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The Electronic Spectra of the Anion Radicals of Substituted Benzenes

By

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The nitrosobenzene, benzonitrile, nitrobenzene, phthalonitrile, isophthalonitrile, terephthalonitrile and pyromellitonitrile anions were prepared by the alkali metal reduction method. Their electronic absorption spectra were measured in parallel with the ESR spectra. Furthermore, the electronic structures of these anion radicals were studied theoretically by combining the open shell SCF procedure with configuration interaction calculation. The observed transition energies and relative intensities were well explained by the present theoretical studies.

Die Anionen von Nitrosobenzol, Benzonitril, Nitrobenzol, Phthalodinitril, Isophthalodinitril, Terephthalodinitril und Pyromellithotetranitril wurden durch Reduktion mit Alkalimetall dargestellt und ihre Elektronenanregungs- und Elektronenresonanz-Spektren (nebeneinander) gemessen. Ferner wurden die Elektronenstrukturen der genannten Anionenradikale mittels der Kombination eines SCF-Verfahrens für offene Schalen mit Konfigurationswechselwirkung ermittelt, wobei sich die beobachteten Übergangsenergien sowie deren relative Intensitäten recht gut ergaben.

Les anions de nitrosobenzène, benzonitrile, nitrobenzène, phthalodinitrile, isophthalodinitrile, terephthalodinitrile et pyromellitotétranitrile ont été préparés par réduction aux métaux alcalins et leurs spectres électroniques et de résonance paramagnétique ont été mesurés. En outre, les structures électroniques de ces radicaux anioniques ont été étudiées théoriquement en combinant la méthode SCF pour les couches ouvertes avec un calcul d'interactions de configurations. Les résultats théoriques expliquent bien les énergies de transitions observées et leurs intensités relatives.

Recently, the studies of electronic structures of anion radicals of aromatic compounds have made remarkable progress [*5, 11, 15*]. Most of them, however, are mainly concerned with ESR spectra. Only HOIJTINK et al. [*2, 3, 4, 7*] have made a lot of works on the electronic spectra of aromatic hydrocarbon anions. We have undertaken to study the electronic spectra of the anion radicals of substituted benzenes containing the nitro [*8*], nitroso and cyano groups. Assignment of the absorption bands has been made by combining experimental results with theoretical studies based on SCF MO method for open-shell systems [*10*].

1. Experimental

Materials. Nitrosobenzene was synthesized by the usual method from nitrobenzene. Purification was done by repeating recrystallization from ethanol (m. p., 67.5 °C).

Benzonitrile of GR grade was dried over calcium chloride and was purified by repeating distillation under reduced pressure. Pyromellitonitrile used in the present study is the same as described in a previous paper [*9*]. Phthalonitrile and isophthalonitrile of GR grade were purified by repeating recrystallization from ethanol. Melting points were 140 °C and 126 °C respectively. Tetrahydrofuran and dimethoxyethane used as solvents were refluxed wiht sodium metal for 2 days, distilled repeatedly and thereafter were kept with K-Na alloy in vacuum line system.

Preparation of Anion Radicals and Measurements. The Nitrosobenzene, benzonitrile, phthalonitrile, isophthalonitrile, terephthalonitrile and pyromellitonitrile anions were prepared by the alkali metal (potassium) reduction method in polar solvents (tetrahydrofuran or dimethoxyethane) [*8*]. Electronic absorption spectra and ESR spectra were measured in parallel with each other in order to make sure of the assignment of the observed electronic absorption spectra to respective anion radicals. They were measured with a Cary recording spectrophotometer model 14 and a Hitachi ESR spectrometer model MPU 2 B (Xband, 100 kc. Modulation) respectively. The preparation of an anion radical and the measurements of the ESR and electronic absorption spectra were made in a vacuum line system shown in Fig. 1.

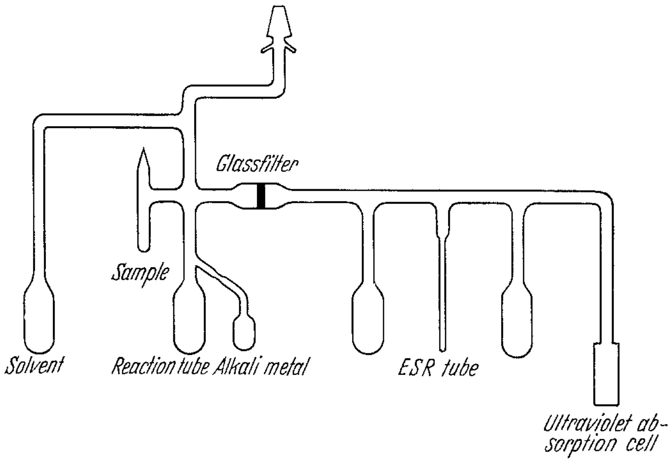

Fig. 1. The vacuum line system

2. Theoretical

We have undertaken to study the π-electron structures of the anion radicals of some substituted benzenes by the method combining open shell SCF procedure of LONGUET-HIGGINS and POPLE [*10*] with the configuration interaction.

Putting $2m - 1$ electrons in the molecular orbitals shown in Fig. 2, we can construct the following ground and excited electron configurations:

Ground configuration,

$$^2\Psi_G = |\varphi_1 \bar{\varphi}_1 \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| \tag{1}$$

four types of excited configurations,

$$^2\Psi_A = |\varphi_1 \bar{\varphi}_1 \cdots \varphi_i \bar{\varphi}_m \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| \qquad \varphi_i \to \varphi_m \tag{2}$$

$$^2\Psi_B = |\varphi_1 \bar{\varphi}_1 \cdots \varphi_{m-1} \varphi_{m-1} \varphi_k| \qquad \varphi_m \to \varphi_k \tag{3}$$

$$^2\Psi_{c\alpha} = \frac{1}{\sqrt{2}} \left(|\varphi_1 \bar{\varphi}_1 \cdots \varphi_i \bar{\varphi}_k \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| + |\varphi_1 \bar{\varphi}_1 \cdots \varphi_k \bar{\varphi}_i \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| \right)$$

$$^2\Psi_{c\beta} = \frac{1}{\sqrt{6}} \left(|\varphi_1 \bar{\varphi}_1 \cdots \varphi_i \bar{\varphi}_k \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| - |\varphi_1 \bar{\varphi}_1 \cdots \varphi_k \bar{\varphi}_i \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| + 2\, |\varphi_1 \varphi_1 \cdots \varphi_i \bar{\varphi}_m \cdots \varphi_{m-1} \bar{\varphi}_{m-1} \varphi_m| \right) \qquad \varphi_i \to \varphi_k \tag{4}$$

φ_i's are the open shell LCAO SCF MO's which are evaluated by the aid of the approximate procedure of LONGUET-HIGGINS and POPLE [10]. In LCAO approximation φ_i can be expressed by $\varphi_i = \sum_\nu C_{i\nu}\chi_\nu$ (here χ_ν represents the atomic orbital function of the ν-th atom). By putting it into the equation $F\varphi_i = E_i\,\varphi_i$, an equation $\sum_\nu F_{\mu\nu}\,C_{i\nu} = E_i\,C_{i\mu}$ was obtained. Furthermore, by adopting the zero-differential overlap approximation, the elements of the secular determinant can be evaluated as follows;

$$F_{\mu\mu} = H_{\mu\mu}^{\mathrm{core}} + \tfrac{1}{2}\,P_{\mu\mu}\,\langle\mu\mu\,|\,\mu\mu\rangle + \sum_{\sigma\neq\mu} P_{\sigma\sigma}\,\langle\mu\mu\,|\,\sigma\sigma\rangle$$

$$F_{\mu\nu} = H_{\mu\nu}^{\mathrm{core}} - \tfrac{1}{2}\,P_{\mu\nu}\,\langle\mu\mu\,|\,\nu\nu\rangle\,. \qquad (5)$$

Here

$$P_{\mu\nu} = \sum_{i=1}^{m-1} 2\,C_{i\mu}\,C_{i\nu} + C_{m\mu}\,C_{m\nu}\,.$$

SCF procedure was carried out by an electronic computer Facom 202 in our Institute and a converged set of MO energies and coefficients were obtained.

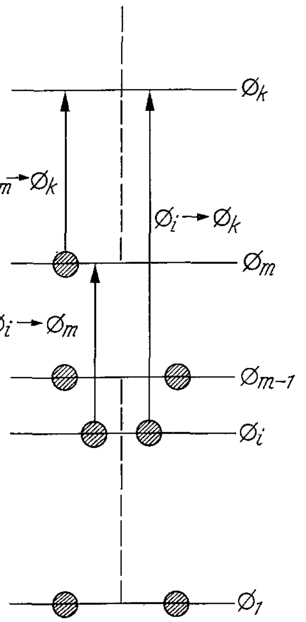

Fig. 2. Molecular orbitals of an anion radical

Configuration interaction calculation is known to improve the reliability of the calculated transition energies and oscillator strengths. In the present calculation, only the singly excited configurations given by Eqs. 1 – 4 were taken into account. Five kinds and twenty-five kinds of general formulae were derived for evaluating the diagonal and off-diagonal elements of the total electronic Hamiltonian respectively. They are shown in Tab. 1.

Electron-electron interaction integrals shown in Tab. 1 like $(mm\,|\,mm)$, $(im\,|\,im)$ and $(ii\,|\,mm)$ were reduced to atomic orbital integrals of the type of

$$(pp\,|\,qq) \equiv \int \chi_p(i)\,\chi_p(i)\,\frac{e^2}{r_{ij}}\,\chi_q(j)\,\chi_q(j)\,d\tau_{ij}\,,$$

which were calculaetd according to the Pariser-Parr approximation [13], the radius of the electron cloud obtained by the effective nuclear charge determined by the Slater rule, and the ionization potentials and electron affinities of appropriate valence states taken from the table of PILCHER and SKINNER [14] being used. The Coulomb integral α_p was obtained by the following equation on the assumption of neglecting penetration integrals

$$\alpha_p = -\,I_p - \sum_{p\neq q} (pp\,|\,qq)\,\gamma_q\,. \qquad (6)$$

Table 1. *General formulae for evaluating the matrix elements necessary for the configuration interaction calculation and transition moments between configurations*

a) Diagonal elements

Ground configuration (Configuration G)	0
A type excited configuration [Configuration A $(i \to m)$]	$F_{mm} - F_{ii} + 1/2\,[(mm \mid mm) + (im \mid im) - 2\,(ii \mid mm)]$
B type excited configuration [Configuration B $(m \to k)$]	$F_{kk} - F_{mm} + 1/2\,[(mm \mid mm) + (mk \mid mk) - 2\,(mm \mid kk)]$
C_α type excited configuration [Configuration C_α $(i \to k)$]	$F_{kk} - F_{ii} + 2\,(ik \mid ik) - (ii \mid kk)$
C_β type excited configuration [Configuration C_β $(i \to k)$]	$F_{kk} - F_{ii} + (im \mid im) + (mk \mid mk) - (ii \mid kk)$

b) Off-diagonal elements

	transition moments $r_{ij} = \int \varphi_i\, r \varphi_j\, d\tau$	Elements
$G - A\ (i \to m)$	r_{im}	$1/2\ (im \mid mm)$
$G - B\ (m \to k)$	r_{mk}	$-1/2\ (mm \mid mk)$
$G - C_\alpha\ (i \to k)$	$\sqrt{2}\, r_{ik}$	0
$G - C_\beta\ (i \to k)$	0	$\sqrt{6}/2\ (im \mid mk)$
$A\ (i \to m) - A\ (h \to m)$	$-r_{hi}$	$1/2\ (hm \mid im) - (hi \mid mm)$
$A\ (i \to m) - B\ (m \to k)$	0	$(im \mid mk)$
$A\ (i \to m) - C_\alpha\ (i \to k)$	$1/\sqrt{2}\, r_{mk}$	$\sqrt{2}/2\ [2\ (ik \mid im) + 1/2\ (mm \mid mk) - (ii \mid mk)]$
$A'\ (h \to m) - C_\alpha\ (i \to k)$	0	$\sqrt{2}/2\ [2\ (hm \mid ik) - (hi \mid mk)]$
$A\ (i \to m) - C_\beta\ (i \to k)$	$\sqrt{6}/2\, r_{mk}$	$\sqrt{6}/2\ [1/2\ (mm \mid mk) - (ii \mid mk)]$
$A'\ (h \to m) - C_\beta\ (i \to k)$	0	$-\sqrt{6}/2\ (ih \mid mk)$
$B\ (m \to k) - B'\ (m \to l)$	r_{kl}	$1/2\ (mk \mid ml) - (mm \mid kl)$
$B\ (m \to k) - C_\alpha\ (i \to k)$	$-1/\sqrt{2}\, r_{im}$	$\sqrt{2}/2\ [2\ (ik \mid mk) + 1/2\ (im \mid mm) - (im \mid kk)]$
$B'\ (m \to l) - C_\alpha\ (i \to k)$	0	$\sqrt{2}/2\ [2\ (ik \mid lm) - (im \mid lk)]$
$B\ (m \to k) - C_\beta\ (i \to k)$	$\sqrt{6}/2\, r_{im}$	$\sqrt{6}/2\ [(im \mid kk) - 1/2\ (im \mid mm)]$
$B'\ (m \to l) - C_\beta\ (i \to k)$	0	$\sqrt{6}/2\ (im \mid kl)$
$C_\alpha\ (i \to k) - C_\alpha\ (i \to l)$	r_{kl}	$2\ (ik \mid il) - (ii \mid kl)$
$C_\alpha\ (i \to k) - C''_\alpha\ (h \to k)$	$-r_{hi}$	$2\ (hk \mid ik) - (hi \mid kk)$
$C_\alpha (i \to k) - C'''_\alpha\ (h \to l)$	0	$2\ (hl \mid ik) - (hi \mid kl)$
$C_\alpha\ (i \to k) - C_\beta\ (i \to k)$	0	$\sqrt{3}/2\ [(mk \mid mk) - (im \mid im)]$
$C_\alpha\ (i \to k) - C'_\beta\ (i \to l)$	0	$-\sqrt{3}/2\ (mk \mid ml)$
$C_\alpha\ (i \to k) - C''_\beta\ (h \to k)$	0	$-\sqrt{3}/2\ (hm \mid im)$
$C_\alpha\ (i \to k) - C'''_\beta\ (h \to l)$	0	0
$C_\beta\ (i \to k) - C'_\beta\ (i \to l)$	r_{kl}	$(ml \mid mk) - (ii \mid kl)$
$C_\beta\ (i \to k) - C''_\beta\ (h \to k)$	$-r_{hi}$	$(hm \mid im) - (hi \mid kk)$
$C_\beta\ (i \to k) - C'''_\beta\ (h \to l)$	0	$-(hi \mid kl)$

Here, φ_m, φ_{m-1} are the lowest unoccupied orbital and the highest occupied orbital of neutral molecule respectively, φ_i, φ_h are occupied and φ_k, φ_l are unoccupied orbitals.

Here I_p is the ionization potential of the π-electron of the p-th atom, and $\gamma_q = 1$ and 2, when the core charges of the qth atom are $+\,e$ and $+\,2\,e$ respectively. The core resonance integral β_{pq} was taken to be proportional to the overlap integral $S_{pq} = \int \chi_p\,(i)\,\chi_q\,(i)\,d\tau_i$ which was taken from the table of Mulliken et al. [*12*].

3. Results and Discussion

Hydrocarbon Anions. First of all, the electronic structures of the naphthalene and anthracene anions were calculated. All atomic distances and bond angles were taken to be 1.39 Å and 120° respectively. The valence state ionization potential and electron affinity of the π-orbitals of the carbon atoms were determined as follow [*14*]:

$$C\ (t_1\, t_2\, t_3\, z) \rightarrow C^+\ (t_1\, t_2\, t_3) \qquad 11.22\ \text{eV}$$

$$C\ (t_1\, t_2\, t_3\, z) \rightarrow C^-\ (t_1\, t_2\, t_3\, z^2) \qquad 0.62\ \text{eV}\,.$$

The value of the core resonance integral β_{cc} was taken to be -2.39 eV. This is the same as that for neutral molecules [*13*].

Table 2. *Observed and calculated transition energies (ΔE) and oscillator strengths (f) for aromatic hydrocarbon anions*

a) Naphthalene anion

No.	ΔE_{obs} (eV)	f^a_{obs}	ΔE_{calc} (eV)	f^{ab}_{calc}
1	1.636	0.29 [*X*]	1.969	0.413 [*X*]
2	hidden		2.657	0.057 [*Y*]
3	3.657	0.40 [*Y*]	3.708	0.486 [*Y*]
4	3.831	0.37 [*X*]	4.286	0.014 [*X*]
5	4.228		5.032	0.876 [*X*]
6	5.443		6.374	2.516 [*X*]

b) Anthracene anion

No.	ΔE_{obs} (eV)	f^a_{obs}	ΔE_{calc} (eV)	f^{ab}_{calc}
1	1.327	– [*Y*]	2.353	0.088 [*Y*]
2	1.686	0.95 [*X*]	1.813	0.874 [*X*]
3	3.161	– [*Y*]	3.504	0.703 [*Y*]
4	3.385	0.70 [*X*]	3.870	0.018 [*X*]
5	3.781	1.50 [*X*]	4.730	1.825 [*X*]
6	hidden	– [*Y*]	4.226	0.004 [*Y*]
7	4.848	– [*X*]	5.775	3.544 [*X*]

[a] [*X*] and [*Y*] mean that the corresponding transition is polarized in the direction of the long and short axes of the anion respectively.

[b] The oscillator strength was calculated by the following equation:
$f_{calc} = 4.704 \times 10^{-7}\, \tilde{\nu}\, Q^2$ ($\tilde{\nu}$ in cm^{-1}, Q in Debye)

By putting π-electrons in the open shell SCF MO's evaluated by the present authors, ground and singly excited configurations were constructed. In the actual configuration interaction calculations, 29 and 33 configurations were taken for the naphthalene and anthracene anions respectively. Diagonal and off-diagonal matrix elements of the total electronic Hamiltonian were evaluated according to the general formulae given in Tab. 1. The finally obtained transition energies and oscillator strengths calculated by the present authors are given in Tab. 2a and 2b for the naphthalene and anthracene anions respectively, together with the experimental results by HOIJTINK et al. [*7*].

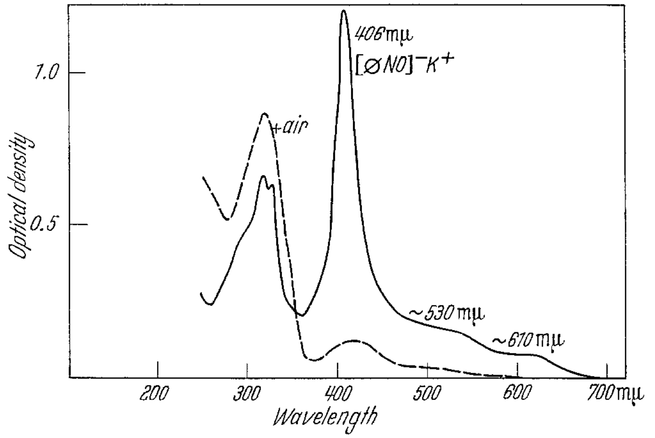

Fig. 3. The electronic spectrum of the nitrosobenzene anion

From Tab. 2a and 2b, it may be said that the theoretical transition energies can explain rather well the observed band positions. Discrepancy of the theoretical transition energy from the observed one becomes larger for higher energy transitions. In order to decrease this discrepancy, we must take the electron configurations with higher energy like doubly excited configurations. In the case of the anthracene anion, the longest wavelength band was observed to be polarized in the Y (short axis) direction [7]. This was contrary to the theoretical expectation made by HOIJTINK et al. on the basis of the refined Hückel MO method. This situation was not improved by the configuration interaction calculation made by the present authors. As for oscillator strengths, the present calculation gave rather improved values compared with that of HOIJTINK et al. However, the theoretical value of transition 4 was still far smaller than the observed value for the both anions.

The Anion Radicals of Substituted Benzenes. The dimethoxyethane solution of nitrosobenzene and the tetrahydrofuran solution of benzonitrile colored respectively orange red and red in contact with potassium film in vacuo. These solutions showed the strong ESR spectra due to the corresponding anion radicals. The ESR spectra of the nitrosobenzene and benzonitrile anion radicals have already been

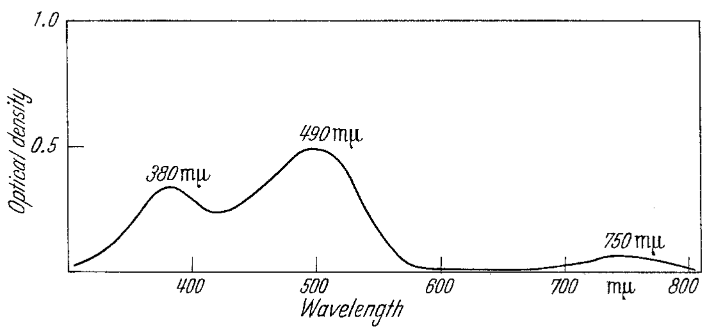

Fig. 4. The electronic spectrum of the benzonitrile anion

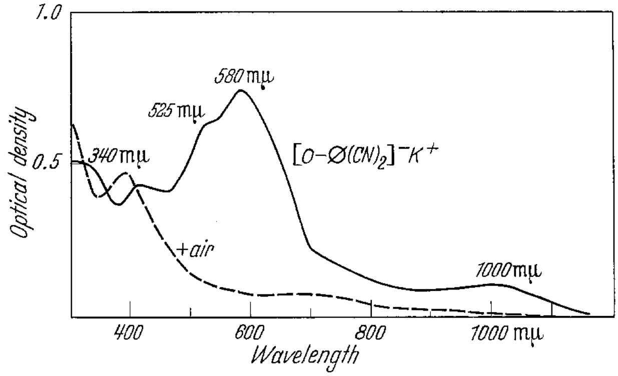

Fig. 5. The electronic spectrum of the phthalonitrile anion

measured by Smentowski [15], and by Carrington and Todd [5] respectively. In parallel with the ESR spectra, the electronic absorption spectra were measured by the present authors with the results shown in Fig. 3 and 4. From the change in the absorption bands caused by exposing the solution to air, three bands were assigned to each of the anion radicals. Their maximum wavelengths are 406, 530, 610 mμ and 380, 490, 750 mμ for the nitrosobenzene and benzonitrile anion radicals respectively. Furthermore, the electronic absorption spectra of the anion radicals of phthalonitrile, isophthalonitrile, terephthalonitrile and pyromellitonitrile were measured in tetrahydrofuran, with the results shown in Fig. 5 – 8.

The open shell SCF MO calculations combined with the configuration interaction procedure described in the theoretical part were carried out with the nitrosobenzene, benzonitrile, nitrobenzene, phthalonitrile, isophthalonitrile, terephthalonitrile and pyromellitonitrile anion radicals.

Values of atomic distances and bond angles, the valence state ionization potentials and electron affinities of the π-electrons, and the values of resonance integrals used in the calculations are summarized in Tab. 3. The energies and characters of SCF MO are given in Tab. 4 for the monosubstituted benzene anions.

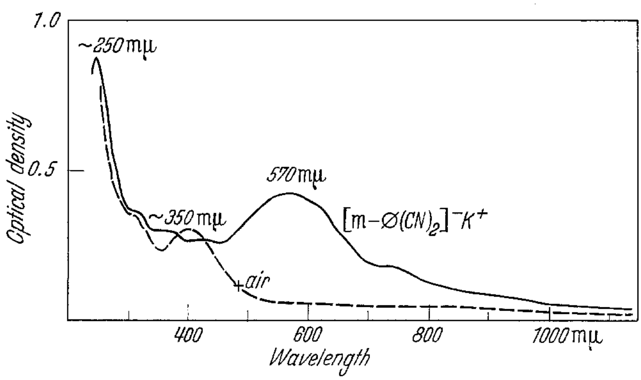

Fig. 6. The electronic spectrum of the isophthalonitrile anion

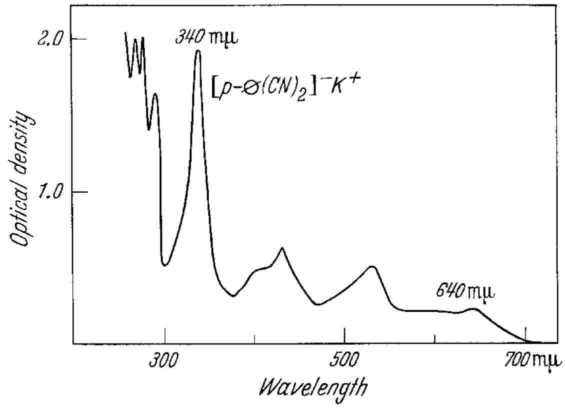

Fig. 7. The electronic spectrum of the terephthalonitrile anion

Configurations considered in the configuration interaction calculation are shown in Tab. 5 for the monosubstituted benzene anions. The energies of the ground and lower excited states finally obtained with the nitrosobenzene, benzonitrile, nitrobenzene, phthalonitrile, isophthalonitrile, terephthalonitrile and pyromellitonitrile anions are shown in Tab. 6. In this table, are also shown the percentages of the configurations mainly contributed to each state. The inspection of Tab. 5 and 6 shows that the configuration interaction exerts a great effect to the energy values and wave functions and is indispensable for the calculation of the excitation energies.

From the wave function given in Tab. 6a, it could roughly be said that the lowest energy transition of the nitrosobenzene anion corresponds to the mixed local excitations within the NO group and within the benzene ring and that the second and the third lowest energy transitions may be regarded as the excitations from the NO antibonding orbital to the benzene e_{2u} orbitals. The calculated transition energies agree well with the observed values and the calculated oscillator strengths can explain the observed tendency as shown in Tab. 7a.

The first excitation of the benzonitrile anion corresponds to the transition between the splitted orbitals of the benzene e_{2u} orbitals. The second excitation is

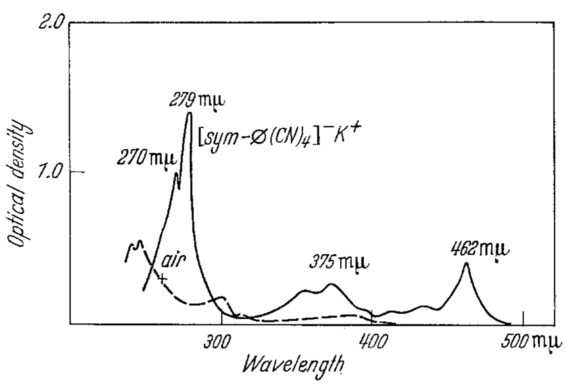

Fig. 8. The electronic spectrum of the pyromellitonitrile anion

Table 3. *Parameters used for the calculations of the substituted benzene anion radicals*[a]

parameters \ materials	Nitrosobenzene	Benzonitrile, *o*-, *m*-, *p*-, dicyanobenzene, Terephthalonitrile	Nitrobenzene
Bond distances and bond angles	C – C, 1.39 Å; C – N, 1.40 Å N – O, 1.35 Å[e] all angles = 120°	C – C′[b], 1.46 Å; C′ – N, 1.16 Å C – C, 1.39 Å[f] < CC′ N – 180° all other angles = 120°	C – N, 1.48 Å; N – O, 1.20 Å C – C, 1.39 Å all angles = 120°[g]
Ionization potentials and electron affinities	N $(t_1^2 t_2 t_3 z) \rightarrow N^+ (t_1^2 t_2 t_3)$ $I_N = 14.51$ eV N $(t_1^2 t_2 t_3 z) \rightarrow N^- (t_1^2 t_2 t_3 z^2)$ $A_N = 1.20$ O $(d_1^2 d_2 x^2 z) \rightarrow O^+ (d_1^2 d_2 x^2)$ $I_O = 17.795$ O $(d_1^2 d_2 x^2 z) \rightarrow O^- (d_1^2 d_2 x^2 z^2)$ $A_O = 3.145$	C′ $(d_1 d_2 xy) \rightarrow C'^+ (d_1 d_2 x)$ $I_{C'} = 11.24$ eV C′ $(d_1 d_2 xy) \rightarrow C'^- (d_1 d_2 xy^2)$ $A_{C'} = 0.58$ N $(d_1^2 d_2 xy) \rightarrow N^+ (d_1^2 d_2 x)$ I_N $I_N = 14.47$ N $(d_1^2 d_2 xy) \rightarrow N^- (d_1^2 d_2 xy^2)$ $A_N = 1.21$	$N^+ (t_1 t_2 t_3 z) \rightarrow N^{++} (t_1 t_2 t_3)$ $I_{N^+} = 28.855$ eV $N^+ (t_1 t_2 t_3 z) \rightarrow N (t_1 t_2 t_3 z^2)$ $A_{N^+} = 12.26$ O $(sx^2 y^2 z) \rightarrow O^+ (sx^2 y^2)$ $I_O = 17.764$ O $(sx^2 y^2 z) \rightarrow O^- (sx^2 y^2 z^2)$ $A_O = 3.87$
Resonance integrals[c]	$\beta_{CC} = -2.39$ eV $\beta_{NO} = -1.27$ $\beta_{CN} = -1.89$	$\beta_{CN} = -3.280$ eV $\beta_{C'C} = -2.082$	β_{CN}[d] $= -2.40$ eV $\beta_{NO} = -2.40$

[a] In this table t and d are sp^2 and sp hybridized orbitals respectively. The values of I_N and A_N were taken from PILCHER and SKINNER's table and the values for sp hybridized oxygen orbital were newly calculated by the aid of the atomic spectral data [*14*].

[b] Here C is the carbon atom of the benzene ring and C′ that of the cyano group.

[c] Resonance integrals between two ajacent atoms.

[d] β_{CN} of the nitrobenzene anion was taken to be equal to the best value for the nitrobenzene molecule [S. NAGAKURA, M. KOJIMA and Y. MARUYAMA: J. Mol. Spectroscopy **13**, 174 (1964)].

[e] Ref. [*6*].

[f] Ref. [*1*].

[g] Ref. [*16*].

Table 4. *Energies, symmetries and characters of* SCF *molecular orbitals of substituted benzene anions*

a) Nitrosobenzene anion

Molecular orbital	Energy (eV)	Character
φ_1	−10.2005	[BZ·a_{2u}[a]]
φ_2	− 7.6519	[BZ·e_{1g} (+ NO·B)]
φ_3	− 7.0856	[BZ·e_{1g}]
φ_4	− 5.9423	[NO·B (+ BZ·e_{1g})]
φ_5	0.1189	[NO·A (+ BZ·e_{2u})]
φ_6	4.3514	[BZ·e_{2u}]
φ_7	5.0851	[BZ·e_{2u} (+ NO·A)]
φ_8	7.9739	[BZ·b_{2g}]

[a] [BZ·a_{2u}] means that this orbial consists mainly of a_{2u} orbital of benzene. NO·B, NO·A are bonding and antibonding orbitals of the nitroso group respectively

b) Benzonitrile anion

Molecular orbital	Symmetry[a]	Energy (eV)	Character
φ_1	(*A*)	− 9.6306	[BZ·a_{2u} (+ CN·B)]
φ_2	(*A*)	− 8.4711	[CN·B (+ BZ·a_{2u})]
φ_3	(*B*)	− 6.2713	[BZ·e_{1g}]
φ_4	(*A*)	− 5.7300	[BZ·e_{1g}]
φ_5	(*A*)	1.8474	[BZ·e_{2u} (+ CN·A)]
φ_6	(*B*)	5.2215	[BZ·e_{2u}]
φ_7	(*A*)	6.4624	[CN·A (+ BZ·e_{2u})]
φ_8	(*A*)	8.7305	[BZ·b_{2g}]

[a] *A* and *B* designate symmetric and antisymmetric about the molecular symmetry axis respectively.

c) Nitrobenzene Anion

Molecular orbital	Symmetry	Energy (eV)	Character
φ_1	(*A*)	−12.6729	[NO_2·B_1]
φ_2	(*A*)	−10.4758	[BZ·a_{2u}]
φ_3	(*B*)	− 8.5996	[NO_2·B_2]
φ_4	(*A*)	− 7.6192	[BZ·e_{1g}]
φ_5	(*B*)	− 7.5667	[BZ·e_{1g}]
φ_6	(*A*)	− 0.4352	[BZ·e_{2u} (+ NO_2·A)]
φ_7	(*B*)	3.8780	[BZ·e_{2u}]
φ_8	(*A*)	4.6979	[BZ·e_{2u} (+ NO_2·A)]
φ_9	(*A*)	7.2517	[BZ·b_{2g}]

of charge-transfer character, that is to say, it is characterized by the unpaired electron migration from the benzene ring to the cyano group. The third excitation corresponds to the $e_{2u} \rightarrow b_{2g}$ transition of the benzene ring. Comparison between the observed and calculated values is shown in Tab. 7b.

The preparation of the nitrobenzene anion and the observations of the ESR and electronic spectra were described in the previous paper [*8*]. The first transition $\Psi_G \rightarrow \Psi_{E1}$ has the characters of the transition between two splitted e_{2u}

Table 5. *Energies and symmetries of the ground and the excited configurations taken in the present calculation of substituted benzene anions*

Configuration	Energy (eV)	Configuration	Energy (eV)
	a) Nitrosobenzene anion		
Ground Configuration	0	$(4 \to 6)_\alpha$	5.8255
$4 \to 5$	3.2182	$(4 \to 6)_\beta$	6.7414
$3 \to 5$	5.9702	$(4 \to 7)_\alpha$	6.3145
$2 \to 5$	5.1024	$(4 \to 7)_\beta$	8.0603
$1 \to 5$	8.8724	$(3 \to 6)_\alpha$	6.2837
$5 \to 6$	2.8511	$(3 \to 6)_\beta$	4.9303
$5 \to 7$	3.3993	$(3 \to 7)_\alpha$	6.8317
$5 \to 8$	5.7512	$(3 \to 7)_\beta$	7.7022

Configuration (*A*)	Energy (eV)	Configuration (*B*)	Energy (eV)
	b) Benzonitrile anion		
Ground Configuration	0	$5 \to 6$	0.6981
$5 \to 7$	2.4489	$3 \to 5$	5.6037
$5 \to 8$	4.1283	$(4 \to 6)_\alpha$	5.8551
$4 \to 5$	4.8751	$(4 \to 6)_\beta$	5.8213
$2 \to 5$	7.7877	$(3 \to 7)_\alpha$	7.8332
$1 \to 5$	8.6245	$(3 \to 7)_\beta$	9.3119
$(3 \to 6)_\alpha$	6.3468		
$(3 \to 6)_\beta$	5.1124		
$(4 \to 7)_\alpha$	7.3386		
$(4 \to 7)_\beta$	8.6965		
	c) Nitrobenzene anion		
Ground Configuration	0	$5 \to 6$	5.1944
$4 \to 6$	4.8993	$3 \to 6$	5.2499
$2 \to 6$	7.8550	$6 \to 7$	2.2531
$1 \to 6$	8.5615	$(5 \to 8)_\alpha$	7.0812
$6 \to 8$	2.8743	$(5 \to 8)_\beta$	8.6434
$6 \to 9$	5.1761	$(4 \to 7)_\alpha$	6.2458
$(5 \to 7)_\alpha$	6.2980	$(4 \to 7)_\beta$	6.3414
$(5 \to 7)_\beta$	5.1168	$(3 \to 8)_\alpha$	8.1879
$(4 \to 8)_\alpha$	7.1417	$(3 \to 8)_\beta$	10.0273
$(4 \to 8)_\beta$	8.6081		
$(3 \to 7)_\alpha$	8.6470		
$(3 \to 7)_\beta$	9.6938		

orbitals and to smaller extent of the charge-transfer transition accompanying the electron migration from the nitro group to the benzene ring. The second transition ($\Psi_G \to \Psi_{E2}$) corresponds to the charge-transfer excitation in the same sense as described in the previous paper [*8*], namely, in the sense that it corresponds to the transition between the two states caused by the resonance interaction between the ground and charge-transfer configurations. The third ($\Psi_G \to \Psi_{E3}$) transition contains two local excitations ($e_{1g} \to e_{2u}$, $e_{2u} \to b_{2g}$) and also charge-transfer excitation. These three excitations correspond in their natures of the respective

Table 6. *Theoretical results of the ground and the lower excited states of substituted benzene anions*

a) Nitrosobenzene anion

Wave function	Energy (eV)	Configurations mainly contributed to each state[a]
Ψ_G	0	Ground Configuration (93)
Ψ_{E1}	2.6466	$4 \to 5$ (52), $2 \to 5$ (16), $5 \to 6$ (24)
Ψ_{E2}	2.7422	$4 \to 5$ (15), $2 \to 5$ (9), $5 \to 6$ (65), $(4 \to 6)_\alpha$ (7)
Ψ_{E3}	2.9515	$5 \to 8$ (6), $2 \to 5$ (8), $5 \to 7$ (70), $(4 \to 7)_\beta$ (5)
Ψ_{E4}	4.7229	$3 \to 5$ (7), $5 \to 8$ (13), $(3 \to 6)_\beta$ (66)

b) Benzonitrile anion

Wave function	Symmetry	Energy (eV)	Configurations mainly contributed to each state[a]
Ψ_G	(A)	0	Ground Configuration (98)
Ψ_{E1}	(B)	0.7133	$5 \to 6$ (98)
Ψ_{E2}	(A)	2.2279	$5 \to 7$ (91), $4 \to 5$ (6)
Ψ_{E3}	(A)	3.4715	$5 \to 8$ (75), $(3 \to 6)_\alpha$ (15)

c) Nitrobenzene anion

Wave function	Symmetry	Energy (eV)	Configurations mainly contributed to each state[a]
Ψ_G	(A)	0	Ground Configuration (92)
Ψ_{E1}	(B)	2.3213	$6 \to 7$ (93)
Ψ_{E2}	(A)	2.6847	$6 \to 8$ (76), $4 \to 6$ (11), $6 \to 9$ (7), Ground (5)
Ψ_{E3}	(A)	4.4855	$6 \to 9$ (43), $(5 \to 7)_\beta$ (43), $(4 \to 8)_\beta$ (5)
Ψ_{E4}	(B)	4.7306	$5 \to 6$ (79), $(5 \to 8)_\beta$ (11), $(4 \to 7)_\beta$ (7)

[a] The number in parentheses represents the contribution (in %) of a corresponding configuration to each state.

transitions to the $W_1 \to W_{10}$, $W_1 \to W_2$ and $W_1 \to W_3$ transitions in the previous paper [*8*] in which the electronic structure of nitrobenzene anion radical was studied theoretically on the basis of the interaction between the benzene anion and the nitro group. The forth ($\Psi_G \to \Psi_{E4}$) transition is composed of the transitions between e_{1g} and e_{2u} and also between e_{1g} and $NO_2 \cdot A$. Comparison between experimental and theoretical values is shown in Tab. 7c. The band of longest wavelength was thought to be hidden in the strong second band.

Concerning the polycyanobenzene anion radicals, the observed and calculated transition energies and the calculated oscillator strengths are given in Tab. 7d – g. In these tables, the directions of the transition moments are also shown. From the inspection of these tables and Fig. 5 – 8, it may be said that the observed absorption spectra are well interpreted by the present theoretical studies. In the cases of the terephthalonitrile and pyromellitonitrile anions, a few bands which could not be expected from the calculated transition energies for the respective anion radicals were observed. For example, extra bands due to unstable specimens appear at 430 mμ and 530 mμ for the terephthalonitrile case. They might be due to some unstable byproducts, probably di-negative ions.

Table 7. *Observed and calculated data for the absorption spectra of the substituted benzenes*[a]

ΔE_{obs} (eV)	ΔE_{calc} (eV)	f^{b}_{calc}	Direction of transition moment
	a) Nitrosobenzene anion		
2.032	2.647	(4.260×10^{-2})	
2.339	2.742	(6.023×10^{-2})	
2.980	2.952	(8.140×10^{-2})	
	b) Benzonitrile anion		
1.653	0.713	$[2.006 \times 10^{-3}]$	$X\ (A \rightarrow B)$[a]
2.530	2.228	$[2.231 \times 10^{-1}]$	$Y\ (A \rightarrow A)$
3.263	3.472	$[8.632 \times 10^{-3}]$	$Y\ (A \rightarrow A)$
	c) Nitrobenzene anion		
–	2.321	6.324×10^{-3}	$X\ (A \rightarrow B)$[a]
2.214	2.685	1.119×10^{-1}	$Y\ (A \rightarrow A)$
–	4.486	1.136×10^{-3}	$Y\ (A \rightarrow A)$
4.052	4.731	2.545×10^{-2}	$X\ (A \rightarrow B)$
	d) Phthalonitrile anion		
1.240	0.619	1.478×10^{-2}	$X\ (B \rightarrow A)$
2.138	2.461	1.234×10^{-1}	$Y\ (B \rightarrow B)$[c]
2.362	2.839	4.537×10^{-2}	$X\ (B \rightarrow A)$
3.646	4.392	6.715×10^{-2}	$Y\ (B \rightarrow B)$
	e) Isophthalonitrile anion		
(1.653 eV) ?	0.350	3.731×10^{-2}	$X\ (B \rightarrow A)$
2.175	1.974	1.753×10^{-1}	$X\ (B \rightarrow A)$
3.542	3.175	5.041×10^{-2}	$Y\ (B \rightarrow B)$[c]
–	4.177	4.019×10^{-2}	$X\ (B \rightarrow A)$
4.959	4.661	1.069×10^{-1}	$Y\ (B \rightarrow B)$
	f) Terephthalonitrile anion		
2.480	1.881	3.866×10^{-1}	$Y\ (B_{1u} \rightarrow B_{3g})$[a]
3.646	4.020	2.196×10^{-1}	$Y\ (B_{1u} \rightarrow B_{3g})$
	4.345		$Y\ (B_{1u} \rightarrow B_{3g})$
	g) Pyromellitonitrile anion		
2.684	1.941	3.366×10^{-1}	$X\ (A_{1u} \rightarrow B_{3g})$
3.306 } 3.492 }	3.379	6.347×10^{-2}	$Y\ (A_{1u} \rightarrow B_{2g})$[d]
4.444	4.413	3.012×10^{-1}	$Y\ (A_{1u} \rightarrow B_{2g})$
4.779	4.592	1.269×10^{-2}	$X\ (A_{1u} \rightarrow B_{3g})$

[a] Transition energies (ΔE) and oscillator strengths (f) for substituted benzene anions. Y and X mean that the corresponding transition is polarized in the direction of the long and short axes of the anion respectively.

[b] The oscillator strength was calculated by the following equation: $f_{calc} = 4.704 \times 10^{-7} \tilde{\nu} Q^2$ ($\tilde{\nu}$ in cm^{-1}, Q in Debye).

[c] Y is symmetry axis.

[d] Y is the axis which connects 3 and 6 position of the molecule.

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