BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1788—1791 (1971)

The Electron-acceptor Strengths of Some Substituted Naphthoquinones

Gunzi SAITO and Yoshio MATSUNAGA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received February 19, 1971)

The electron-acceptor strengths of the substituted naphthoquinones were compared with that of *p*-chloranil in terms of their complexing properties. The following electron affinities were estimated: 2.05 eV for 2,3-dichloro-1,4-naphthoquinone, 2.24 eV for 2,3-dichloro-5-nitro-1,4-naphthoquinone, 2.74 eV for 2,3-dicyano-1,4-naphthoquinone, and 2.78 eV for 2,3-dicyano-5-nitro-1,4-naphthoquinone.

Cyano and nitro groups are strongly electronegative, as is indicated by their large Hammett constants. Consequently, the electron-acceptor strength of aromatic molecules is much enhanced by the introduction of such substituents.[1] For example, *p*-benzoquinone is a rather weak acceptor; it is comparable in strength with *s*-trinitrobenzene. On the other hand, the 2,3-dicyano and 2,6-dinitro derivatives are among the strongest.[2] Their strengths can well be compared with those of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ). The other cyano and nitro compounds so far examined for their acceptor strengths include 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), *p*-cyananil, tetracyano-1,4-naphthaquinodimethane, trinitrophenanthrenequinone, and the nitro derivatives of fluorenemalononitrile.[2-6] However, 1,4-naphthoquinone and its derivatives have scarcely been studied. Continuing the search for a strong electron acceptor,[7] we have examined the acceptor strengths of 2,3-dicyano-1,4-naphthoquinone (DCNQ) and its 5-nitro derivative (DCNNQ) in terms of their complexing properties. In comparison with them, their precursors, 2,3-dichloro-1,4-naphthoquinone (Cl_2NQ) and its 5-nitro derivative (Cl_2NNQ), were also studied.

Experimental

Cl_2NQ and *p*-chloranil were commercially obtained. Cl_2NNQ, DCNQ, and DCNNQ were prepared starting from Cl_2NQ following the procedures of Inoue *et al.* and Wallenfels *et al.*[3,8] They were purified by recrystallization from suitable solvents. DCNQ was finally sublimed in a vacuum. The fourteen aromatic hydrocarbons, twenty-one aromatic monoamines, seven diamines, and eight other compounds listed in Table 1 were employed as electron donors. All the spectra

---

[1] P. R. Hammond, *J. Chem. Soc.*, **1964**, 471.

[2] P. R. Hammond, *ibid.*, **1963**, 3113.

[3] K. Wallenfels, G. Bachmann, D. Hofmann, and R. Kern, *Tetrahedron*, **21**, 2239 (1965).

[4] S. Chatterjee, *J. Chem. Soc. B.*, **1967**, 1170.

[5] T. K. Mukherjee, *J. Phys. Chem.*, **71**, 2277 (1967).

[6] T. K. Mukherjee, *Tetrahedron*, **24**, 721 (1968).

[7] S. Koizumi and Y. Matsunaga, This Bulletin, **43**, 3010 (1970).

[8] A. Inoue, Y. Nomura, N. Kuroki, and K. Konishi, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 536 (1958).

were recorded at room temperature by means of a Beckman DK 2A spectrophotometer, using quartz cells with 1-cm and 5-cm path lengths. The solvent used throughout the measurements was Wako reagent-grade chloroform.

Results and Discussion

Several criteria for the electron-accepting properties of π-acceptors have been proposed by various authors.[9] The comparison of the energies at the charge-transfer (CT) absorption maxima in the molecular complexes of two acceptors with the same series of donors is one of them. The electron affinity estimated by this method may be affected, to some extent, by the kind of solvent and also by the kind of donor. Of course, we must compare the complexes of the same bond type, π–π or n–π. In the present work, we used about fifty π-donors with the hope of averaging the specific effect of the donor molecule on the energy of the CT absorption. McConnell *et al.* have proposed that the energy, $h\nu_{\mathrm{CT}}$, observed in solution can be approximately expressed by:

$$h\nu_{\mathrm{CT}} = I_{\mathrm{D}} - E_{\mathrm{A}} - C, \tag{1}$$

where I_{D} is the ionization potential of the donor, D, where E_{A} is the electron affinity of the acceptor, A, and where C represents the electrostatic energy in the dative-bond structure of the complex and also some other minor terms.[10] The difference in $h\nu_{\mathrm{CT}}$ of the complexes of a given donor with two acceptors, 1 and 2, is, then:

$$(h\nu_{\mathrm{CT}})_1 - (h\nu_{\mathrm{CT}})_2 = (E_A)_2 - (E_A)_1 + (C_2 - C_1). \tag{2}$$

The last term is not necessarily zero. Batley and Lyons estimated the change to be no greater than 0.4 eV.[11] Moreover, one of the present authors has demonstrated that this term is a few kK even if the sizes and shapes of the component molecules are very different.[12] We chose p-chloranil for the reference, as was done in our previous work. The positions of the maxima of the CT absorption bands exhibited by the acceptors and also by the reference mixed with various donors are presented in Table 1. The linear relationships obtained by the least-squares method are as follows:

$$\begin{array}{ll} \mathrm{Cl_2NQ} & (h\nu_{\mathrm{CT}})_1 = 1.003(h\nu_{\mathrm{CT}})_2 + 3.285 \\ \mathrm{Cl_2NNQ} & (h\nu_{\mathrm{CT}})_1 = 0.969(h\nu_{\mathrm{CT}})_2 + 1.785 \\ \mathrm{DCNQ} & (h\nu_{\mathrm{CT}})_1 = 1.034(h\nu_{\mathrm{CT}})_2 - 2.292 \\ \mathrm{DCNNQ} & (h\nu_{\mathrm{CT}})_1 = 0.977(h\nu_{\mathrm{CT}})_2 - 2.603 \end{array} \tag{3}$$

The slopes found here are in good agreement with that required by Eq. (2). The intercepts may be considered as measures of the difference in the electron affinity between the naphthoquinones and the reference. The greater the electron affinity of the acceptor, the smaller the energy of the CT absorption maximum; therefore, the negative intercepts for DCNQ and DCNNQ indicate that these two are stronger electron acceptors than p-chloranil is. If we take the electron affinity of p-chloranil as 2.46 eV, following Farragher and Page,[13] those of the present acceptors are 2.05 eV in $\mathrm{Cl_2NQ}$, 2.24 eV in $\mathrm{Cl_2NNQ}$, 2.74 eV in DCNQ, and 2.78 eV in DCNNQ. These naphthoquinones appear to have acceptor strengths comparable with those of dichloro-p-xyloquinone, p-fluoranil, o-bromanil, and TCNQ respectively. It must be noted that the above-mentioned values cannot be compared directly with the affinities in the literature. Briegleb assumed the affinity of p-chloranil as 1.37 eV, and Batley and Lyons took the iodine molecule as their reference and estimated the affinity of p-chloranil as 2.59 eV. Thus, our values may be about 1 eV higher than the former estimations, but a little less than the latter.

The effect of substituents on the acceptor strength of the naphthoquinones and related compounds will now be examined in more detail. The energies of the CT absorptions in the pyrene complexes fit well the linear relationship given by Eq. (3); that is, the calculated values, 19.5 kK, 17.6 kK, 14.5 kK, and 13.2 kK for the complexes of $\mathrm{Cl_2NQ}$, $\mathrm{Cl_2NNQ}$, DCNQ, and DCNNQ respectively, are in excellent agreement with the observed values presented in Table 1. Therefore, the energies in the pyrene complexes will be used for the purpose of comparing the acceptor strengths in the following discussion.

The difference in energy between the $\mathrm{Cl_2NQ}$ complex and the DCNQ complex is 4.9 kK, while that between the $\mathrm{Cl_2NNQ}$ complex and the DCNNQ complex is 4.3 kK. These values are close to that of 4.5 kK evaluated for the increase in acceptor strength by the replacement of chlorine atoms with cyano groups at the 2 and 3 positions of p-benzoquinone. The latter was obtained on the basis of the following energies: 18.2 kK with the 2,3-dichloro derivative, 13.7 kK with the 2,3-dicyano derivative, 16.2 kK with p-chloranil, and 11.7 kK with DDQ given in an earlier work.[14] When a substituent is introduced to a molecule, its effect on the energy level can be correlated with the π-electron density on the carbon atom to which the substituent is to be introduced.[15] The π-electron distribution in the accepting molecular orbital, in other words, the lowest vacant molecular orbital, of a quinone molecule is, as a first approximation, given by twice the unpaired electron distribution in the semiquinone ion. By the analysis of the hyperfine structure of the electron-spin-resonance spectrum, the latter can be estimated, for the ring-proton splitting constant is approximately proportional to the unpaired electron density on the carbon atom to which the proton is attached.[16] The four equivalent protons in the p-benzosemiquinone ion have been reported by Adams *et al.* to show a spacing of 2.37 oersteds.[17] In the case of the 2,3-dichloro-p-benzosemiquinone ion examined by Venkataraman *et al.*, the splitting due to the two equivalent protons was

---

[9] G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

[10] H. M. McConnell, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[11] M. Batley and L. E. Lyons, *Nature*, **196**, 573 (1962).

[12] Y. Matsunaga, This Bulletin, **42**, 2490 (1969).

[13] A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **62**, 3072 (1966).

[14] Y. Matsunaga and G. Saito, This Bulletin, **44**, 958 (1971).

[15] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

[16] H. M. McConnell, *ibid.*, **24**, 632 (1956).

[17] M. Adams, M. S. Blois, Jr., and R. H. Sands, *ibid.*, **28**, 774 (1958).

TABLE I. ENERGIES OF THE CHARGE TRANSFER ABSORPTION MAXIMA (in kK)
The values in parentheses were not used in computation of Eq. (3).

Donor	*p*-Chloranil	Cl_2NQ	Cl_2NNQ	DCNQ	DCNNQ
Triphenylene	20.1	**	21.2	18.5	17.2
Fluorene	19.6	23.3	21.0	18.0	16.6
Naphthalene	20.2	23.5	21.4	18.7	17.2
Phenanthrene	20.8	24.4	21.6	19.0	17.3
p-Terphenyl	20.3	**	21.6	18.5	16.5
Chrysene	18.6	**	19.6	**	15.0
1,2-Benzanthracene	17.0	20.4	18.2	15.0	13.4
Pyrene	16.2	19.5	17.5	14.6	13.2
Anthracene	15.6	19.2	16.9	13.7	12.5
Perylene	13.2	16.8	14.5	11.7	10.5
Tetracene	12.7	**	13.9	**	**
Mesitylene	23.1	**	**	21.7	20.3
Durene	20.6	24.0	21.6	19.4	18.1
Hexamethylbenzene	19.3	22.5	20.3	18.3	16.9
1,4-Dimethoxybenzene	18.0	**	19.6	15.9	14.7
4,4′-Dimethoxybiphenyl	17.7	21.2	19.0	15.4	13.5
α-Naphthol	17.4	21.0	18.9	15.6	14.1
β-Naphthol	18.3	22.1	20.2	16.4	15.1
3,3′-Dichloro-*o*-tolidine	14.3	17.9	15.6	12.3	10.9
3,3′-Dibromo-*o*-tolidine	14.1	17.8	15.6	12.2	10.8
Benzidine	14.6	17.8	16.2	12.1	10.9
o-Tolidine	13.2	16.6	14.5	11.4	10.4
o-Dianisidine	13.4	16.3	14.8	11.3	10.3
N,*N*,*N*′,*N*′-Tetramethylbenzidine	11.4	14.9	13.0	9.5	9.2
	17.8	**	19.6	16.0	14.6
1,5-Diaminonaphthalene	13.3	16.4	14.3	11.7	**
Phenothiazine	12.3	16.2	13.6	(12.2)	9.9
N-Methylphenothiazine	14.0	17.4	14.8	11.7	10.5
N-Ethylphenothiazine	12.4	(16.9)	14.2	10.7	9.6
Benzo[c]phenothiazine	12.3	16.0	(12.7)	9.9	9.2
Diphenylamine	15.3	19.0	16.6	13.7	12.7
α-Naphthylamine	15.3	18.6	16.3	13.8	12.9*
Phenyl-α-naphthylamine	14.1	(19.2)	15.3	12.3	11.0
Aniline	18.6	21.8	19.4	16.8	*
N-Methylaniline	16.5	19.3	17.7	14.9*	*
N,*N*-Dimethylaniline	15.0	17.9	17.0	13.4	12.1*
N,*N*-Diethylaniline	13.0	16.4	14.5	11.8	*
o-Chloroaniline	19.1	22.4	20.4	17.4	16.3*
m-Chloroaniline	19.4	23.2	20.6	17.9	16.3*
p-Chloroaniline	18.5	22.2	19.6	16.6	15.1*
o-Toluidine	17.5	20.8	18.8	15.7	*
m-Toluidine	18.0	21.1	18.9	16.2	*
p-Toluidine	16.9	20.1	17.9	15.2	*
o-Anisidine	16.7	19.5	17.7	15.1	14.4
m-Anisidine	17.9	*	19.1	16.8*	*
o-Phenetidine	16.8	19.4	18.2	15.0	14.2*
p-Phenetidine	16.2	19.2	17.5	13.7	12.8*
2,4-Xylidine	16.1	19.3	17.5	14.7	*
N-Ethyl-*o*-toluidine	15.2	18.0	(17.9)	13.5	12.4*
N,*N*-Dimethyl-*m*-toluidine	14.7	17.4	*	13.1	11.6*
N,*N*-Diethyl-*m*-toluidine	12.7	16.0	14.0	11.6	10.0*

* These absorptions are transitory.
** The CT absorption band could not be detected.

found to be 2.319 oersteds.[18] On the other hand, the proton splitting constants in the 1,4-naphthosemiquinone ion are 3.22 oersteds at the 2 and 3 positions and 0.57 oersteds at the 5, 6, 7, and 8 positions.[17] An expected quintet with a spacing of 0.6 oersteds has been observed for the 2,3-dichloro-1,4-naphthosemiquinone ion.[19] As the present study indicated that the introduction of an electronegative substituent to the 2 position of 1,4-naphthoquinone affects the acceptor strength as much as the introduction of the same to *p*-benzoquinone does, the substituent situated on the 5 or 6 position of naphthoquinone must be less effective than that introduced to benzoquinone. The increase in the acceptor strength by a nitro group substituted at the 5 position of Cl_2NQ and that of DCNQ is in accordance with this prediction. Hammond has shown that the difference in the energy of the CT absorption maximum between the *p*-benzoquinone complex and the mononitro-*p*-benzoquinone complex is 4.0—4.4 kK, and that between the latter and the 2,6-dinitro-*p*-benzoquinone complex is 2.4 kK.[2] On the other hand, the substitution of a nitro group at the 5 position of Cl_2NQ brings about a change of 2.0 kK in the energy of the CT absorption maximum, and that at the 5 position of DCNQ, a change of 1.4 kK.

The above data clearly show that the effect of substituents on the acceptor strength is mutually dependent. The stronger the acceptor to which an electronegative substituent is introduced, the less the effect. This tendency may be considered as a kind of cumulative influence. Peover has estimated the electron affinity of unsubstituted 1,4-naphthoquinone to be 0.20 e V(1.5 kK) lower than that of *p*-benzoquinone.[20] We have found here that the Cl_2NQ complex shows a CT absorption maximum located 1.3 kK higher than that of the 2,3-dichloro-*p*-benzoquinone complex, while the CT absorption of the DCNQ complex is located only 0.9 kK higher than that of the 2,3-dicyano-*p*-benzoquinone complex. Thus, the difference in the electron affinity between a benzoquinone and the corresponding naphthoquinone becomes progressively smaller when the substituents are more electronegative. This trend sug-

---

[18] B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

[19] Y. Matsunaga, This Bulletin, **33**, 1436 (1960).

[20] M. E. Peover, *Trans. Faraday Soc.*, **58**, 1656 (1963).

gests that the cumulative influence is more pronounced in the benzoquinone series than in the naphthoquinone series.

Finally, we must add that almost all the complexes between DCNNQ and monoamines were found to be transitory. However, Cl_2NNQ and DCNQ gave time-independent colored solutions when mixed with most of the donors examined.