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Studies on 1,3-Dithiolium Cations. III.[1] Stability and Electronic Structure of 4-*p*-Substituted Phenyl Derivatives

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Investigation of substituent effect of 4-*p*-substituted phenyl-1,3-dithiolium cations was undertaken. Determination of pK_{R^+} values for a series of cations has been carried out and it was found that the electron-donating groups stabilized the cations, while the electron-withdrawing groups destabilized the cations. An excellent correlation between pK_{R^+} and Hammett's σ_p constants was established. Determination of $pK_{R'SH}$ has also revealed that there was a linear correlation between $pK_{R'SH}$ and Hammett's σ_p values. The electronic structures and the molecular diagrams of these cations were given by HMO calculation, and pK_{R^+} values were linearly related to the π-electron densities at C-2 positions of these cations.

1,3-Dithiolium cation is an iso-π-electronic with tropylium cation from which it can be formally derived by replacement of two C=C bonds by two sulfur atoms, and is expected to possess a potential "aromatic" sextet.[3] The parent cation was first synthesized by Klingsberg[4] and Leaver, *et al.*[5] Recently, we have found a convenient method for the preparation of a series of 4-*p*-substituted phenyl-1,3-dithiolium cations and reported in the previous paper.[6] C-2 position of these cations was also found to be most reactive toward the nucleophilic reagents.[1] In some respects, these cations showed the chemical and physical similarity to $(4n+2)\pi$ cations (cyclopropenyl or tropylium cations).[7]

Purely theoretical aspects of heterocyclic sulfur compounds including 1,3-dithiolium cation have been discussed by Zahradnik.[8] However, an agreement between the electronic spectra

1) Part II: A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* (Tokyo), **17**, 1931 (1969).
2) Location: *Fukushima-ku, Osaka.*
3) H. Prinzbach and E. Futterer, "Advances in Heterocyclic Chemistry," Vol. 7, ed. by A.R. Katritzky and A.J. Boulton, Academic Press, New York and London, 1966, p. 39.
4) E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962); **86**, 5290 (1964).
5) D. Leaver, W.A.H. Robertson and D.M. McKinnon, *J. Chem. Soc.*, **1962**, 5104.
6) A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* (Tokyo), **17**, 1924 (1969).
7) For review, see; *a*) H. Tanida, "Kōza Yūki Hannō Kikō," Vol. 7, Tokyo Kagaku Dōzin, Tokyo, 1966, p. 1; *b*) I. Murata, "Kaisetsu Riron Yūki Kagaku (Zoku) Kagaku Zōkan 21," Kagaku Dōzin, Kyoto, 1965, p. 135.
8) *a*) R. Zahradník, "Advances in Heterocyclic Chemistry," Vol. 5, ed. by A.R. Katritzky, A.J. Boulton, and J.M. Lagowski, Academic Press, New York and London, 1965, p. 1; *b*) R. Zahradník, and C. Párkányi, *Coll. Czech. Chem. Commun.*, **30**, 3016 (1965); *c*) R. Zahradník and J. Koutecký, *ibid.*, **28**, 1117 (1963).

and the theoretical values was not satisfactory owing to uncomparable experimental conditions, and a systematic and serious study in this field have been required. Nothing has also been reported on pK values of 1,3-dithiolium cations.

Therefore, it will be of great interest to compare the stabilities of 4-*p*-substituted phenyl-1,3-dithiolium cations and to correlate their electronic structures with the experimental data obtained in comparable conditions. The present paper describes the substituent effect on the stabilities of these cations and a discussion on HMO study.

Experimental

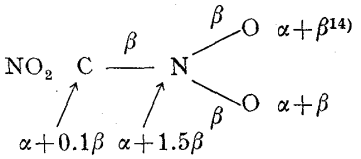
pK Determinations——Apparent $pK_{R'SH}$ value for IVa—e was determined from potentiometric titration by Metrohm potentiometer. Perchlorate (IVa—e) (0.1 mmole) was dissolved in 2 ml of 0.1N HCl and 40 ml of CH_3CN was added to prevent the turbidity during the titration, and titrated with 0.1N NaOH. Half neutralization point of the second pH jump in corrected titration curve was assigned as $pK_{R'SH}$.

pK_{R^+} value for IVa—e was determined spectrometrically from Eq. (1).[9-11]

$$pK_{R^+}=pH-\log\frac{(ROH)}{(R^+)} \qquad (1)$$

Optical densities were measured in 1 cm, quartz cells with a Hitachi EPS-3 recording spectrometer at 25°. MeOH solution of perchlorate (IVa—e) was diluted with aqueous hydrochloric acid to 10% MeOH solution. Measurements were made at four or more acid concentrations covering approximately 10 to 90% ionization at a most suitable point.

HMO Calculations——Calculations were made by HMO method.[12] Empirical parameters are given in the form $\alpha_X=\alpha+h_X\beta$ and $\beta_{C-X}=\rho_{C-X}\beta$; α is the carbon Coulomb integral and β is the resonance integral of the C–C bond, h_X and ρ_{C-X} are numerical constants. The following values were used in the calculations: $K_S=1$,[13] $K_{Br}=2.5$,[13] $K_{CH_3}=3.5$,[13] $K_{CH_3O}=2.0$,[13] $\rho_{C-S}=0.6$,[13] $\rho_{C-Br}=1$,[13] $\rho_{C-CH_3}=1$,[13] $\rho_{C-OCH_3}=1$.[13]



Sulfur's d-orbital was neglected.[8]

Results and Discussion

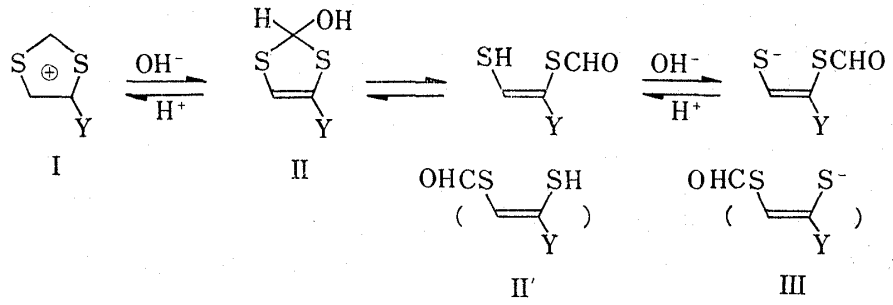
1,3-Dithiolium cation acts as a Brönsted acid,[1] and the first equilibrium between cation and conjugate base (carbinol) is associated with pK_{R^+} value[11] in the following reaction.

$$R^+(I) + H_2O \rightleftharpoons ROH(II) + H^+$$

Ring chain equilibrium ROH (II)⇌R'SH (II') leads to the second equilibrium between thiol and thiolate involved in the following reaction and is associated with $pK_{R'SH}$.

$$R'SH(II') + H_2O \rightleftharpoons R'S^-(III) + H_3O^+$$

9) N.C. Deno, J.J. Jaruzelski, and A. Shriesheim, *J. Am. Chem. Soc.*, **22**, 3044 (1955).
10) I.I. Schuster, A.K. Colter, and R.J. Kurland, *J. Am. Chem. Soc.*, **90**, 4679 (1968).
11) pK_{R^+} is equal to the pH when the carbonium ion is half neutralized. *a*) R. Breslow, "Organic Reaction Mechanisms," W.A. Benjamin, Inc., New York and Amsterdam, 1966, p. 23; *b*) R. Breslow, H. Hover, and H.W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962); *c*) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, 1961, p. 363; *d*) M.A. Battiste and T.J. Barton, *Tetrahedron Letters*, **1968**, 2951; *e*) R.G. Turnbo, D.L. Sullivan, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 5630 (1964).
12) Helpful advice was offered by Dr. M. Yamakawa of this laboratory, thanks of authors being due to him.
13) M. Yamakawa, T. Kubota, H. Akazawa, and I. Tanaka, *Bull. Chem. Soc. Japan*, **41**, 1046 (1968).
14) T. Yonezawa, C. Nagata, H. Kato, A. Imamura, and K. Imokuma "Ryōshi Kagaku Nyūmon," Kakagu Dozin, Kyoto, 1968, p. 56.



IVa—e : R=NO_2, Br, H, CH_3, CH_3O

Chart 1

TABLE I. Apparent $pK_{R'SH}$ of IVa—e (95% CH_3CN)

R	NO_2	Br	H	CH_3	CH_3O
$pK_{R'SH}$	8.95	9.67	10.07	10.30	10.47

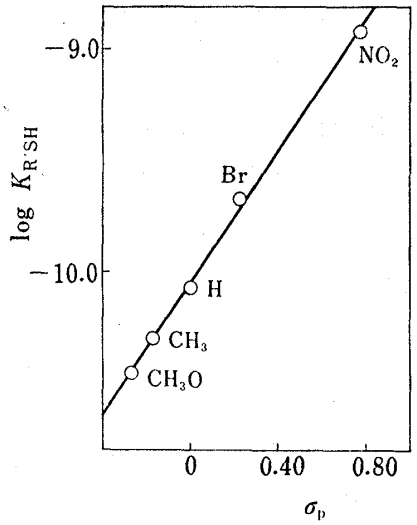


Fig. 1. Correlation of log $K_{R'SH}$ with σ_P Value

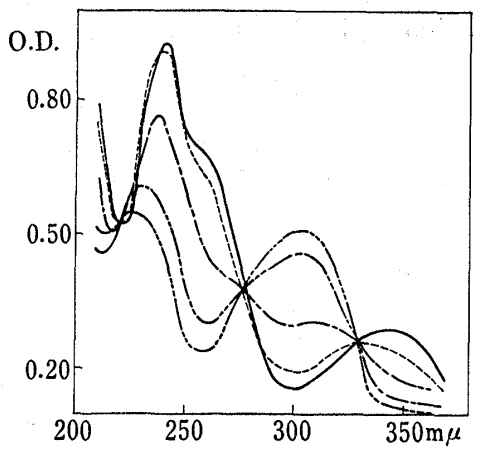


Fig. 2. UV Spectra of IVc at Different pH in 10% MeOH

———: pH 0, I ----------: pH 1
———: pH 2 ———: pH 3
----------: H_2O, II

$pK_{R'SH}$ values for 4-*p*-substituted phenyl-1,3-dithiolium cations (IVa—e) have been measured potentiometrically in 95% CH_3CN[15] and are listed in Table I. The plot of $pK_{R'SH}$ values against the corresponding Hammett's σ_P values gave an excellent linear relationship between $pK_{R'SH}$ value and Hammett's σ_P constant[16] (Fig. 1), and the Hammett equation was given by the least square treatment as presented in Eq. (2).

$$\log K_{R'SH} = 1.46\sigma_p - 10.06 \qquad r = 0.9994 \qquad (2)$$

15) *a*) Insolubility of the covalent carbinol[1] forced to use a mixed-solvent media in the detremination of p*K* values. The values obtained in non-aqueous media are meaningful only in the comparison of a series of these cations.[15b] pK_{R^+} determination by potentiometry taking the first pH jump of the titration curve was failed because of leveling effect and/or other effects caused by non-aqueous media; *b*) E.M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, ed. by S.G. Cohen, A.S. Streitwieser, Jr., and R.W. Taft, Interscience Publishers, New York and London, 1963, p. 223.

16) L.N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewoods Cliffs, New Jersey, 1964, p. 415.

The ultraviolet (UV) absorption spectrum of 4-phenyl-1,3-dithiolium perchlorate (IVc: R=H, X=ClO_4) changed with the pH value of the solvent (Fig. 2). For the solution with pH 0, the spectrum showed a minimum at about 300 mμ, but the intensity at about 300 mμ gradually increased with pH value of the solution examined to give a maximum at 305 mμ in neutral solution. This change corresponds to the equilibrium between cation (I) and its conjugate base (II) as evidenced by the well defined isosbestic points. Thus, pK_{R^+} value of IVc was determined spectrometrically in 10% MeOH giving the value 2.10.

Similarly, pK_{R^+} values for IVa—e were determined in 10% MeOH and were listed in Table II.

Table II. Apparent pK_{R^+} of IVa—e (10% MeOH)

R	NO_2	Br	H	CH_3	CH_3O
pK_{R^+}	0.84	1.73	2.10	2.43	2.59

pK_{R^+} value is a measure of the relative electrophilicities of a series of carbonium ions.[11] Examination of pK_{R^+} values in Table II revealed that the electron-donating groups stabilized the cations (less electrophilic) giving large pK_{R^+} value, while the electron-withdrawing groups destabilized the cation (more electrophilic) to show small pK_{R^+} value. There was a complete linear relationship between pK_{R^+} value and Hammett's σ_p constant as shown in Fig. 3. Hammett equation derived from the least squares treatment was presented in Eq. (3).

$$\log K_{R^+} = 1.67\sigma_p - 2.10 \qquad r = 1.000 \qquad (3)$$

It is noted that pK_{R^+} value was correlated completely with Hammett's σ_p constant rather than Deno's σ^+ constant[17] or Yukawa–Tsuno's σ_π constant.[18] Since pK_{R^+} values au associated

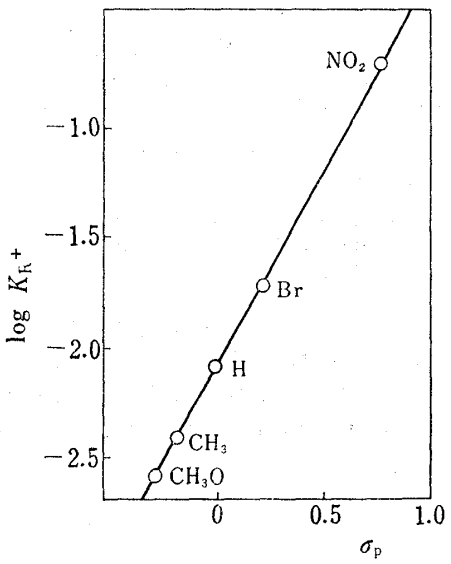


Fig. 3. Correlation of log K_{R^+} with σ_p Value

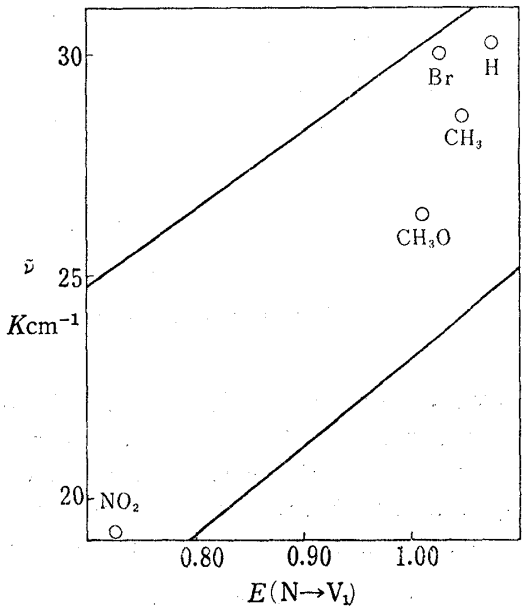


Fig. 4. Energy of the First Intense Absorption Maximum $\tilde{\nu}$(Kcm^{-1}) Plotted against the N→V_1 Transition Energy (β) for IVa—e

1: the regression line for benzenoid hydrocarbons
2: the regression line for tropylium-like ions

17) N.C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3051 (1955).
18) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, 86, 873 (1965).

with carbinol (II) as well as cation (I), inductive factor of σ_p value is effective rather than direct resonance effect of the substituent on the reactive center, C-2 position.

In an attempt to understand further these results and to get the electronic structures of IVa—e, Hückel molecular orbital calculation[8,13] for the cations was performed. The energy characteristics obtained by calculation were presented in Table III. Electronic spectra of the cations in CH_3CN are presented in Table IV. A plot of wave numbers $\tilde{\nu}$ of maxima of the

Table III. Energy Characteristics for Compounds IVa—e

No.	R	n	W	HO	LF	E(N→V_1)
IVa	NO_2	16	23.764	0.58120	−0.14035	0.722
IVb	Br	14	21.124	0.48703	−0.53774	1.025
IVc	H	12	15.846	0.54496	−0.53298	1.078
IVd	CH_3	14	23.056	0.50672	−0.53674	1.044
IVe	CH_3O	14	20.154	0.46783	−0.53846	1.006

number of π-electrons (n), π-electronic Energy (W), energies of highest occupied (HO) and lowest free (LF) π-molecular orbitals, and N→V_1 transition energy, all in β units

Table IV. Electronic Spectra of IVa—e in CH_3CN[6]

No.	R	λ_{max} mμ (log ε)
IVa	NO_2	252.5, 278, 323.5(sh), 286(sh), 520 (4.08, 4.10, 3.81 3.50, 3.16)
IVb	Br	245, 270(sh), 334 (4.25, 4.12, 3.65)
IVc	H	240, 267(sh), 331 (4.24, 3.92, 3.54)
IVd	CH_3	242.5, 268, 350 (4.19, 4.07, 3.55)
IVe	CH_3O	245.5, 284, 379 (4.09, 4.18, 3.57)

longest wave length bands in the UV spectra against the calculated E(N→V_1) values yields a series of points located between the regression lines for benzenoid hydrocarbons and tropylium-like cations[8] as shown in Fig. 4.

Molecular diagrams of IVa—e were presented in Chart 2, and it is clear that C_{4-5} bond has the highest double bond character and the lowest π-electron density in all compounds was assigned to C-2 position. These observations support the exclusive attack of nucleophilic reagents to C-2 position in IVa—e.[6] The plot of pK_R+ value against π-electron density at C-2 position gave a straight line (Fig. 5) indicating that pK_R+ value is linearly related to π-electron density at C-2 position.[19] Although pK_a- π-electron density relationships have

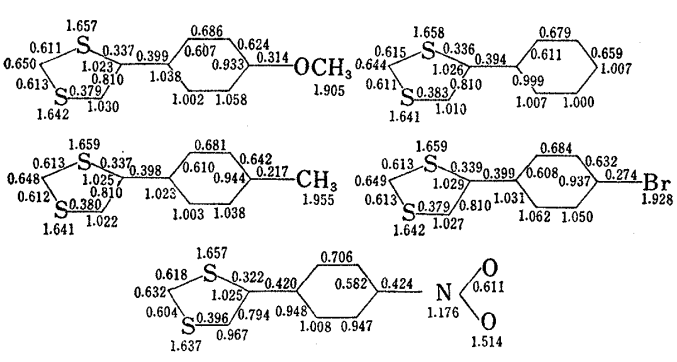


Chart 2. Molecular Diagrams of IVa—e

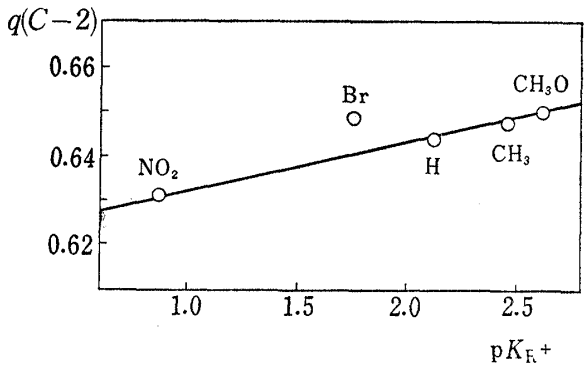


Fig. 5. Correlation of pK_R+ with q(C-2)

19) In the case of Br, a slight deviation was observed. Disagreement of halogen substituents has been reported. M. Kuroki, *Nippon Kagaku Zasshi*, **88**, 463 (1967).

been observed for aromatic amines,[20] it is remarkable that the simplest MO calculations gave such a good correlation between pK_{R^+} value and π-electron density.

It might be expected that phenyl group attached to the C–2 position, the lowest relative electron density position, stabilizes the cation directly giving large pK_{R^+} value. Work on this line is in progress. Attempts will be also made to find the substituent effect on the other physical properties of these cations.

Acknowledgement The authors greately indepted to Prof. S. Nagakura of the Institute for Solid State Physics, the University of Tokyo, for his valuable discussion. They wish to express their deep gratitude to Dr. Ken'ichi Takeda, Director of this laboratory, for his encouragement throughout this investigation. Thanks are also due to Drs. T. Kubota and E. Hirai and M. Yamakawa of this laboratory for their helpful discussion.

20) J.J. Elliott and S.F. Mason, *J. Chem. Soc.*, **1959**, 2352.