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Physicochemical Properties of 1,3-Dithiol-2-ylidene and 1,3-Oxathiol-2-ylidene Derivatives[1]

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The influence of the contribution of the dipolar form to the resonance hybrid structure on the chemical stability of 1,3-dithiol- and oxathiol-2-ylidene derivatives was investigated by means of infrared, ultraviolet, nuclear magnetic resonance, and dipole moment measurement. It is concluded that though the contribution of the polar form to the resonance hybrid is small, it is nevertheless important for double bond isomerization through non-benzenoid aromatic stabilization of its positive charge.

Protonation of the double bond in acid medium does not necessarily occur, since some of the title compounds are not Hammett bases.

In the preceding paper,[1] the syntheses of 1,3-dithiol-2-ylidene (I) and 1,3-oxathiol-2-ylidene (II) derivatives were reported. The positively charged dithiolium or oxathiolium cations being potential aromatic sextets, and the presence of electron-withdrawing groups on the exocyclic carbon of I and II lead to stabilization of the molecules by the contribution of polar structures to the resonance hybrids. Aromaticity of the 1,3-dithiolium cation has been well investigated[3]; however, that of 1,3-oxathiolium cation still remains unexplored. Here we report an investigation of the physicochemical properties of I and II aimed at an understanding of their structures.

Result and Discussion

With regard to the resonance stabilization between neutral and polar structures of 1,4-dithiafulvene[4] derivatives, Campaign and Haaf[5] suggested that the compounds exist in the more stable neutral forms rather than as polar structures, evidenced by the instability of the protonated species of polar structure in alcoholic medium. However, contribution of a polar structure to the resonance hybrid is suggested by the vinyl proton signals in the nuclear magnetic resonance (NMR) spectra of I and II in DMSO-d_6. The chemical shifts of the vinyl protons of Ia and IIa appear at lower fields in DMSO-d_6 than in CF_3COOD (see Table I). The reverse is the case for the chemical shifts of the vinyl protons of Ib and IIb, though that of Ib is at a lower field in DMSO-d_6 than in $CDCl_3$, where it is in the region of the phenyl proton signals, δ 7.67—7.30. Campaign and Haaf[5] reported that the chemical shift of the vinyl proton of the protonated form of 6,6-diacetyl-1,4-dithiafulvene (Ic) was δ 8.12. However, the vinyl proton in the positively charged ring of bis-4-phenyl-1,3-dithiol-2-ylidene (IV)[6] in CF_3COOD

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1) This paper forms Part VII in a series of Studies on Heterocyclic Cation Systems. Preceding paper, Part VI: K. Hirai, T. Ishiba, and H. Sugimoto, *Chem. Pharm. Bull.* (Tokyo), **20**, 1711 (1972).

2) Location: *Sagisu, Fukushima-ku, Osaka, 553, Japan.*

3) H. Prinzbach and E. Futterer, "Advances in Heterocyclic Chemistry," Vol. 7, Academic Press, New York and London, 1966, p. 39; E. Campaign and R.D. Hamilton, *Quart. Rep. Sulfur Chem.*, **5**, 275 (1970); H.C. Sorensen and L.L. Ingraham, *J. Heterocycl. Chem.*, **8**, 551 (1971); K. Fahiam, H. Hartmann, J. Fabian, and R. Mayer, *Tetrahedron*, **27**, 4705 (1971).

4) 1,3-Dithiol-2-ylidene and 1,3-oxathiol-2-ylidene derivatives are conveniently termed as 1,4-diheterofulvenes (see, ref. 1).

5) E. Campaign and F. Haaf, *J. Org. Chem.*, **30**, 732 (1965).

6) A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* (Tokyo), **17**, 1931 (1966).

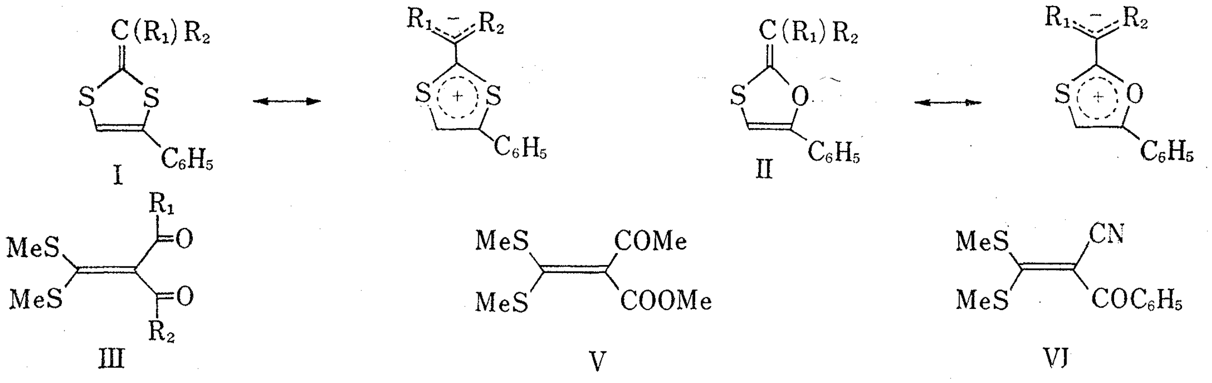


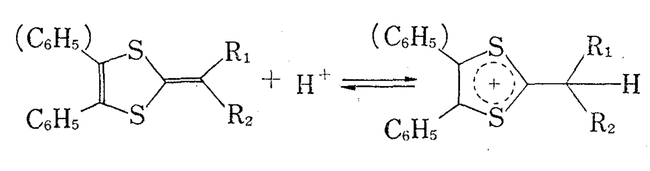
Chart 1

TABLE I. Physicochemical Properties of 1,4-Diheterofulvenes (I, II)[a]

Compd.	R_1	R_2	Dipole moment μ (D)	NMR (chemical shift of vinyl-H)[b] in DMSO-d_6	NMR (chemical shift of vinyl-H)[b] in CF_3COOD	IR $\nu_{C=O}$ cm^{-1} (in $CHCl_3$)
Ia			2.27	8.17	8.02	1635^w, 1587^s
IIa			2.38	7.82	7.55	1663^m, 1604^s
Ib	$COCH_3$	$COOC_2H_5$	2.78	7.95, 7.88	8.08	1665^s, 1600^s
IIb	$COCH_3$	$COOC_2H_5$	4.48	7.65	7.73	1697^s, 1610

a) Prepared and analyzed in the preceding paper (see, ref. 1).
b) δ value in ppm from the internal standard TMS at 60MHz.

was found to appear at the much lower field of δ 8.83. From these results, it is not certain whether the lower shift of the vinyl proton in polar solvents should be ascribed to protonation or to solvent effect. In an acidic solvent, I and II should equilibriate between protonated and nonprotonated species, as shown below, and this would cause the lower field shifts of the vinyl protons. An alternative reason for the shifts in DMSO-d_6 or CF_3COOD being at a lower field than in $CDCl_3$ might be a solvent effect, that is, the contribution of polar structure to the resonance hybrid increases with the polarity of the solvent. To investigate the equilibrium shown above, we measured the visible spectra in H_2SO_4–H_2O solvent. Plots of ε (extinction coefficient) *vs.* $-H_0$ (acidity function) and $\log(\varepsilon-\varepsilon_B/\varepsilon_{BH^+}-\varepsilon)$ *vs.* $-H_0$ are shown in Fig. 1 and 2, respectively. The molecular extinction coefficient increases monotonely with increase in the concentration of H_2SO_4 or $-H_0$, and the slope of $-H_0$ *vs.* $\log(\varepsilon-\varepsilon_B/\varepsilon_{BH^+}-\varepsilon)$ near the inflexion point is about 2 for both species. The slope of this plot for a Hammett base should be unity.[7] Furthermore, there is no isosbestic point on change of acid concentration, and Ia and IIa give almost the same electronic transition energies in protic and aprotic solvents (Table II). It can hardly be concluded from these results that Ia and IIa are in equilibrium with protonated forms, and the spectral change in aq. H_2SO_4 must therefore be due to the solvent effect. Consequently, the difference in the chemical shifts of the vinyl protons in the



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[7] H. Hosoya and S. Nagakura, *Spectrochim. Acta*, **17**, 324 (1961).

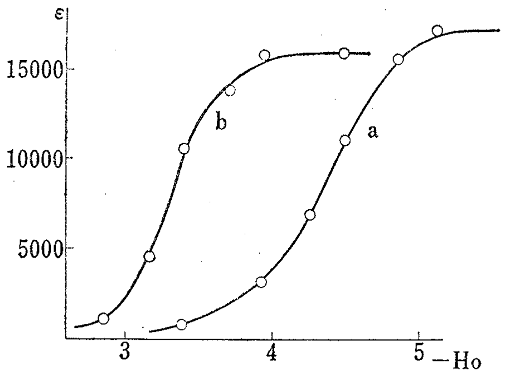

Fig. 1. Plot of ε against $-H_0$ at 24.5°
a: Ia (ε_{385nm}), b: IIa (ε_{365nm})

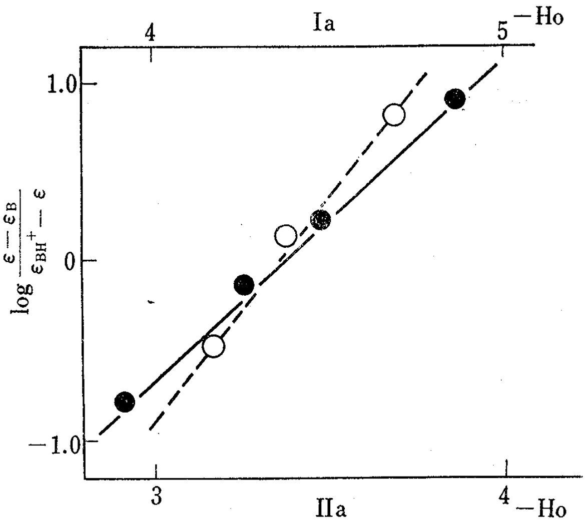

Fig. 2. Plot of log ($\varepsilon - \varepsilon_B/\varepsilon_{BH^+} - \varepsilon$) against $-H_0$
—●—: Ia; —○—: IIa

Table II. The Lowest Electronic Transition Energies of Ia and IIa

Compd.	nm (log ε)	
	in CH_3CN	in 95% EtOH
Ia	395(4.50)	395(4.51)
IIa	359(4.38)	361(4.40)

two solvents, DMSO-d_6 and CF_3COOD, is not due to the formation of protonated species,[8] but is ascribed to the difference in the degree of solvation. However, the lower field shift of vinyl protons of Ib and IIb in a protic solvent than in DMSO, rather than being due to the formation of a single bond by protonation, may due to a less strong hydrogen bonding between the protic solvent and the carbonyl groups of Ib and IIb.[9]

The delocalization of positive charge over the five-membered ring resulting from the increase in the contribution of the polar structure to the resonance hybrid in a polar solvent has a major influence on the chemical shift of the vinyl proton. The structural difference in the delocalization of positive charge can be observed in the lack of a limiting structure of oxathiolium cation to which a vinyl proton is attached. This might result in the observed lower field shift of vinyl protons of Ia and Ib in comparison with those of IIa and IIb in polar solvent. The chemical shifts of the vinyl protons in Ia and Ib were observed at lower field than those in IIa and IIb. This corresponds to the relation of the β proton in thiophene to that in furan, where in the former d orbital participation of sulfur plays an important role.[10]

That the contribution of polar structure to the resonance hybrids of I and II in less polar solvents such as chloroform is small can be further seen from the infrared (IR) spectra of the compounds. As shown in Table I, carbonyl stretching bands of I and II were observed at the same or slightly lower wave numbers than those for ethylenes having two methylthio

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[8] S.V. Tsukerman, L.A. Kutulya, Yu N. Surov, and V.F. Lavrushin, *Zh. Obshch. Khim.*, **41**, 639 (1971).

[9] Arnett, *et al.* have remarked on the difference between proton transfer and hydrogen bonding, E.M. Arnett and E.J. Mitchell, *J. Amer. Chem. Soc.*, **93**, 4052 (1971).

[10] C.C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Company, New York, 1962, p. 28; A.R. Katritzky, "Physical Method in Heterocyclic Chemistry," Vol. 2, Academic Press, New York and London, 1963, p. 114; J. Jonáv, W. Derbyshire, and H.S. Gutowsky, *J. Phys. Chem.*, **69**, 1 (1965).

groups on C_1 and a carbonyl group on C_2 (III). For the latter compounds $\nu_{C=O}$'s were about 1700—1635 cm^{-1}, 40—60 cm^{-1} lower than for a normal carbonyl band. Sandström and Wennerbeck[11] have attributed this shift to a lowering of the barrier to double bond rotation caused by the polar structure, though it does not necessarily signify a large contribution of the polar structure and the carbonyl band observed in III is thought to be a normal band for α,β-unsaturated carbonyl absorption. The lower wave number shift of the carbonyls must be due to the contribution of polar structure to a resonance hybrids of I and II by means of the delocalization of positive charge over the five-membered ring and the negative charge over the electron-withdrawing groups. However, these deviations are small in magnitude as is clear from Table I and the IR data of III.

From this discussion, it appears that the contribution of polar structure to the resonance hybrids of I or II in the ground state in a less polar solvent is not as large as was expected, and this is reflected in the magnitude of the dipole moments of the compounds. The dipole moments measured in dioxane, shown in Table I, are of the same order as the carbonyl group moments.[12] The dipole moments of Ib and IIb are larger than that of IIa. This can be explained by the fact that the direction of the resultant dipole moment of the two carbonyl group moments of Ia and IIa in their neutral form is from the dimedone moiety to the five-membered ring, owing to the fixation of carbonyl groups in the compounds; whereas the reverse is the situation in the polar structure where the direction is from the five-membered ring to the carbonyl groups. The apparent difference between the dipole moments of Ib and IIb can be explained as follows. Existence of two kinds of vinyl proton in Ib, observed in the NMR spectrum in DMSO-d_6, is due to the presence of two geometrical isomers, as discussed later. IIb, however, was obtained in low yield and shows a singlet signal due to the vinyl proton in its NMR. Therefore IIb is not a mixture of two isomers but a single product. This can be further rationalized by consideration that the 6π resonance stabilization due to delocalization is larger for I than for II, because I has two sulfur atoms available for valence shell expansion, leading to the higher barrier to rotation in II than in I. Consequently, only one geometrical isomer of IIb could be isolated in our experiment. The large difference between the dipole moments of Ib and IIb does not arise from the replacement of the oxygen atom in the 1,3-oxathiole ring by a sulfur atom. This is evident from comparison of the dipole moments of Ia and IIa. The difference must originate, therefore, in the direction of the dipole moments. If the dipole moment vectors corresponding to each isomers are d_s and d_s', respectively, and the angle between them is θ, and if the mixture contains equal amounts of each isomer (which is seen to be the case from the NMR spectrum), then the magnitude of the resultant moment is $|d_s| \cos(\theta/2)$. If we suppose the ratio of the dipole moments of Ib and IIb is equal to that of the moments of Ia and IIa, then we obtain $\theta/2=40°$. In the polar structures of Ib and IIb the negative charge is thought to reside more on the oxygen of the acetyl group than on that of the ester group because the Hammett σ_p constant of the former is larger than that of the latter.[13] As a result, a large difference in the dipole moment vector from the molecular axis is plausible.

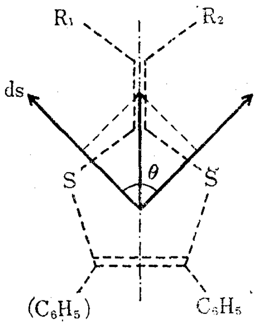

Chart 2

Thus, it can be concluded that 1,4-diheterofulvene exist mainly in the neutral form in a less polar solvent, while there is large contribution of polar structure in a polar medium. Decrease in the double bond character of the exocyclic C–C bonds of I and II is accompanied

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[11] J. Sandström and I. Wennerbeck, *Acta Chem. Scan.*, **24**, 1191 (1970).

[12] E.S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., 1959, p. 62.

[13] H.H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

by contribution of polar structure to the resonance hybrid, in other words, heterocyclic aromaticity of the positively charged five-membered ring of 1,4-diheterofulvenes can be provided by a decrease in the double bond character of the C–C double bond.

The presence of two kinds of proton, observed in the NMR spectrum of Ib, indicates the existence of two geometrical isomers. To study the interconversion of these isomers, the NMR spectrum of Ib was taken at various temperatures (Fig. 3). The signals for the two vinyl protons appearing at δ 7.59 and 7.88, respectively, at 36.5° coalesce at δ 7.77 at 121° ($\Delta G^{\neq}=21.6$ kcal/mole at the coalescence temperature), and become a sharp singlet at δ 7.67 at 170°; furthermore, at each temperature the ratio of the two geometrical isomers is nearly unity, from which the approximation $k_1=k_{-1}$ was made in equation (1). Abnormal behavior of the vinyl proton is observed in that its chemical shift moves to a higher field with increase in temperature; this will be discussed later.

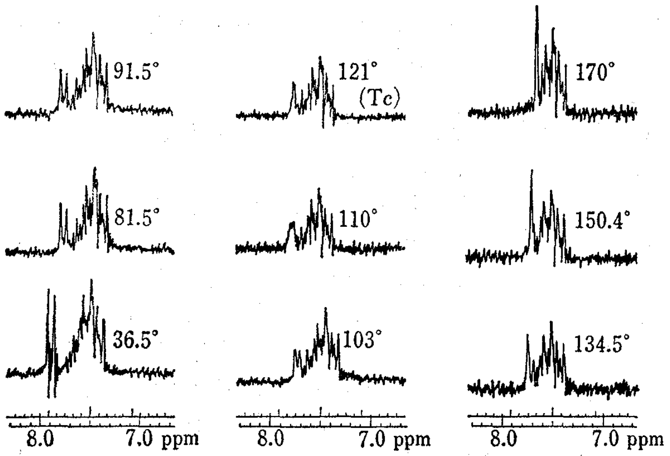

Fig. 3. Temperature Dependent NMR Spectra of Ib in DMSO-d_6

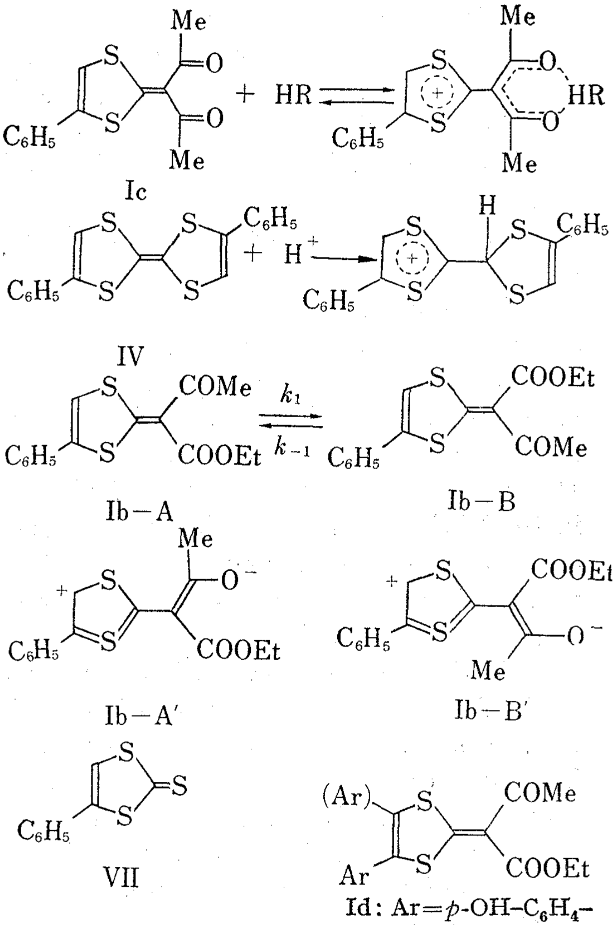

Chart 3

Sandström and Wennerbeck[11] reported that the methyl signal in the NMR spectrum of V is a singlet. As was mentioned previously, the positive charge can be delocalized over the five-membered ring of Ib, and the carbonyl of the acetyl group is more electronegative than that of the ester group. As a result, representations of Ib-A and Ib-B expressing sulfur d orbital participation can be made as shown in Ib-A′ and Ib-B′. The prefered transoid conjugation[14,15] in Ib-A′ gives a lower chemical shift for the vinyl proton than the cisoid conjugation in Ib-B′. In V, lack of this stability results in the singlet methyl signal. The rate of interconversion was obtained from the half-value widths[16] for slow exchange, $k=\pi(\Delta^{T}-\Delta^{\circ})$, and for fast exchange, $k=\pi/2(\Delta\nu^{2}/\Delta^{T}-\Delta^{\circ})$, where $\Delta\nu$ is the difference in the chemical shift of the two isomers and Δ^{T} and Δ° are the half-value widths at temperature T and room temperature, respectively.

The Arrhenius plot of $\log k$ *vs.* $1/T$ obtained is shown in Fig. 4. From this Arrhenius plot we obtained $\Delta H^{\neq}=10.5$ kcal/mole, or $E_a=10.7$ kcal/mole and $\Delta S^{\neq}=-29.0$ e.u. at 300°K.

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14) R.G. Parr, "Quantum Theory of Molecular Electronic Structure," W.A. Benjamin, Inc., New York and Amsterdam, 1964, p. 227.

15) H. Kessler, *Angew. Chem. Intern. Ed. Engl.*, **9**, 219 (1970).

16) H. Grunter, *Tetrahedron Letters*, **1965**, 4085.

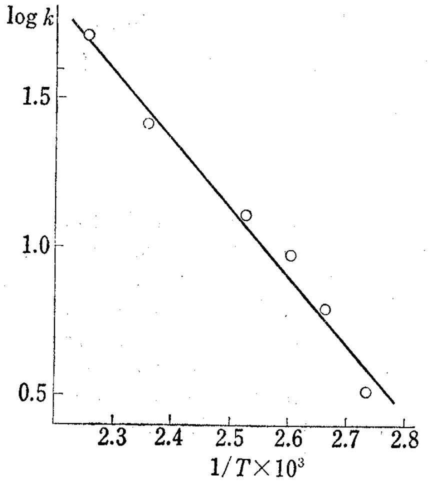

Fig. 4. Arrhenius Plot for Isomerization of Ib

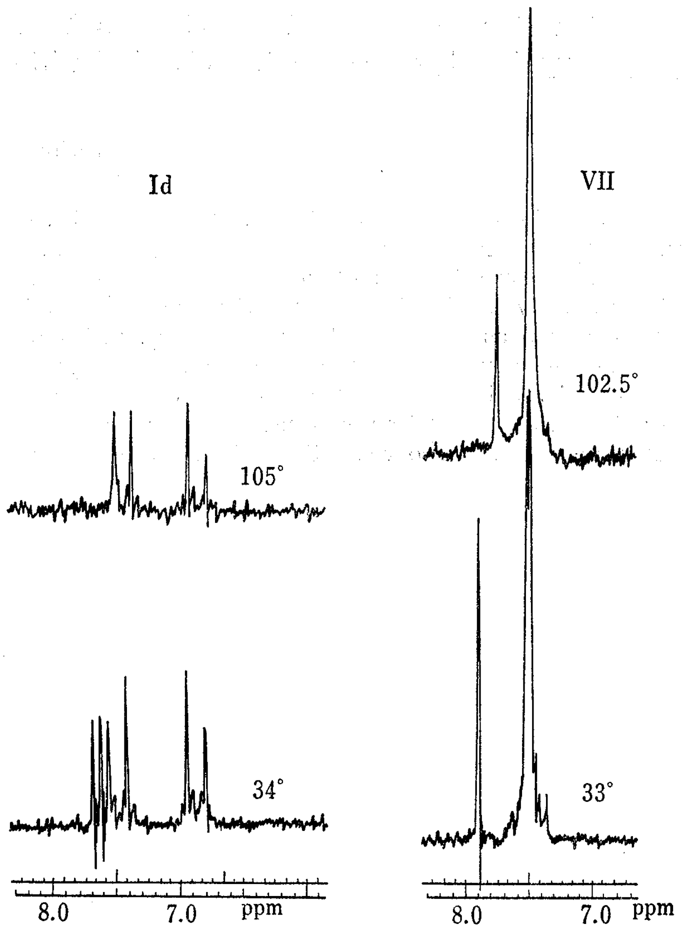

Fig. 5. Temperature Dependence of Vinyl Protons of Id and VII in DMSO-d_6

The rotational barrier for a normal double bond is as high as 60—65 kcal/mole; therefore, the value for Ib is sufficiently reduced from the normal one. Furthermore Sandström and Wennerbeck[11] reported the activation parameters for VI as $\Delta H^{\neq}=15.0$ kcal/mole and $\Delta S^{\neq}=-24.0$ e.u. These results indicate that the easier free rotation of Ib (in polar solvent the E_a value is only about two or three times that of a C–C single bond[15]) than that of VI is attributed to the decrease in double bond character, which in turn is a reflection of the delocalization of positive charge over the five-membered dithiole ring; and the increased activation entropy of Ib over VI is a result of the increased number of atoms involved.[17]

A remaining problem is the abnormal NMR behavior of the vinyl proton with increase in temperature. This can be explained as follows. Concerning the contribution of the polar structure to the resonance hybrid in the ground state, the positive charge is delocalized over the phenyl group attached to the C-2 position, which leads to an increase in the double bond character of the $C_{ph}-C_2$ bond, with the result that in the ground state the phenyl group is nearly coplanar with the 1,3-dithiole ring. The vinyl proton is therefore affected by the anisotropic effect due to the ring current of the phenyl group. With increase in temperature, free rotation around this bond takes place resulting in an averaging of the anisotropic effect of the phenyl ring, and hence a higher field shift of the vinyl proton. To verify this, the NMR spectra of 4-phenyl-1,3-dithiole-2-thione (VII),[18] which is sufficiently polar in its ground state, was measured at different temperatures. The difference in the chemical shift of the vinyl proton of VII at 33° and at 103° is 10 Hz. Furthermore the *p*-hydroxyphenyl derivative (Id) also shows two vinyl protons at room temperature which are shifted to higher field, the difference in chemical shift at 34° and 105° being 11 Hz, while that for Ib is 5 Hz (Fig. 5).

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[17] S. Glasstone, K.J. Laidler, and H. Eyring, "The Theory of Rate Process," McGraw-Hill Book Company, Inc., New York and London, 1941, p. 21.

[18] D. Leaver, W.H. Robertson, and D.M. McKinnon, *J. Chem. Soc.*, **1962**, 5104; H. Behringer and J. Falkenberg, *Tetrahedron Letters*, **1967**, 1895; K. Hirai, H. Sugimoto, and T. Ishiba, to be published.

This means that in Id an electron-releasing substituent conjugates with the 1,3-dithiole ring more than the unsubstituted phenyl group does. Hence the large anisotropic effect of the *p*-hydroxyphenyl group causes the chemical shift difference in Id to be larger than that in Ib.

Experimental

Materials——Compounds (Ia, Ib, IIa, IIb and Id) were prepared according to the method given in the preceding paper.[1] The preparation of compound (IV) has been described in the previous paper.[6]

Dipole Moment——Dipole moments were estimated from the dielectric constant measured in dioxane at 25° and by the density extrapolation method of Halverstadt and Kumler.[19] Atomic polarization was approximated as 5% of electric polarization, which was obtained from the atom refraction.[20]

Electronic Spectra——Hitachi recording spectrophotometer-EPS 3 model was used for the measurement of UV and visible spectra of IIa and Ia in various solvents. Fused quartz cells with glass stoppers of 1 cm liquid path were used for the measurement of aqueous H_2SO_4 solvent. All the solution were prepared just before measurement, concentrations of the solutions being about $10^{-4}-10^{-3}$M.

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[19] I.F. Halverstadt and W.D. Kumler, *J. Amer. Chem. Soc.*, 64, 2988 (1942).

[20] C.P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N.Y., 1955, p. 409.