Experimental and Theoretical Studies on Protonation of Thioketones

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The site of protonation in two classes of thioketones, $(RC_6H_4)_2C{=}S$ (R = H or OCH_3) and $Bu^t_2C{=}S$, was investigated by ^1H and ^{13}C n.m.r. spectroscopy. For aromatic thioketones, protonation occurs on the thiocarbonyl carbon from the side of the π-plane, whereas for the aliphatic compound, protonation of the sulphur atom occurs from the side of the σ-plane as in the case of carbonyl compounds. Electronic absorption spectra also provide information on sites of protonation in these molecules. Results are discussed in terms of total energies, charge-density distributions, and excitation energies of $R_2C{=}S$ and its protonated derivative elucidated by semi-empirical SCF-MO calculations in the CNDO/2 approximation.

IT is well known, from a number of experimental and theoretical investigations,[1] that normal carbonyl compounds ($R_2C{=}O$) are attacked on the oxygen lone pair of the carbonyl group by electrophilic reagents approaching from the σ-plane. For protonation, this conclusion was experimentally confirmed by Olah *et al.*[2] from analyses of low-temperature n.m.r. spectra of such protonated carbonyl compounds as formaldehyde, di-t-butyl ketone, and benzophenone, and was supported by non-empirical and semi-empirical MO calculations[3] on carbonyl derivatives. For thiocarbonyl compounds, however, there is some abnormal experimental evidence,[4] *e.g.*, thiobenzophenone is often attacked by electrophiles on the thiocarbonyl carbon, probably from the side of the π-plane of the thiocarbonyl group. The results of non-empirical SCF-MO calculations on protonated thioformaldehyde were reported by Bernardi *et al.*[5] Recently, we also performed calculations on the same system and found that two different protonated species, $H_2C{=}\overset{+}{S}H$ and $H_3\overset{+}{C}{=}S$, have comparable total energies, or even that a bending form of the latter species is more stable than the former.[6]

These results seem to suggest that the site of protonation of the thiocarbonyl group is determined by substituents on the thiocarbonyl carbon atom. Thus, in order to understand the substituent effect on the orientation of protonation, we studied the ^1H and ^{13}C n.m.r. spectra of typical aliphatic and aromatic thioketones such as di-t-butyl thioketone (DBT),[7] thiobenzophenone (TBP), and 4,4′-dimethoxythiobenzophenone (DTBP).[8] Electronic absorption spectra of protonated thioketones have also been studied and the results are compared with electronic states of various types of protonated thiocarbonyl compounds calculated by means of a semi-empirical CNDO/2 method.[9] The changes in distribution of charge density and excitation energy in the protonated systems are also discussed in comparison with those in non-protonated compounds.

EXPERIMENTAL

Solvents.—Chloroform, deuteriochloroform, and methylene chloride were Spectrograde reagents and used without further purification. Sulphur dioxide was prepared by the usual synthetic method from sodium sulphite and concentrated sulphuric acid and was liquidized with dry ice–methanol before use.

Compounds.—Trifluoroacetic acid and trifluoromethanesulphonic acid were commercial grade and used without further purification. Di-t-butyl thioketone (DBT) was synthesized according to ref. 10. Di-isopropyl disulphide and 1-methylethanesulphenyl perchlorate were prepared from commercial 1-methylethanethiol according to the literature.[11] Thiobenzophenone (TBP) and 4,4′-dimethoxythiobenzophenone (DTBP) were prepared by a conventional synthetic method[12] from benzophenone and hydrogen sulphide. Diphenylmethanethiol was prepared according to the procedure reported by Oster and his co-workers.[13] Bisdiphenylmethyl disulphide[14] was synthesized from butylamine and thiobenzophenone and recrystallized from ethanol–chloroform. Diphenylmethane sulphenyl chloride was prepared from diphenylmethyl disulphide and dry chlorine, according to the usual procedure for preparation of alkanesulphenyl chloride.[15]

Measurements.—^1H N.m.r. spectra for 10—15% v/v solutions of samples in SO_2 were obtained on a 60 MHz

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[1] 'The Chemistry of the Carbonyl Group, ed. S. Patai, vol. 1, 1966, ed. J. Zabicky, vol. 2, 1970, Interscience, New York.

[2] G. A. Olah, M. Calin, and D. H. O'Bien, *J. Amer. Chem. Soc.*, 1967, **89**, 3586; G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 1970, **70**, 561.

[3] For example P. Ros, *J. Chem. Phys.*, 1968, **49**, 4903; S. Nagata, T. Yamabe, K. Hirao, and K. Fukui, *ibid.*, 1973, **79**, 1863.

[4] For instance, A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, 1968, **90**, 7038; P. Beak and J. W. Worley, *ibid.*, 1970, **92**, 4142; 1972, **94**, 597; A. Ohno, K. Nakamura, M. Uohama, S. Oka, T. Yamabe, and S. Nagata, *Bull. Chem. Soc. Japan*, 1975, **48**, 3718.

[5] F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Canad. J. Chem.*, 1975, **53**, 1144.

[6] T. Yamabe, K. Yamashita, S. Nagata, K. Akagi, H. Kato, and K. Fukui, to be submitted for publication.

[7] P. V. Demarco, *Chem. Comm.*, 1969, 1418.

[8] J. Kempf, H. W. Spiess, U. Haeberlen, and H. Zimmermann, *Chem. Phys.*, 1974, **4**, 269.

[9] (*a*) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 129, 136; (*b*) J. A. Pople and G. A. Segal, *ibid.*, 1966, **44**, 3289.

[10] A. Ohno, K. Nakamura, Y. Nakazima, and S. Oka, *Bull. Chem. Soc. Japan*, 1975, **48**, 2403.

[11] D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3627; see also ref. 17.

[12] B. F. Goffon and E. A. Braude, *Org. Synth.*, 1963, Coll. Vol. 4, 927.

[13] G. Oster, L. Citarel, and M. Goodman, *J. Amer. Chem. Soc.*, 1962, **84**, 703.

[14] A. Ohno and N. Kito, *Internat. J. Sulfur Chem. A*, 1971, **1**, 26; H. Staudinger and H. Feudenberger, *Org. Synth.*, 1931, **11**, 94.

[15] H. Lecher, *Ber.*, 1925, **58**, 409; H. Brintzinger, K. Phannsteil, H. Koddebusch, and K. E. Kling, *Chem. Ber.*, 1950, **83**, 87; 'Organic Sulfur Compounds,' ed. N. Kharasch, Pergamon, New York, 1961, vol. 1, p. 350.

Hitachi spectrometer. The temperature was kept at −55 °C and tetramethylsilane was used as an external standard. The measurements of ^{13}C n.m.r. spectra for 25—30% v/v solutions of samples in $CDCl_3$ were carried out using a JEOL LNM-PFT-100 system (25.15 MHz) at room temperature (24 °C), where an internal ^{2}D lock was employed and tetramethylsilane was used as an internal standard. Electronic absorption spectra were measured on a Hitachi ESP-3T spectrophotometer at 15 °C.

Method of Calculation.—Calculations were carried out by means of the CNDO/2 method,[9a] with the following parameters for sulphur atom:[9b] β_S^0 −18.15, ζ_S 1.816 67, $\frac{1}{2}(I_s + A_s)_S$ 17.65, $\frac{1}{2}(I_p + A_p)_S$ 6.989 (energy values in eV). The *d* orbitals on sulphur were not included in this calculation.[*] We used the geometries of acetone and acetophenone for those of dimethyl thioketone (DMT) and phenyl methyl thioketone (PMT), respectively, except for the C=S bond distance. The value of R(C–S) was taken from non-empirical calculations on $H_2C{=}S$[17] as the initial distance in the optimization.

RESULTS AND DISCUSSION

N.m.r. Measurements.—Figure 1a presents the 60 MHz ^{1}H n.m.r. spectrum of DBT in CCl_4 at −55 °C. Figure 1b shows the 60 MHz ^{1}H n.m.r. spectrum of DBT in liquid SO_2 at −55 °C in the presence of an equimolar amount of a protonating reagent, CF_3COOH.[†] A new signal at δ 2.6 appeared in the spectrum of protonated DBT. Table 1 gives the results of protonation and relevant chemical shifts for analogous compounds. The signal at δ 2.6 is too high to be attributed to a *C*-protonated species; chemical shifts of protons in compounds of similar structure to the *C*-protonated species $Bu^t_2CHS^+$ appear at δ *ca.* 5.2, *e.g.* for $(CH_3)_2CHS^+ClO_4^-$. Even if the degree of protonation is somewhat weak, the signal from the CH proton of R_2CHS^+-type compounds is expected to appear at δ *ca.* 4—5. The value δ 2.6 is quite reasonable for the formation of the *S*-protonated species $Bu^t_2\overset{+}{C}{-}SH$. The values for chemical shifts of thiol protons are in the range δ 1.3—2.3[18] (Table 1). In particular, δ 2.3 for $Bu^t_2C(CN)SH$ is quite close to 2.6 observed for the DBT + H^+ system.

TABLE 1

Proton chemical shifts (δ) of DBT + H^+, TBP + H^+ system, and relevant molecules

	δ(C–H*)	δ(S–H*)	Ref.
$Bu^t_2C{=}S + B^+$	2.60[a]		
$Ph_2C{=}S + H^+$	7.00[a]		
$Ph_2CH^*{-}SH^*$	5.35	2.20	*b*
$Ph_2CH^*{-}SS{-}CH^*Ph_2$	4.79		*c*
$Ph_2CH^*S{-}Cl$	6.30		*c*
$Ph_2CH^*{-}S{-}C_6H_{11}$[f]	5.20		*b*
$Bu^t_2CH^*{-}SH^*$	2.67	1.33	*d*
$Bu^t_2C(CN){-}SH^*$		2.30	*d*
$Bu^t_2CH^*{-}SS{-}CH^*Bu^t$	2.54		*e*
$Me_2CH^*{-}SH^*$	3.00	1.40	*c*
$Me_2CH^*{-}SS{-}CH^*Me_2$	2.90		*c*
$Me_2CH^*S{-}Br$	3.20		*c*
$Me_2CH^*{—}ClO_4$	5.17		*c*

[a] Liquid SO_2 at −55 °C. CF_3COOH was used as a proton donor. [b] Ref. 25. [c] This work (in $CDCl_3$). [d] A. Ohno, K. Nakamura, M. Uohama, and S. Oka, *Chem. Letters*, 1975, 983. [e] Ref. 6. [f] Cyclohexyl diphenylmethyl sulphide.

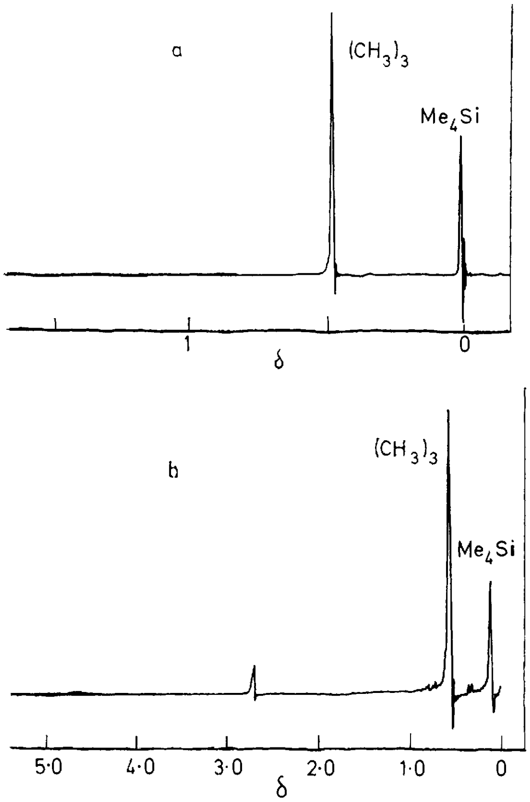

FIGURE 1 a, ^{1}H N.m.r. spectrum of DBT in CCl_4 solvent at −55 °C; b, ^{1}H N.m.r. spectrum of DBT + CF_3COOH in liquid SO_2 at −55 °C

The ^{1}H n.m.r. spectra of TBP (Figure 2a) and its protonated form, taken under the same conditions as those for DBT, show that the proton chemical shift due to protonation appears at δ 7.0 (Figure 2b). By comparing the locations of the chemical shifts of the TBP + H^+ system with those of the corresponding thiol and its derivatives listed in Table 1, one can recognize that protonation of TBP occurs on the carbon atom of the thiocarbonyl group rather than on the sulphur atom. If the protonation of TBP occurred on the sulphur atom, a

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[*] For organic compounds with a bivalent sulphur atom, the contribution of 3*d* orbitals to the excitation energy cannot necessarily be neglected for the far-u.v. region. At present, however, we deal mainly with absorption bands of comparatively small excitation energies in the u.v.–visible region, where we can neglect the contribution of sulphur 3*d* orbitals.[16]

[†] The species produced from the reaction of CF_3COOH and thioketones are thought to be protonated ions and to be fairly stable in liquid SO_2 at −55 °C on the basis of the extensive studies on the protonation of carbonyl compounds by Olah *et al.*[2]

[16] For instance, J. R. Sabin, *J. Amer. Chem. Soc.*, 1971, **93**, 3613; J. S. Rosenfield and A. Moscowitz, *ibid.*, 1972, **94**, 4797; V. B. Koutecký and J. I. Musher, *Theor. Chim. Acta*, 1974, **33**, 227.

[17] We also carried out calculations on acetone with the same CNDO/2 method. See J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, 1959, **31**, 1562; P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, *Chem. Phys.*, 1974, **3**, 35; see also refs. 5 and 22.

[18] R. H. Silverstein and G. C. Bassler, ' Spectrometric Identification of Organic Compounds,' Wiley, New York, 1967, ch. 4 gives proton chemical shifts for thiol protons at δ 1.2—1.6 and 2.6—3.6 for alkyl and aromatic thiols, respectively.

signal would be expected to appear below δ 3. *C*-Protonation is strongly supported by the chemical shift for the CH proton (δ 6.3) in Ph_2CHSCl in $CDCl_3$, since the ionic nature of this compound in polar solvents is supposed to be similar to that of protonated TBP.[19] From this experimental evidence from ^1H n.m.r. spectroscopy, we may conclude that protonation takes place on a lone pair of the sulphur atom in the case of DBT, whereas it occurs on carbon in the case of TBP.

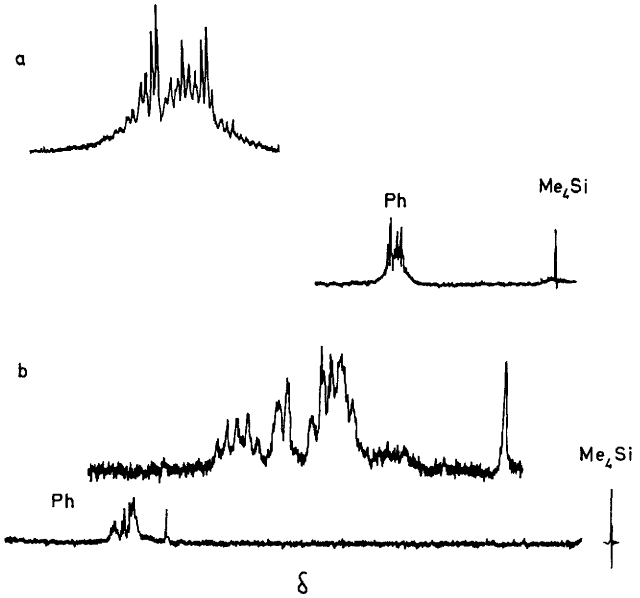

FIGURE 2 a, ^1H N.m.r. spectrum of TBP in CCl_4 solvent at −55 °C; b, ^1H n.m.r. spectrum of TBP + CF_3COOH in liquid SO_2 at −55 °C

Additionally, we measured the ^{13}C n.m.r. chemical shifts for the signals from DBT and DTBP and their protonated systems in $CDCl_3$ at room temperature.

TABLE 2

^{13}C N.m.r. chemical shifts [δ (p.p.m.) from Me_4Si] of DBT, DBT + H^+, DTBP, and DTBP + H^+ systems in $CDCl_3$

$Bu^t{}_2C{=}S$		32.9		53.6		278.4
$Bu^t{}_2C{=}S + H^+$		28.2		47.1		250.2
Δδ		+4.7		+6.5		+28.2
Assignment		$C(^*CH_3)_3$		$^*C(CH_3)_3$		$^*C{=}S$
$(CH_3OC_6H_4)_2C{=}S$	55.5	133.3	132.2	141.0	163.3	233.6
$(CH_3OC_6H_4)_2C{=}S + H^+$	56.6	116.9	138.9	130.9	171.9	206.0
	−1.1	−3.6	−6.7	+10.1	−8.6	+27.6
Assignment	$-O^*CH_3$	C(3)‡	C(2)†	C(1)‡	C(4)‡	$^*C{=}S$

† C(1)—(4) designate aromatic carbon atoms directly connected with, and *ortho*, *meta*, and *para* to the thiocarbonyl group, respectively.

The data for DBT and DTBP and their protonated species are given in Table 2, which shows similar changes in the carbon chemical shift to higher field for the thiocarbonyl group upon protonation. However, these results did not show so clear a difference as the ^1H spectra.

Electronic Spectra.—Electronic absorption spectra of DBT in CH_2Cl_2 at 15 °C with various concentrations of trifluoromethanesulphonic acid (TFA) are shown in Figures 3a and b. The bands at 5.18 (log ε 3.90) and 2.33 eV (1.03) for DBT, assigned to $\pi_{C=S} \longrightarrow \pi_{C=S}^*$ and $n_S \longrightarrow \pi_{C=S}^*$ transitions,[10] respectively, become weak and finally disappear without being shifted upon increasing the concentration of TFA. On the other hand, DTBP–TFA behaved quite differently from DBT–TFA (see Figure 4). A new absorption band appeared at 2.60 eV (log ε 3.04) * upon protonation, and this was followed by a slight weakening of the intensity of the band at 2.15 eV (log ε 2.50) due to the $n_S \longrightarrow \pi_{C=S}^*$ transition of DTBP. We could not find, however, any marked change in the

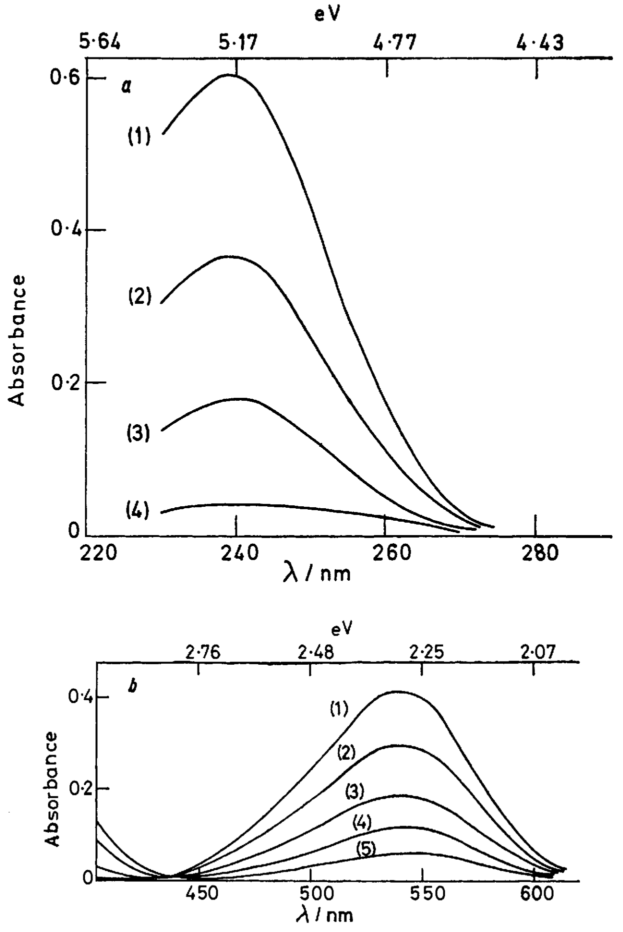

FIGURE 3 a, Electronic absorption spectra of DBT–TFA in CH_2Cl_2 at 15 °C. [DBT] 7.61 × 10^{-5}M. [TFA] (1) 0; (2) 1.40 × 10^{-5}; (3) 2.81 × 10^{-5}; (4) 8.70 × 10^{-5}M. λ < 230 nm not observed because of solvent absorption b, Electronic absorption spectra of DBT–TFA in CH_2Cl_2 at 15 °C. [DBT] 3.80 × 10^{-2}M. [TFA] (1) 0; (2) 0.57 × 10^{-2}; (3) 0.72 × 10^{-2}; (4) 1.41 × 10^{-2}; (5) 2.85 × 10^{-2}M

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* This new absorption band increased sharply in intensity as TFA was added. Therefore, we have adopted the maximum value as its intensity. This large intensity suggests that the new band may be of an electronically allowed transition.

[19] T. Yamabe, S. Nagata, Y. Kikuzono, and K. Fukui, *Bull. Chem. Soc. Japan*, 1975, **48**, 1349.

absorption bands in the u.v. region.* It should be noted that protonated DTBP (brown) regenerates DTBP (blue) when the system is diluted by a polar solvent such as EtOH or H_2O, which indicates that the bond formed by the protonation is weak and tends to dissociate in a polar solvent.

These results imply that there is a remarkable difference between the protonation of DBT and of DTBP. Such an interesting phenomenon seems to be consistent with the results obtained from ^1H n.m.r. measurements. In order to confirm the remarkable change found in the electronic absorption spectra, we decided to carry out MO calculations in the CNDO/2 approximation.

Molecular Orbital Calculations.—Aliphatic thioketones usually have characteristic absorption bands due to the $n_S \longrightarrow \pi_{C=S}^*$ and $\pi_{C=S} \longrightarrow \pi_{C=S}^*$ transitions of the thiocarbonyl group. The positions and intensities of these bands are not so largely affected by the change of alkyl substituents. Therefore, for the present MO calculations, we employed a simple system, dimethyl thioketone (DMT),[20] in place of DBT. As for DTBP on the other hand, it is thought that one phenyl group is twisted to some extent out of a plane defined by the other phenyl ring and the thiocarbonyl group and hence does not participate in conjugation to a great extent. This is supported by the fact that DTBP showed a shoulder at 2.05 eV (log ε 2.47) in addition to a band at 2.15 eV (log ε 2.50) in ethanol (the shoulder may also be due to an $n_S \longrightarrow \pi_{C=S}^*$ transition, although it was not sufficiently distinct to be regarded as an absorption band). This phenomenon may be associated with a conformation of DTBP in which one of phenyl groups is out of π-conjugation with the thiocarbonyl group, which is especially important in polar solvents.[21] Therefore, it is reasonable for a theoretical calculation to employ phenyl methyl thioketone (PMT) [20] as a model of DTBP.

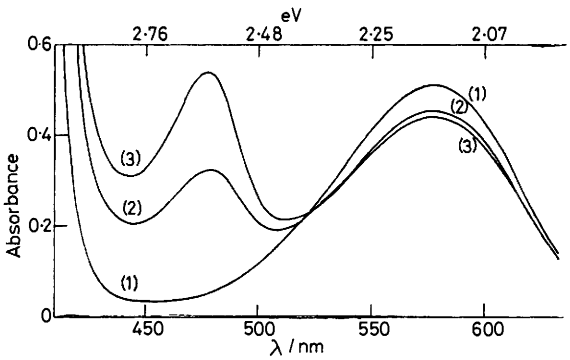

FIGURE 4 Electronic absorption spectra of DTBP–TFA in CH_2Cl_2–EtOH (99 : 1 v/v) at 15 °C. [DTBP] 1.27 × 10^{-3}M. [TFA] (1) 0; (2) 0.71 × 10^{-2}; (3) 1.40 × 10^{-2}M

The formal charge density of the C=S bond of the thiocarbonyl group of DMT obtained after optimization with respect to the C=S distance [with optimized geometry R(C=S) = 1.761 Å] is listed in Table 3. From Table 3 the following features for DMT can be observed: the π-bond of the thiocarbonyl group is considerably polarized and the π-bond order is remarkably small compared with that for a carbonyl group (*e.g.* in acetone 0.93).[21] This fact implys that the π-bond has a zwitterionic character $(\gt\overset{+}{\mathrm{C}}-\overset{-}{\mathrm{S}})$ to some extent. On the other hand, σ charge density is polarized in the opposite direction, different from that in carbonyl groups where the direction of polarization is the same from both π and σ bonds. The net charge of thiocarbonyl group indicates slightly positive and negative charges on the carbon and sulphur atoms, respectively. Such a polarization, however, is too small to be compared. with those in carbonyl compounds.[22]

TABLE 3

Formal charge densities, bond orders, and total energies (E_T) of DMT and DMT—H^+ systems A—D

		Formal charge density		Bond order	E_T(a.u.)	r(X–H′)Å [b]
		C	S			
DMT	σ	−0.25	+0.25	$\pi_{C=S}$; 0.78	−36.581	
	π	+0.42	−0.55			
A	σ	+0.01	−0.20	$\pi_{C=S}$; 0.48	−37.049	1.200
	π	+0.06	+0.67	$\sigma_{C-H'}$; 0.80		
B	σ	−0.21	+0.14	$\pi_{C=S}$; 0.53	−37.042	1.215 [c]
	π	+0.46	+0.06	$\sigma_{C-H'}$; 0.48		
				$\sigma_{S-H'}$; 0.72		
C	σ	−0.37	+0.22	$\pi_{C=S}$; 0.30	−36.982	1.470
	π	+0.67	−0.12	$\sigma_{S-H'}$; 0.91		
D	σ	−0.33	+0.99	$\pi_{C=S}$; 0.51	−36.993	1.400
	π	+0.61	−0.83	$\sigma_{S-H'}$; 0.94		
		C	O			
Acetone	σ	+0.07	−0.02	$\pi_{C=O}$; 0.93	−44.228	
	π	+0.18	−0.27			

[a] The optimized bond distance R(C=S) of DMT is 1.761 Å, for which the four types of protonated configuration were calculated. [b] H′ Designates the proton which attacks the carbon or sulphur atom of the thiocarbonyl group. [c] In type B, r is the distance between the proton and the centre of the thiocarbonyl group.

For calculations on protonated DMT, four types of structures, A—D, were taken into account. A—C are representative of those in which a proton attacks the carbon, the centre of the C=S π-bond, and the sulphur atom, respectively, along the π-plane. D is a structure in which protonation occurs on a sulphur lone pair through the σ-plane as normally accepted. Based on the optimum geometry of DMT, the most stable configuration for each of the four types of protonated species

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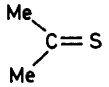
* In ethanol, DTBP showed several absorption bands due to the $\pi \longrightarrow \pi^*$ transitions, *i.e.*, 5.57 (log ε 4.33), 4.94 (4.22), 4.18 (4.11), and 3.52 eV (4.44). In methylene chloride or chloroform, however, these bands were not sufficiently distinguished to allow changes resulting from protonation to be followed.

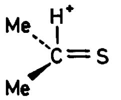
[20] J. G. Calvert and J. N. Pitt, jun., ' Photochemistry,' Wiley, New York and London, 1966. From the data therein one can compare $n_S \longrightarrow \pi_{C-S}^*$ transition energies of the model systems with those of the compounds of interest, *i.e.*, 2.70 and 2.33 eV for DMT and DBT, respectively, and 2.07 and 2.15 eV for PMT and DTBP, respectively.

[21] E. J. Moriconi, W. F. O'Connor, and W. F. Forbes, *J. Amer. Chem. Soc.*, 1960, **82**, 5454; W. A. Lees and A. Burawoy, *Tetrahedron*, 1964, **20**, 1527, 1533, 2229; O. Korver, J. U. Veenland, and Th. J. de Boer, *Rec. Trav. chim.*, 1965, **84**, 289, 304; see also ref. 20.

[22] R. H. Lumbroso and C. Andrieu, *Bull. Soc. chim. France*, 1966, 3201; N. C. Baird and J. R. Swenson, *J. Phys. Chem.*, 1973, **77**, 277. See also ref. 6.

was determined as a function of r (the distance of C–H$^+$ or S–H$^+$) and R(C=S) as well as θ (C$\widehat{S}$H) for type D. Furthermore, since R(C=S) is expected to be lengthened and tends to have the nature of a single bond as a proton approaches the carbon or sulphur atom of the thiocarbonyl group, the four protonated configurations were reoptimized in regard to R(C=S) after the optimization of r and δ. The value obtained for R(C=S) was found to be 1.81—1.82 Å in all cases. The optimized values of r, R, and θ as well as the total energies and charge density distributions are also presented in Table 3. From the viewpoint of total energy, type A with r(C–H$^+$) 1.20 Å is the most stable structure and the stability decreases in the order A > B > D > C. The calculated results are quite different from those for carbonyl compounds, where protonation takes place on the oxygen lone pair, *i.e.* through the type D process. The differences of total energy may be reasonably explained by the charge density distribution and the weakness of π-bonding in the thiocarbonyl group by comparison with those in a carbonyl group. Since the formal charge on sulphur atom in a σ-framework including σ 3p-lone pair electrons is positive, protonation of type D may be not so easy as that on the usual unpolarized 3p lone pair. It may be as weak as type C, where proton attacks the π electron of sulphur in the zwitterionic form ($>\overset{+}{C}-\overset{-}{S}$), and the destabilization due to the cleavage of the C=S π-bond may be not so large because of the weakness of this π-bond. The difference in total energy (*ca.* 6.90 kcal mol^{-1}) of type C and D protonation, however, is within the usual limits of rotational barriers.[5] In type C protonation, the 2p_z orbital of the carbon atom is almost empty as a result of newly formed S–H σ-bond, and this can be contrasted to the type A protonation where a strong C–H bond is formed in place of the weak C=S bond. Usually C–H σ-bonds are much stronger than S–H σ-bonds and, as a consequence, type A protonation may appear to be most favoured among these four types of protonations. The conclusion is partly supported by the fact that the resultant species (CH$_3$)$_2$CH–S$^+$ is stable in acidic solvents.[11] The discrepancy between theoretical and experimental results may be accounted for by the steric effect of bulky t-butyl group or even by the modification of π-conjugation caused by aromatic substituents [23] in the case of aromatic thioketones.


DMT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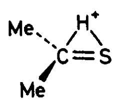
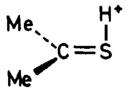
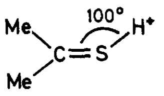

B


C


D

The excitation energies were calculated on the basis of optimal geometries for protonated DMT including the configurational interaction (CI) technique. It is noteworthy that the contribution of sulphur 3d orbitals is usually not appreciable for transitions with such small excitation energies as those of bivalent sulphur compounds and, therefore, was neglected for the present calculation.[16] The calculated excitation energies and oscillator strengths for DMT and DMT–H$^+$ systems are shown in Figure 5 together with several molecular orbital levels. Based on the results shown in this Figure, the theoretical absorption spectra were synthesized and are illustrated in Figure 6. According to

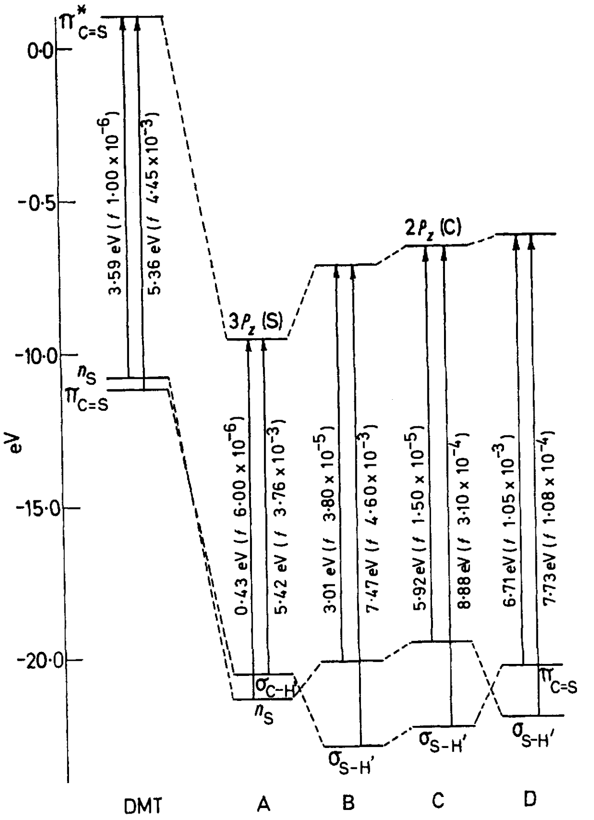


FIGURE 5 Partial MO diagram, electronic transition energies, and oscillator strengths (f) for DMT and DMT–H$^+$

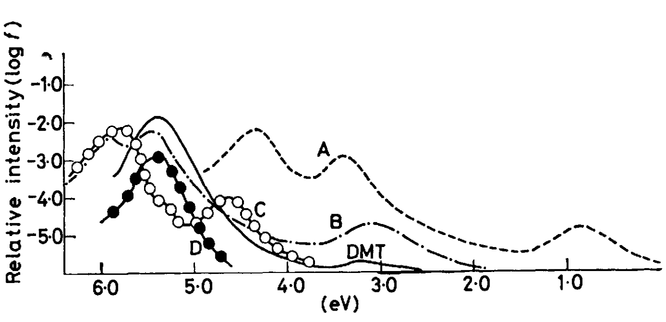


FIGURE 6 Schematic absorption spectra based on the calculated transition energies for DMT and DMT–H$^+$ systems A—D

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[23] For instance, L. Kaper, J. U. Veenland, and Th. J. de Boer, *Spectrochimica Acta*, 1967, **23A**, 2605.

the calculated results, as is seen in Figures 5 and 6, two absorption bands at 2.33 and 5.18 eV of DBT are assigned to $n_S \longrightarrow \pi_{C=S}^*$ and $\pi_{C=S} \longrightarrow \pi^*_{C=S}$ transitions, respectively, which are also supported by other experimental evidence.[10]

In type A protonation, the original $\pi_{C=S}^*$ orbital is converted into a low-lying empty orbital with almost the nature of sulphur $3p_z$, owing to the cleavage of the $\pi_{C=S}$ bond by protonation and hence the band due to $n_S \longrightarrow \pi_{C=S}^*$ transition shifts towards the longer wavelength region. On the contrary, the band for the $\pi_{C=S} \longrightarrow \pi_{C=S}^*$ transition would shift towards shorter wavelength with the nature of $\sigma_{C-H'} \longrightarrow 3p_z$ transition, because $\pi_{C=S}$ orbital changes into lower $\sigma_{C-H'}$ orbital by the protonation, as found in Figure 5. (The approaching proton in protonation is denoted as H′.) Furthermore, a new band due to the $\sigma_{C-S} \longrightarrow 3p_z$ transition is also expected at shorter wavelength than that for the $n_S \longrightarrow \pi_{C=S}^*$ one of DMT. The calculated results therefore seem to be far from the pattern of absorption spectra obtained for DBT–TFA system. Moreover, in the actual process of protonation of the thiocarbonyl-carbon atom of DBT, the proton would be affected by the large steric influence of a bulky substituent such as the t-butyl group.[10] The possibility of type A protonation, therefore, may be small even though it is predicted to be the most stable configuration from the calculated total energy of the DMT–H$^+$ system.

In type B protonation, the band for the $n_S \longrightarrow \pi_{C=S}^*$ transition shifts somewhat towards the longer wavelength region with increasing intensity, whereas the band for the $\pi_{C=S} \longrightarrow \pi_{C=S}^*$ transition, which is similar to $\sigma_{S-H'}$ (and/or $\sigma_{C-H'}$) $\longrightarrow \pi_{C=S}^*$, would shift largely towards the shorter wavelength region and then disappear in the region considered.

In type C protonation, both $n_S \longrightarrow \pi_{C=S}^*$ and $\pi_{C=S} \longrightarrow \pi_{C=S}^*$ transitions would largely shift the corresponding bands towards the shorter wavelengths of $n_S \longrightarrow 2p_z(C)$ and $\sigma_{S-H'} \longrightarrow 2p_z(C)$ transitions, respectively. [$2p_z(C)$ is the empty π-type orbital on the thiocarbonyl carbon atom.] In the present case, however, there appears a new band attributable to the $n_S \longrightarrow \sigma_{S-H'}^*$ transition. Thus, the features for type B and C protonations are inconsistent with the pattern experimentally observed.

Type D protonation leads to a possible configuration for the protonated thioketone predicted from ^1H n.m.r. measurements. Two transitions, $n_S \longrightarrow \pi_{C=S}^*$ and $\pi_{C=S} \longrightarrow \pi_{C=S}^*$, would disappear accompanying the change of sulphur lone pair n_S into the $\sigma_{S-H'}$ bond and to the distortion of C=S π-bond by protonation. Thus the results obtained by calculations on type D protonation reflect the experimental results better than other models: both absorption bands disappeared when the amount of TFA added to DBT solution was increased (see Figure 6).

We next considered the PMT–H$^+$ system, where the optimized value of R(C=S) for PMT was 1.71 Å and those of four types of protonated configurations with respect to r, R, and θ were found to have the same trend as the DMT–H$^+$ system. Type A protonation was also predicted to be the most stable from the total energy with the same trend (A > B > D > C) as the protonated DMT system. The stability of type A protonation could be also explained in terms of a weak π-bond characteristic of the thiocarbonyl group. The calculated excitation energies[22] in the PMT–H$^+$ system change similarly to those in the DMT–H$^+$ system (Figure 7) with the change of protonating site. The assignment for a new absorption band at 2.60 eV observed in DTBP–TFA system may afford significant information on the orientation of protonation for an aromatic thioketone. Three possible transitions can be predicted for this band with the aid of the calculated excitation energies and oscillator strengths, *i.e.* $n_S \longrightarrow 3p_z$ and $\sigma_{C-S} \longrightarrow 3p_z$ for type A protonation, and $n_S \longrightarrow \pi_{C=S}^*$ for type B. The band for the first transition, however, would appear in the extremely longer wavelength region and its intensity would be increased because the molecular symmetry is distorted to some extent. The third transition is expected to be similar to the first. Thus, the predicted energies for these two transitions contradict the experimental result that there is no band in a region of longer wavelength than that for the $n_S \longrightarrow \pi_{C=S}^*$ transition of PMT. On the other hand, the second transition ($\sigma_{C-S} \longrightarrow 3p_z$ in type A protonation) results in a band at a wavelength close to the position for the $n_S \longrightarrow \pi_{C=S}^*$ transition of PMT. In addition, the band has intensity (f *ca.* 10^{-3}) sufficient to provide an absorption spectrum in the visible region. The appearance of

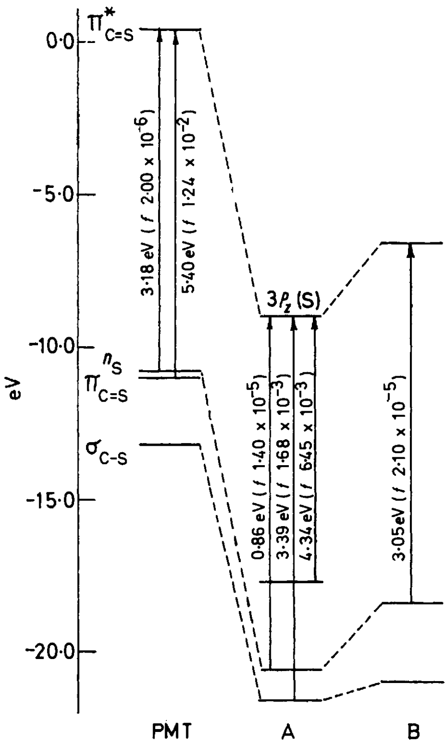

FIGURE 7 Partial MO diagrams, electronic transition energies, and oscillator strength for PMT and PMT–H$^+$

this transition may be accounted for by the facts that the energy level of σ_{C-S} orbital is raised by the elongation of the C–S bond as a result of protonation and that the energy level of $\pi_{C=S}^*$ is lowered to the level almost equivalent to that of $3p_z$(S), which is an empty orbital on the sulphur atom. It can be asserted that this second transition accords better with the experimental results than the others, that is, the new absorption band observed at 2.60 eV may be assigned to the $\sigma_{C-S} \longrightarrow 3p_z$ transition in the type A structure. Thus, the present calculations predict that protonation takes place on the thiocarbonyl carbon and sulphur atoms in PMT–H^+ and DMT–H^+ systems, respectively, which is in accord with the absorption spectra of the DTBP–TFA and DBT–TFA systems.

It should be mentioned that there is no distinct difference in total energies between type A and B protonations in the PMT–H^+ system (*ca.* 2.5 kcal mol^{-1}), although the spectral pattern changes. Therefore, the middle of type A and B protonation may be considered to be the actual protonated structure. In fact, the C–H′ bond formed is so weak that protonated DTBP regenerates DTBP in polar solvents such as EtOH or H_2O. The final protonated configuration, however, should be so stable that the two aryl substituents are bent out of the plane of thiocarbonyl group and the C–H^+ bond is rehybridized to form an sp^3 hybridized orbital on the thiocarbonyl carbon atom.[6]

Conclusion.—From the analyses of the ^1H n.m.r. and electronic absorption spectra, it was found that a proton attacks the thiocarbonyl carbon of aromatic thioketones and sulphur of the aliphatic thioketone, respectively. The results can be interpreted by CNDO/2 calculations. This characteristic of a thiocarbonyl π-bond has also been demonstrated from the reaction with nucleophilic reagents[4] as well as electrophilic ones such as H^+. Thus various types of reactions may be expected for double bonds containing second-row elements.

We thank Dr. S. Kobayashi for measurements of ^1H n.m.r. spectra. We also express our appreciation to Dr. K. Yoshikawa, Mr. S. Kitagawa, Dr. T. Imagawa, and Miss M. Sugiura for the measurements of ^{13}C n.m.r. spectra and their helpful discussions.

[6/1027 *Received, 28th May,* 1976]