π-System Properties of Pyromellitonitrile[1]

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The absorption spectra of charge-transfer complexes of polycyclic aromatic hydrocarbons with pyromellitonitrile (I) and the polarographic half-wave reduction potential of I have been measured. The e.s.r. spectrum of the anion-radical obtained from I and potassium in dimethoxyethane (DME) is reported. Hückel molecular orbital calculations are made and compared to the experimental properties.

Pyromellitonitrile[2,3] (1,2,4,5-tetracyanobenzene) is the most highly substituted simple cyanobenzene compound known.[3a] The other known cyanobenzenes containing three or more nitrile groups, are 1,2,4-tricyanobenzene and 1,3,5-tricyanobenzene.[4] No cyanobenzene derivatives apparently are known with three or more nitrile groups situated on adjacent sites of the aromatic nucleus.[3a,5] Since unsaturated compounds with multiple nitrile substitutions have strongly electron-deficient π-systems,[6] it was of interest to examine the electron-accepting properties of polycyanobenzenes. Pyromellitonitrile (I) was chosen for initial investigation because simple molecular orbital calculations and symmetry considerations suggested that its lowest unfilled molecular orbital would have the same energy as penta- and hexacyanobenzenes,[7] and because of the report[8] that the corresponding quinone, cyanil (2,3,5,6-tetracyano-p-benzoquinone), is a very powerful π-acid.

Pyromellitonitrile was prepared and its properties matched those described in the literature (cf. Experimental). Its ultraviolet spectrum, not previously reported, had the longest wave length absorption maximum occurring at 316 mμ (log ε 3.58) in ethanol.

Polarographic Reduction.—The first half-wave reduction potential of I in acetonitrile occurs at −0.66 v. (vs. SCE). It is a one-electron wave, $I_D = 4.18$. A second wave was also observed at −1.63 v. The first half-wave reduction potential suggests an electron affinity[9] for I between p-benzoquinone[10] ($\epsilon_{1/2} = -0.52$ v.) and p-duroquinone[10] ($\epsilon_{1/2} = -0.84$ v.), and very close to the electron affinity of pyromellitic dianhydride[10] ($\epsilon_{1/2} = -0.60$ v.).

(1) Part III in a series on Cumulative Effects of Substituents on the π-System Properties of Aromatics. Paper II: A. Zweig, J. E. Lehnsen, and M. A. Murray J. Am. Chem. Soc., **85**, 3933 (1963).

(2) E. A. Lawton and D. D. McRitchie, J. Org. Chem., **24**, 26 (1959).

(3) An extensive study of the e.s.r. spectra of 12 aromatic and unsaturated nitriles, including pyromellitonitrile, together with Hückel and approximate configuration interaction calculations was reported after this work had been completed: P. H. Rieger and G. K. Fraenkel, J. Chem. Phys., **37**, 2795 (1962).

(3a) NOTE ADDED IN PROOF.—Since the submission of this paper, the preparation of hexacyanobenzene has been reported by K. Wallenfels and K. Friedrich, Tetrahedron Letters, No. 19, 1223 (1963).

(4) 1,2,4-Tricyanobenzene: R. Engelhardt and H. Arledter, U. S. Patent 2,591,415 (1952), German Patent 842,045 (1952), m.p. reported 127.5°; A. V. Willett, Jr., and J. R. Pailthorp, U. S. Patent 2,716,646 (1955), no m.p. reported. 1,3,5-Tricyanobenzene: G. M. Bennett and R. L. Wain, J. Chem. Soc., 1108 (1936), m.p. 261–263°; A. V. Kusanov and E. A. Abrazhanova, Sbornik Statei Obshchei Khim., **2**, 865 (1953); Chem. Abstr., **49**, 6820c (1955), m.p. 210–212°; D. J. Hadley and B. Wood, U. S. Patent 2,838,558 (1958), no m.p. reported.

(5) A number of heterocyclic analogs of benzene are known which contain three or more adjacent cyano groups: E. L. Little, et al., J. Am. Chem. Soc., **80**, 2832 (1958); C. D. Weis, J. Org. Chem., **27**, 3514 (1962); C. D. Weis, ibid., **27**, 3695 (1962).

(6) T. L. Cairns, et al., J. Am. Chem. Soc., **80**, 2775 (1958).

(7) The lowest unfilled molecular orbitals of all three compounds have a node passing through their common plane of symmetry.

(8) K. Wallenfels and G. Bachmann, Angew. Chem., **73**, 142 (1961).

(9) While the absolute values of the electron affinities of these molecules are not known, there is considerable evidence that polarographic reduction potentials are proportional to electron affinities: M. Batley and L. E. Lyons, Nature, **196**, 573 (1962).

(10) M. E. Peover, ibid., **191**, 702 (1961).

Charge-Transfer Complexes.—It was found that pyromellitonitrile (I) has certain advantages over other compounds of similar π-acidity for study of molecular complexes. The longest wave length electronic transition of I occurred at about 9×10^3 cm.⁻¹ higher frequency than p-benzoquinone or p-duroquinone.[11] This allowed the study of the charge-transfer spectra of I with most aromatic hydrocarbons without the interference of absorptions due to pure acceptor transitions. Such absorptions seriously interfere with the examination of charge-transfer spectra of many aromatic hydrocarbons with acceptors such as 1,3,5-trinitrobenzene, p-benzoquinone, and p-duroquinone. Compound I is moderately soluble in organic solvents while the corresponding dianhydride is insoluble in all but the most polar solvent.[12]

It has been demonstrated by Dewar and co-workers[13–15] that the long wave length absorption maximum of polycyclic aromatic hydrocarbons with π-acceptors such as 1,3,5-trinitrobenzene,[13] tetracyanoethylene,[14] and 2,4,7-trinitro-9-fluorenone[15] are related to the energies of the highest filled molecular orbitals of the donors and the lowest unfilled orbitals of the acceptors, as calculated by the Hückel molecular orbital (HMO) method. Because the interaction of the acceptor and donor in these complexes is weak, the ground state interaction of the molecular orbitals of the separate molecules is regarded as negligible,[16] and may be neglected in the calculations. This allows the use of a simple relationship between the energy of the charge-transfer absorption and the molecular orbitals of the donor and acceptor. This relationship is expressed by eq. 1 where D_i is the energy of the highest filled

$$\Delta E_{i,j} = D_i - A_j \tag{1}$$

orbital of the donor and A_j is the energy of the lowest unfilled orbital of the acceptor. The energies of these molecular orbitals, as calculated by the Hückel molecular orbital theory, are expressed in eq. 2 and 3

$$D_i = \alpha + \beta X_i \tag{2}$$

$$A_j = \alpha + \beta X_j \tag{3}$$

where α and β are the carbon coulomb integral and the carbon–carbon resonance integral, respectively, both integrals regarded as constants, and X_i and X_j are numbers, characteristic of the molecule, which may be evaluated theoretically.[17] Since in this study the acceptor molecule, I, is always the same, eq. 1 reduces to

$$\Delta E_{i,j} = D_i - \text{a constant} \tag{4}$$

A straight line plot of E_i vs. D_i will give the value of β.

(11) The longest reported ultraviolet absorption for p-benzoquinone is 450 mμ; for p-toluquinone, 440 mμ (CCl₄): W. Flaig, T. Ploetz, and A. Küllmer, Z. Naturforsch., **64b**, 668 (1955).

(12) L. L. Ferstandig, W. G. Toland, and C. D. Heaton, J. Am. Chem. Soc., **80**, 2778 (1958).

(13) M. J. S. Dewar and A. R. Lepley, ibid., **83**, 4560 (1961).

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

(15) A. R. Lepley, ibid., **84**, 3577 (1962).

(16) The absorption bands of the donors and acceptors in these complexes appear virtually unchanged from those of the separated substances.

(17) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 2.
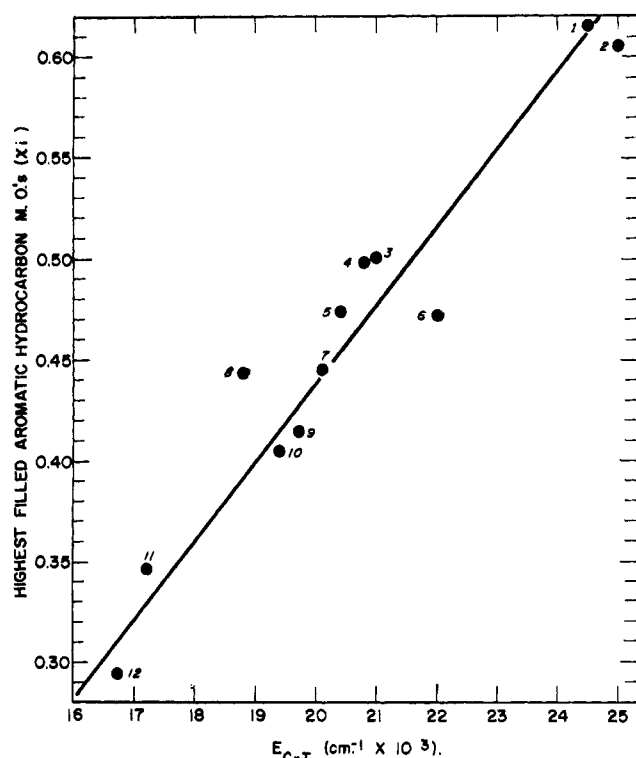
Fig. 1.—Hydrocarbon–pyromellitonitrile π-complex transition energies plotted against the highest filled MO's of the hydrocarbons.

Since β is constant, the slope of the line should be invarient regardless of which charge-transfer donors or acceptors are being studied. Previous results[13–15] affirmed this; measured slopes resulted in values of β in the narrow range 3.00–3.12 e.v.

The intercept of the plot of $\Delta E_{i,j}$ vs. D_i with the $E_{i,j}$ axis gives the value of A_j. This is a useful experimental method of measuring the energy of the lowest unfilled molecular orbital of the acceptor.

We have examined a number of charge-transfer complexes of I with polycyclic aromatic hydrocarbons. Complexes of I have not previously been reported. Table I lists the wave lengths and frequencies of the

TABLE I

Charge-Transfer Bands of π-Complexes of Aromatic Hydrocarbons with Pyromellitonitrile and the Highest Filled MO's of the Hydrocarbons

Compound	Number	Wave length of c.-t. band, mμ, in CHCl$_3$	Frequency of c.-t. band $\times$ 10^3, cm.$^{-1}$	X_i
Naphthalene	1	408	24.5	0.616
Phenanthrene	2	400	25.0	.605
Picene	3	475	21.0	.501
1,2,3,4-Dibenzanthracene	4	480	20.8	.499
1,2,5,6-Dibenzanthracene	5	490	20.4	.473
1,2,7,8-Dibenzanthracene	6	455	22.0	.471
Pyrene	7	497	20.1	.445
1,2,4,5-Dibenzpyrene	8	535	18.7	.442
Anthracene	9	508	19.7	.414
3,4-Benztetraphene	10	515	19.4	.405
Perylene	11	583	17.2	.347
Naphthacene	12	600	16.7	.294

first charge transfer bands of I with twelve alternate polycyclic aromatic hydrocarbons. The HMO values of X_i for the hydrocarbons as defined in eq. 2 are also listed in Table I. The breadth of the charge-transfer
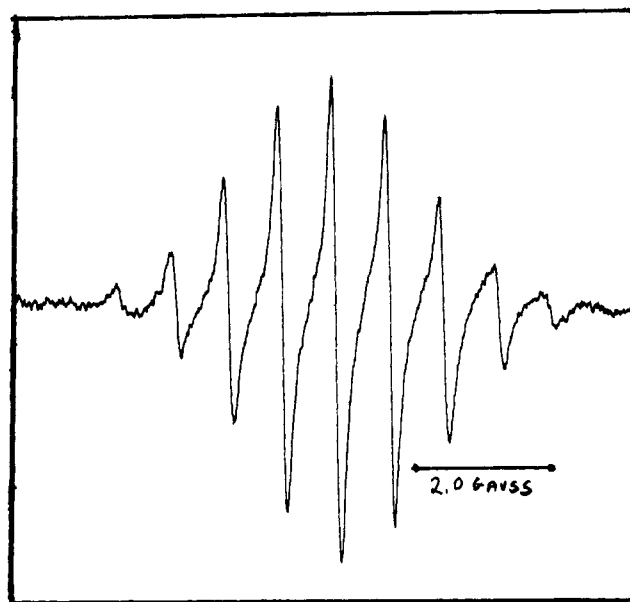

Fig. 2.—E.s.r. derivative spectrum of pyromellitonitrile anion-radical in DME.

absorptions was such as to result in a 5–10 mμ uncertainty in the positions of the maxima.

The values of X_i are plotted against the observed transition energies in Fig. 1. A reasonable straight line correlation is obtained. The line drawn was fitted by the method of least squares. The slope of the line gave a value of -3.21 e.v. for β and the intercept of the line with $E_{i,j} = 0$ resulted in a value of -0.335 for X_j.[18] Deviations of individual points from the line are in part due to the measurement uncertainties and in part due to oversimplification in the Hückel method of calculating the X_i's. The slightly larger value for β obtained for the complexes of I than for complexes of other acceptors[13–15] may in part be ascribed to the fewer complexes examined here.

Comparison with Pyromellitic Dianhydride.—It appeared from their reduction potentials (vide infra) that tetranitrile I is comparable to pyromellitic dianhydride in electron acceptor properties. If this is the case, the charge-transfer maxima of I and the dianhydride should be similar. Table II compares the positions of maximum absorption of both acceptors with four representative hydrocarbon donors.

TABLE II

Charge-Transfer Bands of π-Complexes of Aromatic Hydrocarbons with Pyromellitonitrile and Pyromellitic Dianhydride

Donor	Wave lengths of c.-t. bands, mμ, in CHCl$_3$	
	Pyromellitic dianhydride	Pyromellito-nitrile
Naphthalene	411	408
Anthracene	518	508
Pyrene	505	497
Perylene	595	583

Although the numerical differences are probably within experimental error, these results, together with the polarographic data, consistently suggest that the dianhydride is a slightly stronger π-acceptor than the tetranitrile.[19]

Electron Spin Resonance.—The reaction of a dilute solution of I in 1,2-dimethoxyethane with potassium in

(18) Since β is negative, the energy of the orbital A$_j$ is positive (antibonding) with regard to the energy zero (α).

(19) Further investigations of the acceptor properties of anhydrides are in progress.

a sealed tube, using a previously described technique,[20] resulted in formation of the straw-colored radical-anion II. The e.s.r. derivative spectrum of II is shown in
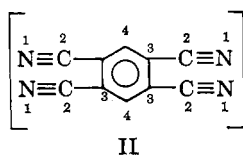
$$
\begin{bmatrix}
\underset{1\ 2}{N\equiv C}\text{—}\overset{4}{\underset{3}{\bigcirc}}\overset{3}{\underset{3}{}}\text{—}\underset{2\ 1}{C\equiv N} \\
\underset{1\ 2}{N\equiv C}\text{—}\underset{4}{}\text{—}\underset{2\ 1}{C\equiv N}
\end{bmatrix}
$$

II

Fig. 2. Under conditions of higher resolution, the e.s.r. spectrum of electrolytically reduced pyromellitonitrile showed an asymmetric triplet for each of the lines in Fig. 2.[21] The coupling constants thus obtained for the pyromellitonitrile anion-radical are $a^N = 1.15$ gauss and $a^H = 1.11$ gauss.[21]

Molecular Orbital Calculations.—In order to make molecular orbital calculations on π-systems containing heteroatoms, appropriate changes must be made in the empirical α and β parameters associated with each atom and bond. These changes are made in terms of the standard α_c and β_{cc} of benzene, and take the form of eq. 5 and 6.
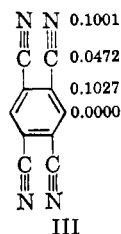
$$\alpha_x = \alpha_c + h_x\beta_{cc} \qquad (5)$$

$$\beta_{cx} = k_{cx}\beta_{cc} \qquad (6)$$

Few Hückel molecular orbital treatments of conjugated nitriles have been reported. In connection with an investigation of the anion-radical of tetracyanoethylene,[22] h_N was taken as 1.0 and k_{CN} as 1.2, although these parameters had originally been chosen for sp$_2$ bonding of nitrogen to carbon.[23] For Hückel molecular orbital calculations on I, the hetero parameters chosen were $h_N = 0.5$[24] and $k_{CN} = 1.2$.[25] Solution of the secular determinant was made by factoring, taking advantage of the high (D$_{2h}$) symmetry of pyromellitonitrile.[26]

The energy of the eight lowest molecular orbital (X$_8$), the lowest unfilled molecular orbital, of I calculated in this way is $0.3135|\beta|$. This is in good agreement with the energy of this orbital estimated from the molecular complexes of I with aromatic hydrocarbons $(0.335|\beta|)$ and with methoxybenzenes $(0.301|\beta|)$.[1]

The unpaired electron distribution in the eight molecular orbital of I as calculated with these parameters is shown in III.

$$
\begin{array}{c}
\underset{C\ \ C}{N\ \ N}\quad 0.1001 \\
\quad\quad 0.0472 \\
\quad\quad 0.1027 \\
\quad\quad 0.0000 \\
\underset{N\ \ N}{C\ \ C}
\end{array}
$$

III

The molecular orbital (X$_8$) of I containing the un-

(20) A. Zweig and A. K. Hoffmann, *J. Am. Chem. Soc.*, **84**, 3278 (1962).

(21) P. M. Reiger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

(22) W. D. Phillips, J. C. Rowell, and S. A. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

(23) L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

(24) Reference 17, p. 121.

(25) The nitrile carbon coulomb integral and the ring to nitrile carbon resonance integral were taken to be the same as the standard benzene α_c and β_{cc}.

(26) Reference 12, Chapter 3.

paired electron has a node at the proton-bearing positions and thus Hückel MO calculations predict no splitting of the e.s.r. spectrum due to these protons. The Hückel approximation neglects configuration interaction, and it has been shown in other instances[27] that when such electron correlation effects are considered, negative spin densities are predicted which agree in magnitude with the observed splittings.

There is evidence that the e.s.r. hyperfine splitting due to the N^{14} nucleus is linearly related to the unpaired electron density on nitrogen. Thus for aza-aromatics, the nitrogen hyperfine coupling constant has been reported to be proportional to the unpaired electron density on nitrogen as calculated by the Hückel method.[28] The relationship is expressed by eq. 7 where Q_N is the proportionality constant.

$$a_N = Q_N \rho_N \qquad (7)$$

The experimental value of Q_N for aza-aromatics was found to be ~ -25 gauss, when $h_N = 0.75$ and $k_{CN} = 1.00$.[28] For unpaired electrons in delocalized π-systems which include the nitrile group, the value of Q_N has not been established, nor has the direct proportionality between spin density and hyperfine coupling constant, as described by eq. 7, been adequately demonstrated. On theoretical grounds[3,29] there are good reasons to believe that other factors, such as 1s-orbital spin polarization, must be considered in assessing hyperfine coupling constants. If the direct proportionality relationship of eq. 7 is assumed to hold for unsaturated nitriles, however, the observed nitrogen coupling constant together with the hetero parameters employed in these calculations suggest a value of Q_N for this nitrile of ~ -11 gauss.

A valence bond treatment has also been proposed[30] as a method for estimating the hyperfine constants of polysubstituted anion-radicals from the measured constants of the monosubstituted species. This method has been used to treat proton splittings in the anion-radicals of the isomeric phthalonitriles and pyromellitonitrile.[3]

Experimental[31]

(27) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(28) A. Carrington and J. dos-Santos-Veigas, *Mol. Phys.*, **5**, 21 (1962).

(29) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(30) J. C. Schug, T. H. Brown, and M. Karplus, *ibid.*, **37**, 330 (1962).

(31) All melting points are uncorrected.

(32) As obtained from the Explosives Department, E. I. du Pont de Nemours and Co., Wilmington, Del.