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ELECTRON AFFINITIES OF POLYNUCLEAR ACCEPTORS

NITRO DERIVATIVES OF FLUOREN-$\Delta^{9,\alpha}$-MALONONITRILE

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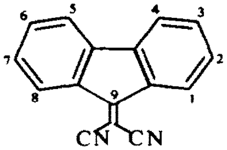
Abstract—Electron affinities of a number of polynitro derivatives of fluoren-$\Delta^{9,\alpha}$-malononitrile have been examined. The order of electron affinities, as determined by d.c. polarography, is found to be 2,4,5,7-tetranitro > 2,4,7-trinitro > 3,6-dinitro > 2,6-dinitro > 2,4-dinitro ≈ 2,5-dinitro > 2,7-dinitro. The half wave potentials of similarly substituted fluoren-9-ones were measured. Further confirmation of the relative order of electron affinity of the acceptors (**1a–1g**) was obtained from their charge-transfer spectra with a number of donor hydrocarbons. From this experiment, however, 2,4; 2,5 and 2,7-dinitro isomers, were found to have the same electron affinity. An attempt has been made to explain the contribution of inductive and resonance-interaction effects of the nitro groups on the electron acceptor strengths of these compounds. A number of solid anion radical salts of 2,4,5,7-tetranitro fluoren-$\Delta^{9,\alpha}$-malononitrile have been synthesized.

Strongly electronegative substituents enhance π-electron acceptor strengths of aromatic molecules. Acceptor strength, measured as electron affinity (EA), depends on the number and relative positions of electron withdrawing substituents.[1] Some information about the substituent effect on the electron affinities of nitrobenzenes[2] and *p*-benzoquinones[3] is available. However, no systematic investigation of polynuclear acceptors has been reported. Colter *et al.*[4] found that the rates of phenanthrene catalyzed acetolysis of polynitro-9-fluorenyl *p*-toluenesulfonates depend on the number and position of the nitro groups on the fluorene ring; the latter behaves as an acceptor with respect to phenanthrene. The electron acceptor properties of 2,4,7-trinitro (**1f**)[5] and 2,4,5,7-tetranitro (**1g**)[6] derivatives of fluoren-$\Delta^{9,\alpha}$-malononitrile have been briefly described. With the availability of a number of dinitro derivatives (**1a–1e**),[7] it is now possible to compare the electron affinities of various isomers of polynitro-fluoren-$\Delta^{9,\alpha}$-malononitrile.



(**1**)

a: 2,4-dinitro d: 2,7-dinitro
b: 2,5-dinitro e: 3,6-dinitro
c: 2,6-dinitro f: 2,4,7-trinitro
g: 2,4,5,7-tetranitro

Polarography

The electron affinity (*EA*) of an acceptor (*A*) can be determined from the reversible one electron reduction potential ($E_{\frac{1}{2}}$) by Hedges and Matsen relationship[8]

$$E^\circ_{\frac{1}{2}} = EA + \Delta E_{sol} - \Phi_{Hg} - E^\circ_{Hg:Hg^{2+}} \tag{1}$$

where ΔE_{sol} is the solvation energy associated with

$$A^-_{gas} + A^\circ_{sol} \rightarrow A^\circ_{gas} + A^-_{sol}$$

Φ_{Hg} is the work function of mercury, 4·54 eV, and $E^\circ_{Hg:Hg^{2+}}$ is the absolute value of calomel electrode, 0·53 V. Although ΔE_{sol} may vary from compound to compound, it is safe to assume as constant for a series of closely similar structures.[9] In absence of an appropriate ΔE_{sol} an average value of 3·66 eV has been used.[10] Eq. 1, then is reduced to

$$EA = E_{\frac{1}{2}} + 1{\cdot}41 \tag{2}$$

The acceptors (**1a**–**1g**) were reduced at the dropping mercury electrode giving two waves before the reduction potential of lithium ion of the lithium perchlorate supporting electrolyte was reached. The number of electrons associated with each wave were determined by the use of Tome's relationship $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 59$ mV, for one electron reversible reduction.[11] Whereas, the first wave corresponded with one electron reduction, the second wave was found to involve 3-4 electron process. In Table 1, the first half wave potentials ($E_{\frac{1}{2}}$), limiting current constants (I), and electron affinities (EA) are tabulated. The electron affinities of the acceptors (**1a**–**1g**) were in the following order, 2,4,5,7 > 2,4,7 > 3,6 > 2,6 > 2,4 ≈ 2,5 > 2,7.

TABLE 1. POLAROGRAPHY OF FLUOREN-$\Delta^{9,\alpha}$-MALONONITRILES IN ACETONITRILE (SUPPORTING ELECTROLYTE 0·1M $LiClO_4$)

Compound	$E_{\frac{1}{2}}$, V vs. s.c.e.	$-(E_{\frac{3}{4}}-E_{\frac{1}{4}})$ mV	I^a	EA^b
1. Unsubstituted	−0·71	56	3·04	0·70
2. 2,4-Dinitro (**1a**)	−0·343	58	3·09	1·06
3. 2,5-Dinitro (**1b**)	−0·343	62	3·17	1·06
4. 2,6-Dinitro (**1c**)	−0·280	60	3·06	1·13
5. 2,7-Dinitro (**1d**)	−0·380	59	2·87	1·03
6. 3,-6-Dinitro (**1e**)	−0·253	60	3·10	1·15
7. 2,4,7-Trinitro (**1f**)	−0·100	58	3·38	1·31
8. 2,4,5,7-Tetranitro (**1g**)	+0·115	50	3·20	1·52

[a] Limiting current constant, $I = id/m^{\frac{2}{3}}t^{\frac{1}{6}}C$
[b] From Eq. 2.

Since, nitro groups are reduced at considerably higher potentials[12] (e.g. nitrobenzene, −1·147 V, 1,4-dinitrobenzene, −0·69 V), it can be assumed that the first electron is used in the reduction of dicayanomethylene function. The inductive and resonance effects of the nitro groups are relayed through the benzene rings to the electron deficient carbon atom at position 9. An idea about the electron densities at different positions of the fluorene ring system can be obtained from the experimentally determined, and calculated spin densities of fluorenone anion radical.

Dehl and Fraenkel[13] found that the spin densities on carbon atoms at 1, 2, 3 and 4 are 0·083, 0·011, 0·130 and 0·027, respectively. It is reasonable to expect the same relative order in the case of fluoren-$\Delta^{9\alpha}$-malononitrile anion-radical. Consequently, the nitro groups at 2,4 and equivalent 7 and 5 positions will show less resonance interaction and will influence the electron deficiency at 9 position predominantly by inductive effect only. The inductive effect is further enhanced by the non-planarity of the nitro groups at positions 4 and 5. X-ray crystallographic studies show that the nitro group at 4-position of 2,4,7-trinitro derivative (**1f**) is twisted 19·3° out of the plane of the molecule.[14] Similarly, an examination of the space filling model of 2,4,5,7-tetranitro derivative (**1g**) reveals that the two groups at 4 and 5 positions are locked at nearly 75° out of the planes of respective benzene rings. In the case of the dinitro isomers, the high electron densities at 3 and equivalent 6 positions, are depleted by the electron withdrawing nitro groups by resonance interaction, consequently 3,6 (**1e**) and 2,6 (**1c**) dinitro isomers have higher electron affinities. Conversely, the 2,7-dinitro isomer (**1d**) is expected to be the weakest acceptor.

Further confirmation of the substituent effect was sought from the reduction potentials of similarly substituted 9-fluorenones (Table 2). Although the first half-wave potentials are not strictly consistent with one electron reversible reduction process, it is apparent that 2,7-dinitro fluoren-9-one is the weakest acceptor among the other dinitroketones.

TABLE 2. POLAROGRAPHY OF FLUOREN-9-ONE IN ACETONITRILE (SUPPORTING ELECTROLYTE 0·1M $LiClO_4$)

Compound	$E_{\frac{1}{2}}$	No. of electrons	EA^{a}
2,4-Dinitro	−0·484	1	0·926
2,5-Dinitro	−0·498	1·3	0·912
2,6-Dinitro	−0·555	2	0·856
2,7-Dinitro	−0·645	0·7	0·765
3,6-Dinitro	−0·538	1·2	0·873
2,4,7-Trinitro	−0·465	1	0·945
2,4,5,7-Tetranitro	−0·250	1	1·16

[a] From Eq. 2.

Charge-transfer spectra

Charge-transfer energy, as derived from simple molecular orbital treatment is given by

$$E_{\pi} = B_j - (\alpha + \chi_i\beta) \tag{3}$$

where B_j is the energy of the acceptor orbital involved in the interaction with the donor, α is the Coulomb integral of carbon, β is the carbon carbon resonance integral, and χ_i is the energy coefficient of the highest filled orbital of the donor.[15]

TABLE 3. THE CHARGE-TRANSFER ABSORPTION MAXIMA FOR HYDROCARBON COMPLEXES OF THE

No.	Donor	$X_i\beta^a$	TNF^b	2,4,5,7-Tetranitro **1g**		2,4,7-Trinitro^c **1f**	
			E_π (mμ)	E_π (mμ)	EA^d	E_π (mμ)	EA
1	Anthracene	0·414	541	740	1·581	662	1·364
2	1,2-Benzanthracene	0·452	525	701	1·538	640	1·370
3	1,2-Benzopyrene	0·497	510	667	1·517	600	1·309
4	3,4-Benzopyrene	0·371	590	785	1·467	726	1·339
5	3,4-Benzotetraphene	0·405	561	—	—	686	1·355
6	1,2,3,4-Dibenzanthracene	0·499	505	670	1·549	610	1·367
7	1,2,5,6-Dibenzanthracene	0·473	525	685	1·497	—	—
8	1,2,4,5-Dibenzopyrene	0·442	562	710	1·405	689	1·354
9	Decacyclene	0·470	518	675	1·402	625	1·355
10	Pyrene	0·445	520	710	1·583	650	1·421
11	Perylene	0·347	620	810	1·414	745	1·281
	Average Electron Affinity (EA)			·	1·49		1·35

[a] Energy of highest occupied MO; C. A. Coulson and R. Daudel, Dictionary of Values of Molecular Constants.
[b] Ref. 17.
[c] Ref. 5.
[d] Equation 4.
[e] Shoulder.

The intercept of the plot of E_π again $\chi_i\beta$ gives the value of $(B_j - \alpha)$, a measure of the acceptor strength. In Table 3, the charge transfer absorption maxima (E_π) of the acceptors with ten hydrocarbon donors are tabulated. A second charge transfer band was observed in several instances with 2,4,5,7-tetranitro (**1g**) and 2,4,7-trinitro (**1f**) compounds. For a given donor, the blue shift of the maxima is indicative of weakening of acceptor strength. As expected, close linear relationship has been observed between E_π and $\chi_i\beta$ for each acceptor. The plots in Fig. 1 represents four distinctly separated straight lines.[16] It has been generally observed that the slope is constant for all acceptors ($\beta = 3{\cdot}06$ eV).[17] In the present case, the deviations are due to the fewer number of hydrocarbons taken. Since Eq. (3) itself is derived from an oversimplified use of the Huckel theory, such deviations are to be expected.

Alternatively, electron affinities of an acceptor can be compared against a standard acceptor by measuring their charge transfer bands with a given donor. Thus if $(EA)_i$ and $(EA)_k$ are the electron affinities of an acceptor and the standard acceptor, respectively, their charge transfer energies are related by

$$(E_\pi)_i - (E_\pi)_k = (EA)_k - (EA)_i \qquad (4)$$

This relationship holds only when the complexes are of the same bond type and configuration. Electron affinities derived from the use of iodine as standard has been criticized on these grounds. Instead, chloranil has been used as a standard.[10] In the present case of polynuclear acceptors, it is assumed that the π-complexes will bear close similarity in bond type and configuration with those derived from 2,4,7-trinitrofluorenone. Further, the electron affinity $(EA)_k$ derived from polarography is free from the experimental uncertainty inherent in the EA value measured via charge

NITRO DERIVATIVES OF FLUOREN-$\Delta^{9,\alpha}$-MALONONITRILE AND THEIR RELATIVE ELECTRON AFFINITIES

3,6-Dinitro **1e**		2,6-Dinitro **1c**		2,4-Dinitro **1a**		2,5-Dinitro **1b**		2,7-Dinitro **1d**	
E_π (mμ)	*EA*	E_π (mμ)	*EA*	E_π (mμ)	*EA*	E_π (mμ)	*EA*	E_π (mμ)	*EA*
630	1·273	607	1·194	538	0·942	590	1·135	582	1·107
603	1·251	584	1·184	566	1·116	569	1·128	560	1·093
572	1·200	555	1·142	550	1·122	530	1·037	545^{d}	1·101
670	1·195	665	1·182	645	1·125	637	1·101	637	1·101
—	—	635	1·202	—	—	608	1·116	601	1·092
570	1·224	547	1·129	545^{e}	1·125	553	1·158	555	1·166
590	1·204	567	1·120	550^{e}	1·047	545	1·112	545^{d}	1·012
605	1·107	637	1·204	615	1·135	605	1·102	600	1·084
585	1·219	580	1·201	572	1·169	570^{e}	1·164	570^{d}	1·164
607	1·288	592	1·235	578	1·183	565	1·135	568	1·145
680	1·110	715	1·211	656	1·053	692	1·153	695	1·161
	1·20		1·18		1·10		1·12		1·11

Mathematical Institute, Oxford, England, and the Centre de Chimie Theorique de France, Paris, France (1955).

transfer spectra. For this purpose, the charge transfer energies of 2,4,7-trinitrofluorenone have been included in Table 3. It will be observed that the order of electron affinities determined by the use of equation 4 agree with that obtained polarographically. Although polarography differentiates the variation of electron deficiency

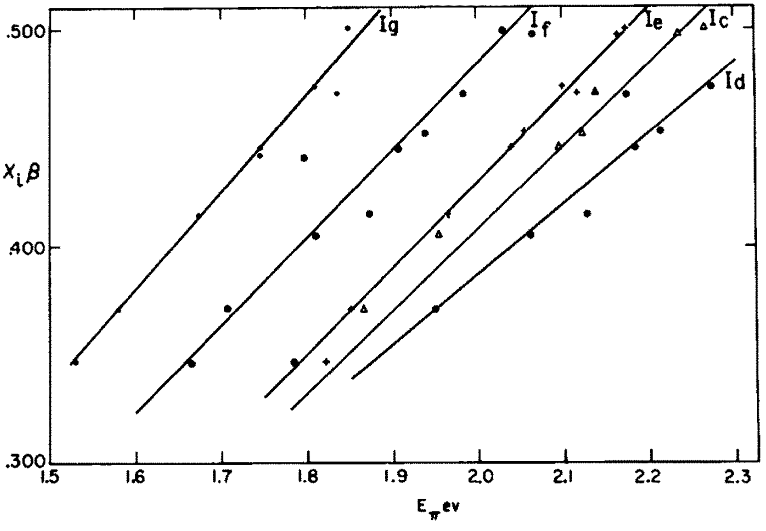


FIG. 1 Plots of the charge-transfer transition energies E_π for the π-complexes of hydrocarbons with the nitro derivatives of fluoren-$\Delta^{9,\alpha}$-malononitrile against the highest filled orbital of the hydrocarbons. Designations are those given in Table 3.

TABLE 4. 2,4,5,7-TETRANITRO FLUOREN-$\Delta^{9\alpha}$-MALONONITRILE (TFM) ANION RADICAL SALTS

Product	Cation Source	Yield	Dec[a]	Analyses, %					
				Calc			Found		
			°C	C	H	N	C	H	N
$\text{Li}^{+}\text{TFM}^{\dot{-}}\text{H}_2\text{O}$	LiI H_2O	50%	>400°	44·35	1·39	19·39	44·18	1·78	19·28
$\text{Cs}^{+}\text{TFM}^{\dot{-}}$	CsI	42%	315	38·73	1·02	14·12	38·88	1·05	14·26
$(\text{Cs})_2^{+}(\text{TFM}^{\dot{-}})_2\text{TFM}$	CsI	25%	305	38·67	0·81	16·91	39·35	1·10	17·01
(N-Methylphenazinium)$^{+}\text{TFM}^{\dot{-}}$	$\text{C}_{13}\text{H}_{12}\text{N}_2\text{I}$	82%	208	57·75	2·50	18·58	57·54	2·49	18·71
(N-Methyltriethylammonium)$^{+}\text{TFM}^{\dot{-}}$	$\text{C}_7\text{H}_{18}\text{NI}$	45%	270	52·80	4·22	18·72	53·11	4·09	18·90
(Methyltriphenylarsonium)$^{+}\text{TFM}^{\dot{-}}$	$\text{C}_{19}\text{H}_{18}\text{AsI}$	39%	226	57·62	3·04	11·53	57·48	3·14	11·71
(Methyltriphenylphosphonium)$^{+}\text{TFM}^{\dot{-}}$	$\text{C}_{19}\text{H}_{18}\text{PI}$	50%	235	61·31	3·23	12·55	61·29	3·11	12·65
(N-Methylquinolinium)$^{+}\text{TFM}^{\dot{-}}$	$\text{C}_{10}\text{H}_{10}\text{NI}$	—	245	56·52	2·55	17·74	58·85	2·83	18·61

[a] At this temp, decomposition sets in. Final decomposition temperature could not be determined due to dark color of the melt. The range is usually 5–10°.

at the exo-double bond at carbon 9 in **1a**, **1b** and **1d**, any change in the overall π-electron deficiency of these isomers could not be detected from their charge transfer behavior.

Anion radicals

2,4,5,7-tetranitro fluoren-$\Delta^{9,\alpha}$-malononitrile (**1g**), being a strong acceptor, is expected to form stable anion radical by capturing one electron from a donor of sufficiently low ionization potential. Deep colored paramagnetic anion radical salts were prepared by mixing acetonitrile solutions of **1g** and iodides of various types of cations.[18] In Table 4, a number of the anion radical salts are listed. These salts are quite stable in the solid state; in solution, however, the paramagnetism gradually decays indicating dimerization or other oxidative processes.

EXPERIMENTAL

Materials. Syntheses of the compounds have been described earlier.[5–7] By following the same procedure, 3,6-dinitrofluoren-$\Delta^{9,\alpha}$-malononitrile was obtained from 3,6-dinitrofluoren-9-one,[19] m.p. 305–309° (d). (Found: C, 60·62; H, 2·05. Calc. for $C_{16}H_6N_4O_4$: C, 60·38; H, 1·90%.)

Polarography. Both a Sargent Model XV and a Sargent Model XXI polarograph were used. All polarographic measurements were made in spectral grade acetonitrile solns of 0·1M lithium perchlorate. Tetra-n-butyl ammonium perchlorate (TBA) and tetra-n-ethyl ammonium perchlorate (TEA) were tried as supporting electrolyte but the results indicated slow kinetically controlled reduction. The d.c. polarography was carried out at room temp in a three electrode Arthur and Vanderkam cell.[20] The IR drop in the cell was compensated by a Sargent Model A compensator. The half-wave potentials were measured vs aqueous saturated calomel electrode under conditions of "long immersion".[21] The observed reproducibility of half-wave potential measurements was ±5 mV. Maximum current values were used in calculating limiting current constant $I = i_d/m^{2/3}t^{1/6}C$, where i_d is the limiting current in microamperes, m in mg. of Hg/sec., t in sec, and C in mmoles/liter.

Charge-transfer spectra. Solns of the π-complexes were prepared in CH_2Cl_2 by adding a soln of the acceptor to the soln of large excess of the aromatic hydrocarbon donor. In several cases solns of **1f** and **1g** gave immediate ppt with donor solns. The filtrate, after removal of the solid, was used for spectral determination. The charge-transfer absorption spectra were measured in a Cary Model 14 recording spectrophotometer using quartz cells of 1 cm path lengths, the reference cell containing solns of the donors. The donor hydrocarbons were used in the form obtained from Rutgerswerke-Aktilgensellschaft, Frankfurt-am-Main, West Germany.

General method of preparing anion-radical salts. To a boiling soln of 1 mmole of (**1g**) in 75 ml of spectrograde acetonitrile was added a filtered soln of 3 mmole of iodide in 75 ml of the same solvent. The highly coloured soln was concentrated under N_2. After cooling, the dark crystals were filtered and washed with cold acetonitrile. All operations were carried out in acid washed glassware. When 1 mmole of cesium iodide was used, the resulting product analysed for $(Cs)_2^{+}\,(C_{16}H_5N_5O_6)_2^{\dot{-}}\,.\,(C_{16}H_5N_5O_6)$.

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