. Robert J. Harder and Hertler noted that such formation of complex anion-radical salts, which included a formally neutral TCNQ molecule as well as the TCNQ radical anion, was fairly general. The complex salts are abbreviated $[\mathrm{Cation}][\mathrm{TCNQ}]_n$ $(n > 1)$.[24]

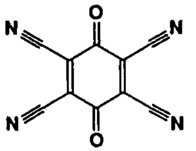
To this point the methods for generating TCNQ anion-radical salts involved the one-electron reduction of TCNQ and comcomitant oxidation of a donor and/or iodide salt. The propensity for complex salts to form under these conditions frustrated attempts to make many simple salts, [Cation][TCNQ], which were needed for comparison with the complex salts. The key solution to the problem was provided by Walter Mahler, who discovered that the lithium salt, $\mathrm{Li}^{+}[\mathrm{TCNQ}]^{\cdot -}$, was soluble in water (as the deep blue $[\mathrm{TCNQ}]_2^{2-}$ dimer dianion) as well as organic media (as the deep green $[\mathrm{TCNQ}]^{\cdot -}$ monoanion) to permit the preparation of $[\mathrm{TCNQ}]^{\cdot -}$ salts by metathesis with quaternary ammonium and other organic or inorganic salts.[24] Using this technique L. Russell Melby prepared [*N*-methylphenazenium][TCNQ], which was the first organic compound to show metal-like conductivity, *i.e.*, the conductivity increased with decreasing temperature.[29] It was the ESR studies of William D. Phillips, Donald B. Chesnut, and M. Thomas Jones[30] and the electrical conductivity studies of Glen Kepler and Paul Bierstedt[31] that brought the first understanding of the physics of these new electronic materials and excited worldwide interest in the chemistry and physics of highly conducting and in some cases superconducting organic materials.

FERROMAGNETIC CHARGE TRANSFER SALTS

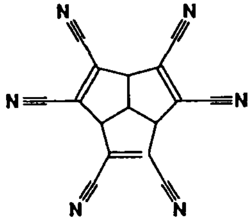
The quest for a molecular/organic based ferromagnet has not escaped the imagination.[32,33] The delocalization of an electron over an entire crystal coupled with partial occupancy of an electron energy band fulfills the basic criteria of a metal and, as discussed above, many examples, including processable conducting polymers, confirming these concepts exist today. Different concepts and materials, however, need to be considered for ferromagnetic behavior. Ferromagnetism, like superconductivity (but not metal-like conductivity) is a cooperative phenomenon, and localized spins must couple three dimensionally. The stable charge transfer salts of $[\mathrm{TCNE}]^{\cdot-}$ and $[\mathrm{TCNQ}]^{\cdot-}$ provide the means to achieve cooperative magnetic behavior. The decamethylferrocene charge transfer salts of TCNE and TCNQ are ferromagnetic and metamagnetic, respectively, and the former charge transfer salt is the only reported example of a molecular based material with a ferromagnetic ground state. For crystals aligned parallel to the applied magnetic field the saturation magnetism is 36% greater than that reported for iron metal on either an iron or mole basis.

CYANOCARBONS OF THE FUTURE

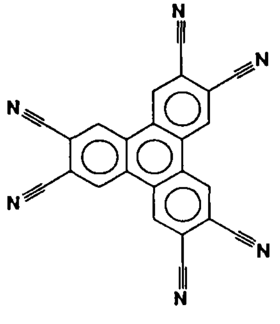
In addition to those cyanocarbons easily prepared and already characterized, many cyanocarbons would benefit from improved synthetic routes. Some obvious examples include hexacyanobenzene, cyanil (2,3,5,6-tetracyanobenzoquinone), and 2,3,5,6-tetracyano-7,7,8,8-tetracyano-*p*-quinodimethane. The quest to prepare organic ferromagnets brings the need for donors and/or acceptors with D_{2d} or C_n ($n > 2$) symmetry.[33] Examples of such materials are rare and, owing to the ability of multiple cyano groups to increase the electron affinity of the compound enabling the stabilization of anion as well as radical anions, several exemplary compounds, *e.g.*, hexacyanoacepentalenide, hexacyanotriphenylene, or dodecacyanodecacyclene are challenging species to prepare.[34]



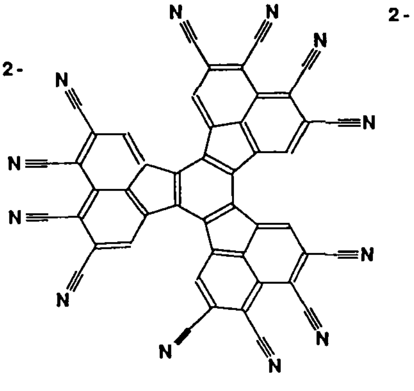
cyanil



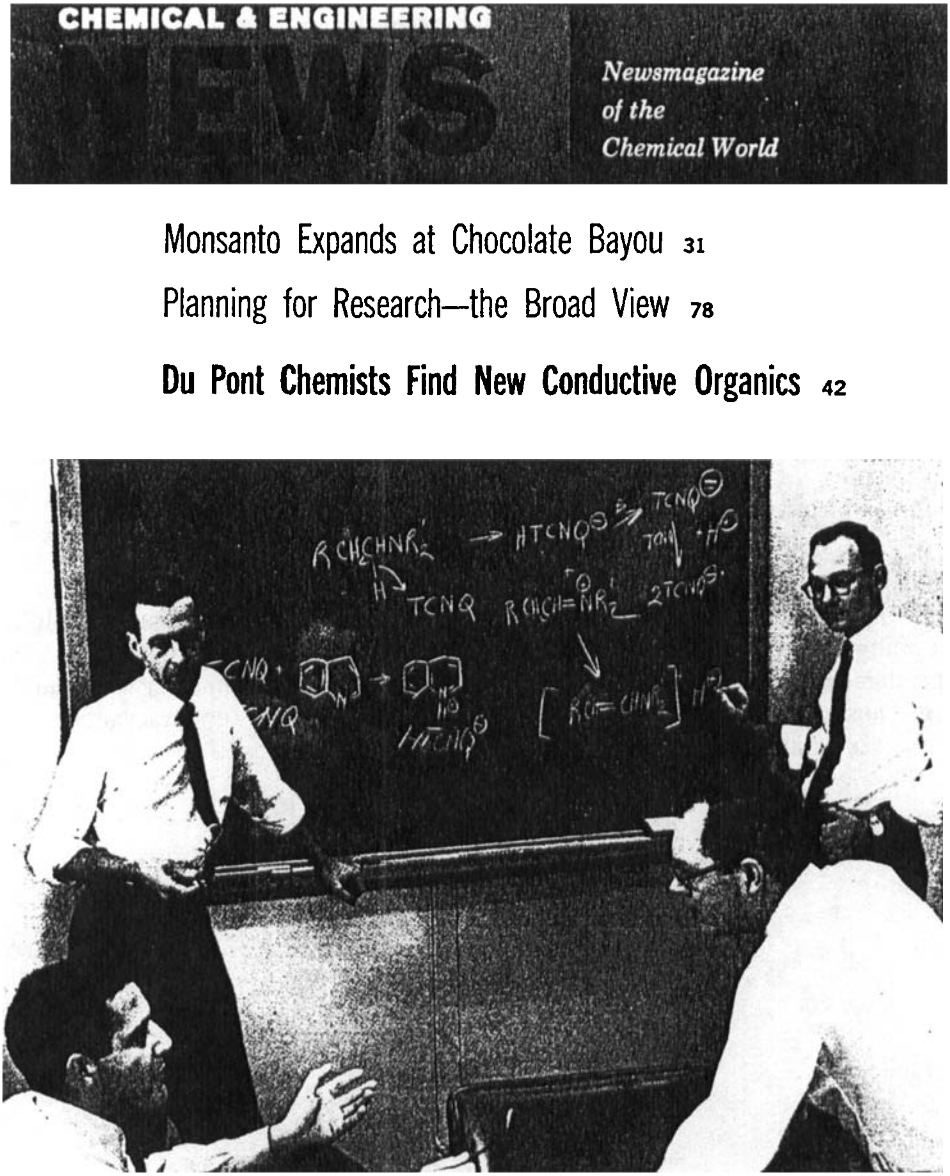
hexacyanoacepentalene



hexacyanotriphenylene



dodecacyanodecacyclene



CHEMICAL & ENGINEERING NEWS

Newsmagazine of the Chemical World

Monsanto Expands at Chocolate Bayou 31

Planning for Research—the Broad View 78

Du Pont Chemists Find New Conductive Organics 42

FIGURE 1 Photograph of L. Russell Melby (top left), Donald S. Acker (bottom left), Walter R. Hertler (top right), and Richard E. Benson (bottom right) discussing TCNQ chemistry [*Chemical & Engineering News*, Jan. 9, 1961 front cover] (reproduced with permission).

TABLE II

Cyanocarbons

Cyanocarbon	Formula		IR ν_{CN}, cm^{-1}		
			0	1-	2-
$(CN)^-$	$(CN)^-$			2080[a]	
NCCN	$(CN)_2$		2158[e]		
$[C(CN)]_x$	$[C(CN)]_x$		1635		
$[C(CN)_3]^-$	$[C(CN)_3]^-$			2162[b]	
$C(CN)_4$	$C(CN)_4$		2273[9]		
$[C(CN)]_2$	$C_2(CN)_2$		2236,2246[f]		
$C_2(CN)_4$	$C_2(CN)_4$	*	2121,2159[c]	2144,2183[c]	2069,2167[c]
$C_2(CN)_6$	$C_2(CN)_6$	*	2273		
$[C_3(CN)_5]^-$	$[C_3(CN)_5]^-$	*		2193[d]	
$C_4(CN)_6$	$C_4(CN)_6$	*	2238,2247, 2253,2211[c]	2168,2185, 2207,2220[c]	2123,2151, 2200[c]
$\{C([C(CN)_2]_3\}^{2-}$	$C_4(CN)_6$	*			2158,2173[6]
$C_4[C(CN)_2]_4$	$C_8(CN)_8$				2200[13]
$[C(CN)]_{5-}$	$[C_5(CN)_5]^-$	*		2237[8]	
$[C(CN)]_6$	$C_6(CN)_6$				
$C_3[C(CN)_2]_3$	$C_6(CN)_6$	*		2196,2210[c]	2150,2192[c]
$C_6H_4[(C(CN)_2]_2$	$C_6H_4C_2(CN)_4$	*	2222,2226[c]	2153,2179[c]	2105,2150[c]
$C_6F_4[(C(CN)_2]_2$	$C_6F_4C_2(CN)_4$	*	2228[c]	2178,2196[c]	2133,2167[c]
$C_6(CN)_4[(C(CN)_2]_2$	$C_6(CN)_4C_2(CN)_4$				2160,2190, 2215,2226[18b] 2237,2257[14b]
p-$C_6O_2(CN)_4$	$C_6O_2(CN)_4$				

*Discovered at Du Pont.

[a] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed., 1970, John Wiley and Sons, New York, NY, p. 178.

[b] D. A. Dixon, J. C. Calabrese and J. S. Miller, *J. Amer. Chem. Soc.*, **108**, 2582 (1986).

[c] J. S. Miller and D. A. Dixon, *Science*, **235**, 871 (1987).

[d] U. Mazur and K. W. Hipps, *J. Phys. Chem.*, **86**, 2854 (1982).

[e] G. D. Craine and H. W. Thompson, *Farad. Soc.*, **49**, 1273 (1953).

[f] F. A. Miller and R. B. Hannan, Jr., *J. Chem. Phys.*, **21**, 110 (1953).

EPILOG

The late 1950's–1960's was an exciting period at the Du Pont Central Research and Development Department due in part to the study of cyanocarbons.† Many collaborative investigations on both the chemical or the physical aspects of these materials flourished (Figure 1), and many new compounds through the years have been isolated and characterized as summarized in Table II. The scientific progress made in the past thirty years in the area of cyanocarbon chemistry has not passed without recognition. Several papers have been acknowledged as the pioneering work in the area of molecular (organic, organometallic, and/or polymeric) conductors and more recently ferromagnets. Two principal papers, *i.e.*, the Merrifield

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†Other research areas that contributed to the overall research excitement during this time period included: organometallic chemistry, boron hydride chemistry, fluorocarbon chemistry, polymers syntheses, metal oxide chemistry, and crown ether chemistry. The latter discovery received international recognition via the awarding of the 1987 Nobel Prize in Chemistry to Charles J. Pedersen.

and Phillips and Melby, Harder, Hertler, Mahler, Benson, and Mochel, papers, References 22 and 25, respectively, have been classified by the Institute for Scientific Information® as Citation Classics.[35,36] The 1958 Merrifield and Phillips paper reported that TCNE was a strong π acceptor that formed strong donor/acceptor

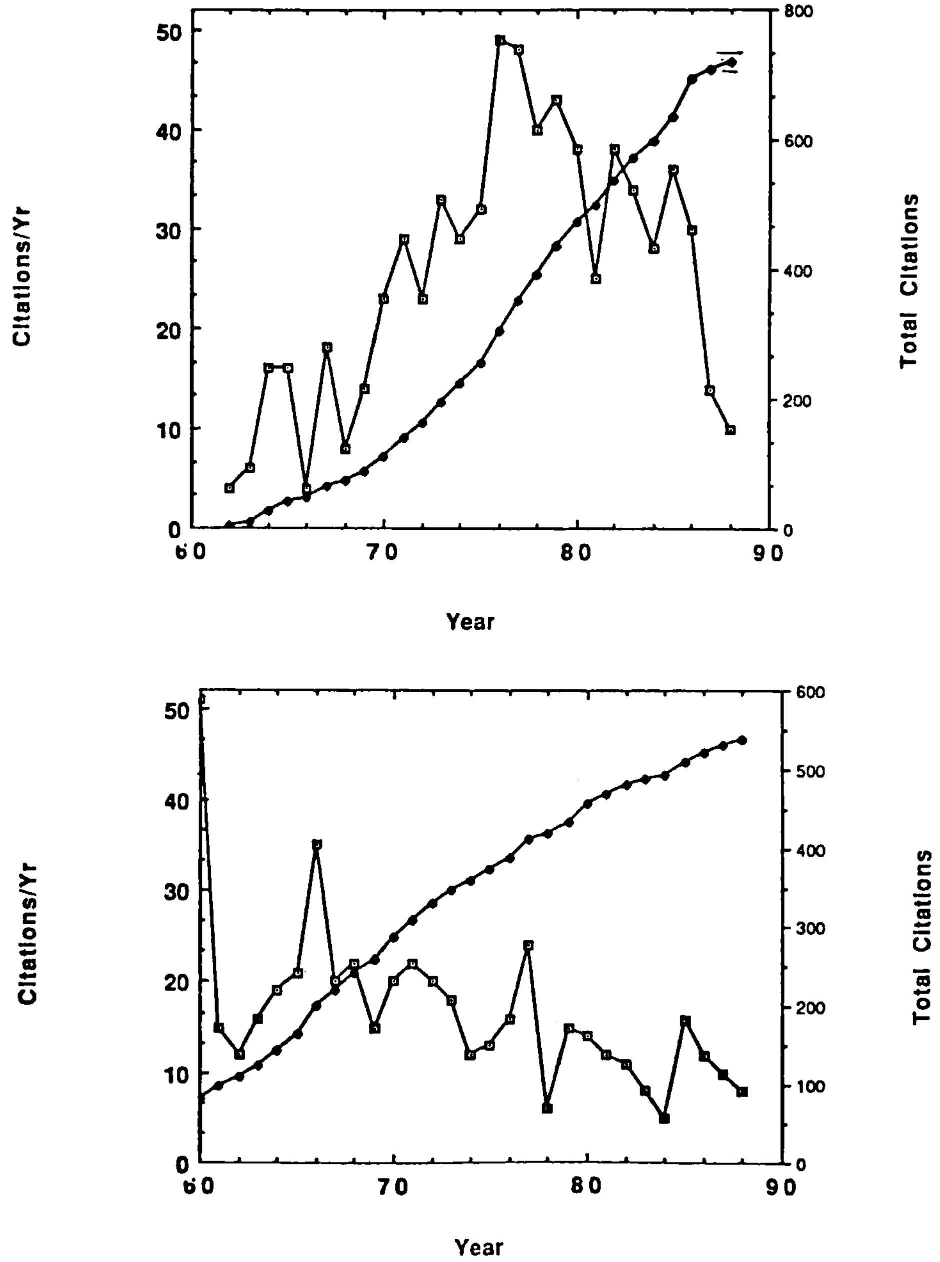

FIGURE 2 Citation frequency for the Melby, Harder, Hertler, Mahler, Benson, and Mochel (Reference 24) (top) and Merrifield and Phillips (Reference 22) (bottom) Citation Classics.

complexes with many electron rich aromatic donors. The 1962 Melby and coworker's paper disclosed that the TCNQ radical anion, $[TCNQ]^{\cdot -}$, was stable and that numerous electron transferred ion radical salts—some of which exhibited high dc electrical conductivity—could be isolated as crystalline solids. The citation history for these key papers is depicted in Figure 2.

Cyanocarbons continue to play an important role in both chemistry and physics. Subsequent work in many laboratories during the intervening quarter century has confirmed the importance of organic compounds as electronic materials. The pioneering work has led to the development of polymeric metal-like conductors and molecule-based organic superconductors and ferromagnets. In recent years applications based on conducting polymers have emerged and it is anticipated that they will be important in future generations of electronic devices. The emerging area of second and third order nonlinear optical properties of organic compounds may well make use of the high polarizability of cyanocarbons and their anions and their investigation continues in many laboratories.

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