On the Basicities of the Nitro-derivatives of Benzoanthrones

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Benzene is considered to be a weak base or electron-donor in relation to bromine and iodine owing to the existence of its π-electrons. Its trinitro-derivative, however, behaves as an acid or electron-acceptor in relation to naphthalene, anthracene and other highly condensed aromatic hydrocarbons. This is a result of the strong electron-accepting power of the nitro-group, which is due to the group's inductive and resonance effect. In the nitro-derivatives of aniline, it is observed that the influence of the substituted nitro-group on the lone-pair electrons of the nitrogen atom of the amino-group reduces its proton-affinity or basicity.

The present author has observed that the influence of electron-donating methyl-groups on the basicities of matrix-benzenes in the methyl-derivatives of aromatic compounds can be explained in terms of the amount of decrease in empirical resonance energies among such complexes as solvated ions and original compounds. The influence can be expressed as $\log(N^*/N)$ with the application of Carter's equation by estimating the number of resonance structures of polarized polymethylbenzene, including polarization on methyl-groups, on the assumption that the resonance structures polarized on methyl-groups possess the same weight or maintain a constant ratio (α) of weights to those polarized in a matrix compound. The details of these studies will be submitted elsewhere1).

In this paper, the influence of the nitro-group on the decrease in basicity of the carbonyl-oxygen atom of the nitro-derivatives of benzoanthrone is explained with reference to the resonance effect.

Experimental Procedures

The measurement of optical absorption was carried out with a Beckman DU-type spectrophotometer according to the method of Hammett and Dingwall2). The observed values satisfied Beer's law considerably well in the range of concentration from 10^{-5} to 10^{-6} mol. per liter.

The applied specimens were synthesized in the manner proposed by M. Shioda of the University of Tokyo.3) These were recrystallized from *o*-dichlorobenzene and further purified by means of sublimation in vacuo of the order of 10^{-3} mmHg. The solutions were prepared by a dilution method from the standard solution with a definite concentration. The chemical structures of the specimens used in this experiment are shown in Table I.

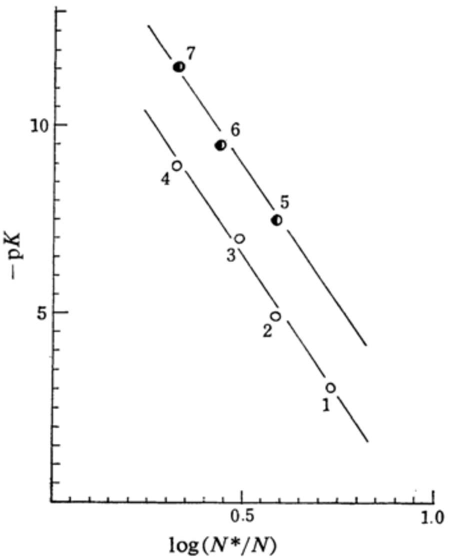

Fig. 1. The correlation of pK with $\log(N^*/N)$ in nitro-derivatives of benzoanthrone and anthraquinone.
(1) Benzoanthrone (Bz), (2) 3-NitroBz, (3) 3,9-DinitroBz, (4) TrinitroBz, (5) Anthraquinone (An), (6) 1-NitroAn, (7) 4,5-DinitroAn.

Results and Discussion

The absorption spectra of mono-nitrobenzoanthrone, di-nitrobenzoanthrone and tri-nitrobenzoanthrone in concentrated sulfuric acid of various acidities are shown in Figs. 2–4. From these spectral curves, the pK-value of each compound is obtained as listed in Table I according to the method of Hammett2). The substitution of one nitro-group decreases the basicities of benzoanthrone by the amount of two in a pK unit as shown in Table I.

Similar results were obtained in the nitro-substitution of aniline and also of anthraquinone, as illustrated in the table. In order to explain this decrease in basicity by nitro-substitution from the point of view of the change of empirical resonance energy, in such

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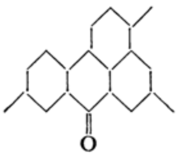
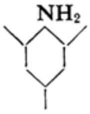
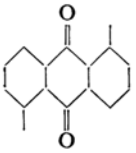
1) T. Handa, This Bulletin, to be published.

2) L. P. Hammett and J. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

3) M. Shioda and S. Kato, *J. Soc. Org. Synth. Chem., Japan*, **15**, 361 (1957).

TABLE I. THE pK-VALUE OF NITRO SUBSTITUTED AROMATICS

Matrix compound	pK-Value			
	Unsubstituted	Mono-NO$_2$	Di-NO$_2$	Tri-NO$_2$
	−3.2	−5.1	−7.1	−9.2
	ca. 5.3	*ortho-* −0.16 *para-* 1.4	−4.1	−9.1
	−7.5	−9.5	ca. −12.1	Not measured

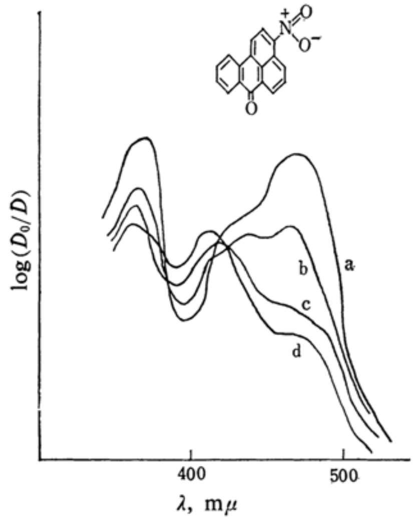


Fig. 2. The spectral response curves of mononitrobenzoanthrone in concentrated sulfuric acid.
(a) 90∼100% H$_2$SO$_4$, (b) 78% H$_2$SO (c) 70% H$_2$SO$_4$, (d) 67% H$_2$SO$_4$.

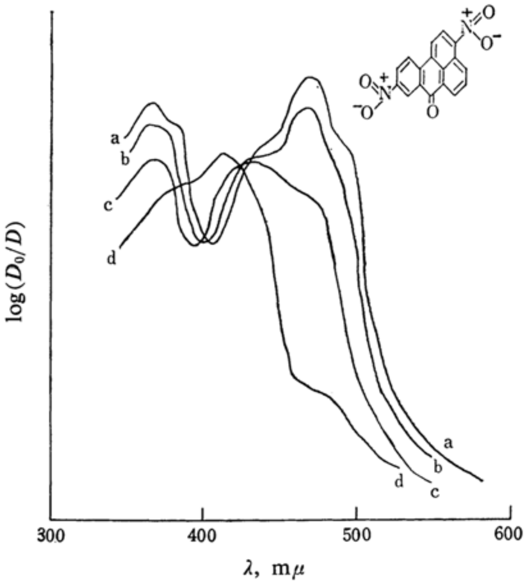


Fig. 3. The spectral response curves of dinitrobenzoanthrone in 100% (a), 82% (b), 75% (c), and 70% (d) sulfuric acid.

a manner as we have used to explain the basicities of hydrocarbons and their related quinones, it is necessary to estimate the number of Kekùle resonance structures in the ground-state of the original compound and those in the ground-state of a complex such as solvated ion protonated at its carbonyl-oxygen atoms.

In the preceding papers(1,4), in the explanation of the basicities of polymethylbenzenes as measured by McCanlay, et al.(6), we estimated structure I due to the resonance in the matrix and structure II due to the resonance of the polarized methyl-group, as shown in Fig. 5 in the previous report(4), equally or with a definite ratio of weights, for the purpose of making a rough estimation of the number of resonance structures, explaining the contribution of methyl-groups to basicity as a change in empirical resonance energy with the use of Carter's empirical equation.

In the case of nitro-derivatives of benzoanthrone, structures I and II are the principal structures, where it is estimated that II possesses a weight equal to that of I, or where the weight of I is in a definite ratio to that of II

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4) T. Handa, ibid., **14**, 338, 550 (1956).

5) P. G. Carter, *Trans. Faraday Soc.*, **45**, 597 (1947).

6) D. A. McCanlay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951); D. A. McCanlay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

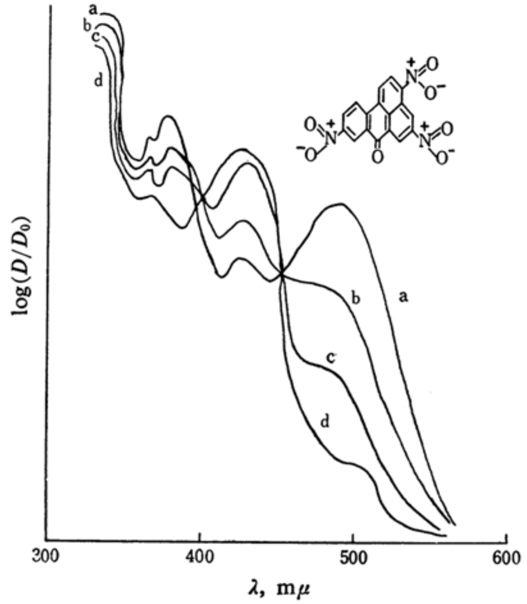

Fig. 4. The spectral response curves of trinitrobenzoanthrone in 100% (a), 95% (b), 90% (c), and 85% (d) sulfuric acid.

in nitrobenzoanthrone, though that ratio may in fact be considerably small.

As for the structures of the protonated nitrobenzoanthrone, structures III and IV belong to the localized non-bonding part, as in the case of the quinones[1,4]*, and structures V and VI belong to the dative part of that complex. The contribution of the VI structures with a double charge in the same molecule may be very small.

In the same manner, for protonated dinitro- and trinitrobenzoanthrone, we assume the contribution of various structures to the resonance energy. Structures X, XI and XII, with weights equal or in a definite ratio (α) to those the former group, are the principal structures belonging to the non-bonding part of the complex, and XV, XVI and XVII are the structures of trinitrobenzoanthrone. Structures XIII and XIV, with weights equal or in a definite ratio (α) to that of XIII, are also principal factors in the dative part of the complexes in the ground-state, while XIX and XX are such factors for trinitrobenzoanthrones.

Therefore, as was explained in the previous reports[1,4], Eq. 1 is derived approximately for the nitro-derivatves of benzoanthrone:

$$\varDelta H_G \fallingdotseq \varDelta R_G + C' \fallingdotseq R_2 - R_1 + C'$$
$$= C_0 + C_2{}^2(R_H{}^+ - R)\ ^{4)} \qquad (1)$$

or $\varDelta R_G \fallingdotseq C + 69\beta^2 \log N_D/N\ ^{1)}$ kcal./mol.

where $R_H{}^+$ and R represent the resonance energies of the protonated ion and the original compound, and C_2 is the coefficient of the wave function expressing the dative part in the ground-state of the complex-ion. $\varDelta R_G$ is the change in empirical resonance energy in the ground-state as a result of complex-formation, and β^2 and N_D are the coefficients of the wave function expressing the dipole-oriented state and the number of the resonance structures in this state respectively. The meaning of $R_H{}^+$ is taken to be the same in this case as in that of R_D.

In estimating the resonace energy of the nitro-derivatives of benzoanthrone, when we assume that the contribution from the nitro-group (an) can be included in the estimation independently from that of the matrix polarized by the resonance of the charge of the nitro-group, it is expressed in terms of Eq. 2, as was described by Carter for hydrocarbons:

$$R = a_0 + an + bD + c \log N \qquad (2)$$

where a_0, a, b and c are constants, n is the number of nitro-groups, D is the number of double bonds, and N is the number of Keküle resonance structures, which are explained above.

When we take α as 1.0**, pK may be plotted versus $\log(N^*/N)$ lineary in Fig. 1, as well as in the case of nitroanthraquinones. By the application of Eq. 2, we can roughly estimate the weights of the dipole-oriented structure in the ground-state of the complex from the gradient observed in Fig. 1.

Thus, we are able to explain the decrease in the basicities of benzoanthrone by the nitro-substitution from the resonance effect of the nitro-groups.

When we plot the pK values of the chloro-derivatives of benzoanthrone versus $\log(N^*/N)$,

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* Basicity which corresponds to the change in the total energy in the ground-state, $\varDelta H_G$, between the complex and its matrix is estimated as follows; assuming the term $T\varDelta S$ to be constant for a series of compounds:

$$\varDelta H_G = C + 69b^2\{\log(N_{Ip}/N) - \beta^2 \log(N_D/N)\}$$
$$+ 69\,\beta^2 \log(N_D/N) \qquad (3)$$

where N_{Ip} is the number of cannonical resonance structures in the ionized-state, N_D is that of those in the dipolar excited state, and b and β are the coefficients of the wave-function expressing the dative part of the ground-state of the complex and the dipole oriented-states respectively. The energy of the dipole-oriented state W_{00} is assumed to be as follows:

$$W_{00} = \alpha^2 W_0 + \beta^2 W_{01} \qquad (4)$$

where W_0 is the energy of the original hydrocarbons in the ground-state and W_{01} is that of the perturbed dipole-oriented state. This relation is discussed in detail in another report[1]. In the case of proton-complexes which existed as solvated ions (σ-from), the term $b^2\{\log(N_{Ip}/N) - \beta^2 \log(N_D/N)\}$ becomes very small owing to the greatly increased values of β^2 in strongly acidic media, as compared to the second term in Eq. 3, $69\,\beta^2 \log(N_D/N)$.

** The real value of α can be estimated by comparing the empirical resonance energies of this series of nitro-compounds with the gradient of 69 kcal./mol. in Carter's equation.

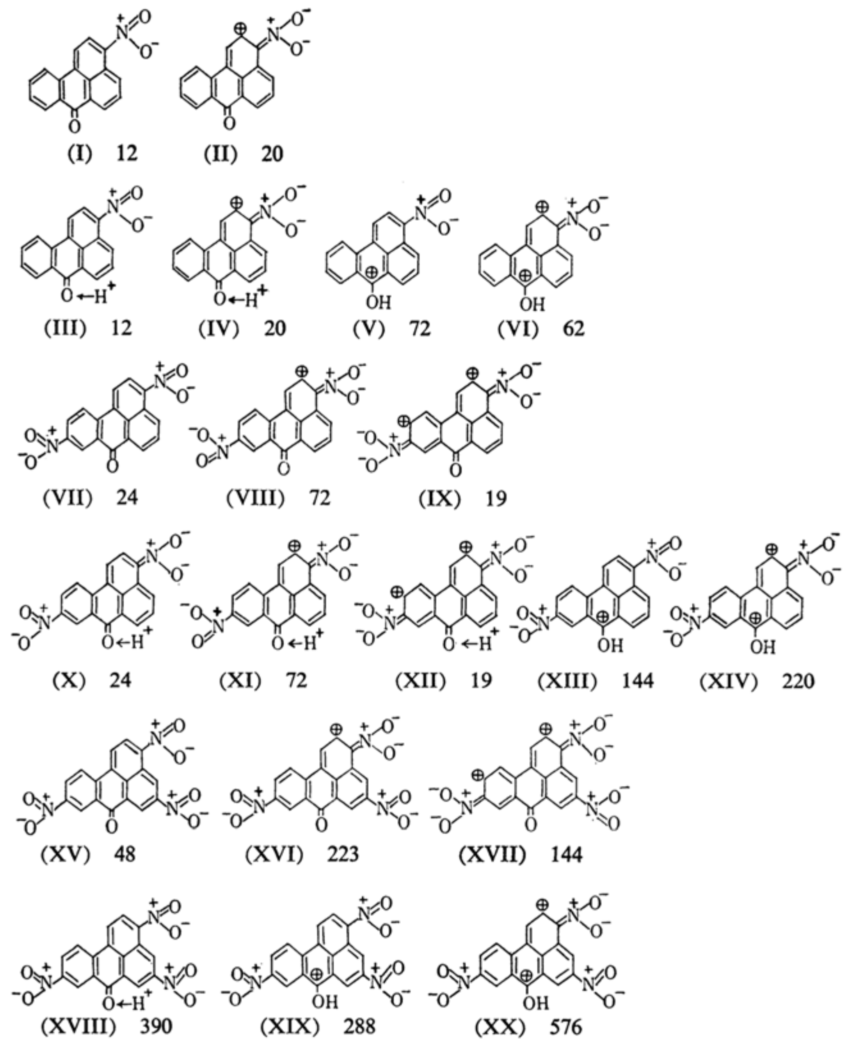

Fig. 5. The resonance srtuctures of nitrobenzoanthrone derivatives.

values which are estimated formally as in the case of nitrobenzoanthrones, they correspond with $\log(N^*/N)$ approximately linearly. In this case, the gradient of the line is smaller than that in the case of the nitro-derivatives. This means that the contribution of the polarized structure in the ground-state is larger in the case of nitro-derivatives than in the case of chloro-derivatives.

Summary

The basicities of the nitro-substituted benzoanthrones were measured. One nitro-substitution decreases the basicity of beazoanthrone by about two pK units, as in the case of nitro-substituted aniline and anthraquinone. This is explained qualitatively not by the inductive effect but by the resonance effect of the nitro groups on the carbonyl group of benzoanthrone in such way as to estimate approximately the change of resonance energies in the cases of both hydrocarbons and their related quinones. The gradient of the straight line of pK plotted versus $\log(N^*/N)$ in the case of nitro-substitution is greater than in the case of chloro-substitution. This means that the contribution of the polarized structure in the ground state to resonance effect is greater in the case of the nitro-derivatives of benzoanthrone than in the case of the chloro-derivatives.

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