

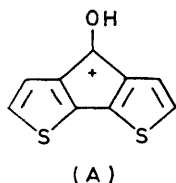
Proton Nuclear Magnetic Resonance Studies of Protonated Cyclopentadithiophenones and Cyclopentadithiophens

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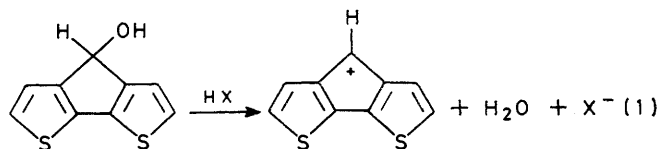
The ^1H n.m.r. spectra of protonated fluorenone, cyclopentadithiophenones ($\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ at -60°), and cyclopentadithiophens ($\text{CF}_3\text{CO}_2\text{H}$ at -15°) are discussed. Di- and mono(carbonyl)-protonation occurred. Cyclopenta[1,2-*c*:3,4-*c'*]dithiophen-7-one and fluorenone are found to be protonated first at the carbonyl group. PPP Calculations show that carbonyl protonated ketones having a cyclopentadiene carbocyclic ring are energetically less favourable than those having a cyclopentane or cyclopentene carbocyclic ring. From the values of the chemical shift of the $=\overset{+}{\text{O}}\text{H}$ protons it is concluded that the C-O bond remains largely a double bond. Three cyclopentadithiophens are easily protonated in $\text{CF}_3\text{CO}_2\text{H}$ at -15° at corresponding positions in the *b*-annulated thiophen ring. The absorption frequencies in the electronic absorption spectra of these protonated cyclopentadithiophens are in good agreement with transition energies calculated by PPP methods.

THE study of the n.m.r. spectra of stable carbonium ions in extremely strong acids has given much information about these ions,¹⁻⁸ *i.e.*, the site of protonation, the conformation, the basicity, and the reactions which they undergo. Thiophen and alkyl-substituted thiophens^{9,10} are protonated at the α -carbon atom, whereas in thienyl ketones¹¹ the oxygen atom is the most basic position. Diprotonation is reported to occur with mesityl 2-thienyl ketones,¹¹ where the protons are attached to the carbonyl group and the mesityl ring. In neither case was sulphur protonation observed.

Our interest in protonated cyclopentadithiophenones was partly based on the assumption that they might provide systems related to the anti-Hückel dithienyl cyclopentadienyl cations, *e.g.* (A). The corresponding

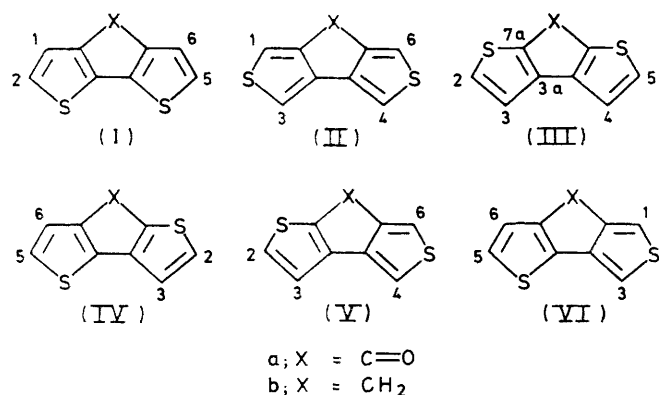


anions have been studied.¹² The simple cations obtained from the alcohols by reaction with acid [reaction (1)]



proved to be unstable. The cations probably react with the thiophen ring of neutral molecules.¹³ U.v. measure-

ments of cyclopentadithiophenones (Ia)—(VIa) in strong acids gave results that could not be interpreted by assuming simple protonation of the carbonyl group.¹⁴ In order to gather more information about the protonation of the ketones they were studied by n.m.r. spectroscopy in $\text{FSO}_3\text{H}-\text{SbF}_5(1:1)-\text{SO}_2$ at -60° . A comparable study was made of the closely related cyclopentadithiophens (Ib)—(VIb) in order to establish the influence of the carbonyl group. Cyclopentadithiophens (Ib), (IVb), and (VIb) are protonated in the relatively



weak acid $\text{CF}_3\text{CO}_2\text{H}$ at -15° . Compounds (IIb), (IIIb), and (Vb) are insufficiently soluble in this solvent although an intensive colour indicates that protonation takes place to some extent. Decomposition of cyclopentadithiophens occurred when they were dissolved at low temperature in stronger acids, such as H_2SO_4 and $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$.

⁷ R. v. d. Linde, J. W. Dornseiffen, J. U. Veenland, and Th. J. de Boer, *Tetrahedron Letters*, 1968, 525.

⁸ R. v. d. Linde, J. W. Dornseiffen, J. U. Veenland, and Th. J. de Boer, *Spectrochimica Acta*, 1968, **24A**, 2115.

⁹ H. Hogeveen, *Rec. Trav. chim.*, 1966, **85**, 1072.

¹⁰ U. E. Wiersum and H. Wynberg, *Tetrahedron Letters*, 1967, 2951.

¹¹ L. Kaper and Th. J. de Boer, *Spectrochim. Acta*, 1970, **26A**, 2125.

¹² M. J. Janssen and J. de Jong, *Rec. Trav. chim.*, 1967, **86**, 1246.

¹³ G. J. Heeres, Thesis, Groningen, 1972.

¹⁴ P. B. Koster, J. Runsink, and M. J. Janssen, unpublished results.

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¹ H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, 696.

² G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, 1967, **89**, 3582.

³ G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, 1967, **89**, 3586.

⁴ M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 1735.

⁵ T. Birchall and R. J. Gillespie, *Canad. J. Chem.*, 1965, **43**, 1045.

⁶ Th. J. Sekuur and P. Kranenburg, *Tetrahedron Letters*, 1966, 4793.

RESULTS

In general, the n.m.r. spectra are characterized by absorptions of six (cyclopentadithiophenones) and seven (cyclopentadithiophens) protons in three distinct regions.

(1) *The $\overset{+}{\text{O}}\text{H}$ Region.*—The protonated ketones absorb at very low field, δ 13.5–14.7, a region characteristic of $\overset{+}{\text{O}}\text{H}$ protons. The protonated ketone (IIa) displays a second $\overset{+}{\text{O}}\text{H}$ absorption at δ 11.49. The only exception is found with ketone (VIa). Possibly this ketone is not protonated at the carbonyl group, or else rapid exchange occurs with the excess of acid present (see Discussion section).

(2) *The δ 5–11 Region.*—In this region all compounds give absorptions due to five protons. Additional peaks are found for ketones (IIa) and (VIa), which can be combined to sets of four aromatic protons. This second set is present in the standard acid system (IIa) or appears only when the amount of acid is reduced (VIa) and must belong to a second species in solution [*cf.* also the two $\overset{+}{\text{O}}\text{H}$ absorptions in protonated ketone (IIa)]. In all but one of the compounds three protons absorb between δ 7.50 and 10.59 and two protons between δ 5.34 and 6.05. The exception is (IIIa), where five separate protons are found between δ 7.43 and 11.01. All peaks in the δ 5–11 region are present as more or less complicated multiplets.

(3) *The CH_2 Bridge.*—Finally, the cyclopentadithiophens show a singlet (2 H) at δ *ca.* 4 which must belong to the CH_2 bridge. It is shifted to lower field compared to the CH_2 singlet of the neutral compounds by 1 p.p.m. or less.

It is clear from this first survey of the results that all compounds become protonated at the carbon skeleton and ketones (Ia)–(Va) also at the carbonyl group. Apparently in (IIa) this main species is accompanied by a mono-(carbonyl) protonated substance. Obviously in all compounds except (IIIa) carbon protonation takes place at carbon atoms already bearing a hydrogen atom, thus giving rise to the CH_2 absorption between δ 5.34 and 6.05. This range is in accordance with the absorptions found for the CH_2 groups in diprotonated 5-methyl- and 5-methoxy-2-thiophencarboxylic acid¹¹ (δ 5.76 and 5.44, respectively) and in protonated (methyl)thiophens⁹ (δ 5.2–5.4). The spectrum of (IIIa) in region (2) then must be due to a carbon protonated species where the proton is attached to one of the carbon atoms of the central ring.

The structure of the protonated ketones has further been elucidated with the aid of double resonance techniques and the known thiophen ($J_{2,3}$ *ca.* 5 and $J_{2,5}$ *ca.* 2 Hz) and protonated thiophen coupling constants⁹ ($J_{2,3}$ 4 and $J_{2,5}$ 2.4 Hz). The assignment of all protons for the individual ketones is as follows.

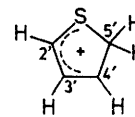
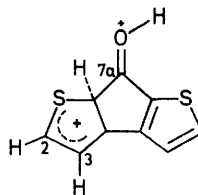
Compound (Ia).—In the spectrum of protonated (Ia) the resonances at δ 8.93 and 8.06, because of their thiophen 2,3 coupling of 5.0 Hz, arise from H(5) and H(6) of the non-protonated ring. The resonances at δ 6.03 (2 H) and 8.67 (1 H) are coupled (J 2.0 Hz). From the results of H–D exchange experiments¹⁵ it is clear that protonation occurs at the α -position. The CH_2 group shows a long range coupling with H(5) (J 1 Hz) which fortifies the supposition of α -carbon protonation.

Compound (IIa).—On the basis of peak integration the two protonated forms of ketone (IIa) are assigned to di- (A, 62%) and mono-protonated (B, 38%) ketone. The $\overset{+}{\text{O}}\text{H}$

¹⁵ P. B. Koster, M. J. Janssen, and E. A. C. Lucken, *Spectroscopy Letters*, 1973, 6, 253.

proton in mono-(carbonyl)protonated ketone (IIa) is less deshielded than in the case of diprotonation. Ketone (IIa; B) is stabilized by an allylic type of resonance, which resonance stabilization is responsible for the difference in chemical shift of $\text{H}_B(1)$ (δ 8.45) and $\text{H}_B(3)$ (7.13). The resonance of $\text{H}_B(1)$ is found to be shifted downfield whereas that of $\text{H}_B(3)$ shows only a small (upfield) shift as compared with the chemical shifts of, respectively, δ 7.88 and 7.30 in SO_2 at -60° . In diprotonated ketone (IIa; A) the resonances at δ 8.54 and 8.98 are coupled with J 1.5 Hz, a normal value for thiophen 2,5 coupling, and, therefore, must belong to the non-protonated ring. Protonation is thought to occur at position 3, because this position is not subject to conjugative deactivation of the carbonyl group. Moreover, H–D exchange experiments have shown that only H(3) and H(4) are exchanged against deuterium in $\text{DCl}-\text{CH}_3\text{CO}_2\text{D}$.¹⁵ The large deshielding of $\text{H}_A(1)$, δ 10.59, demonstrates that the positive charge, brought into the thiophen ring by the captured proton, resides for the greater part in that ring. Due to the mode of annulation of the thiophen rings, the conjugative interaction between these two rings is small.

Compound (IIIa).—The n.m.r. spectrum of protonated ketone (IIIa) deviates somewhat from the other spectra.



$$\delta(\text{H}_{7a}) \ 7.43 \ J_{7a,2} \ 2.5 \text{ Hz}$$

$$\delta(\text{H}_2) \ 11.01 \ J_{3,2} \ 4.0 \text{ Hz}$$

$$\delta(\text{H}_3) \ 8.13$$

$$\delta(\text{H}_{5'}) \ 5.44 \ J_{5',2} \ 2.4 \text{ Hz}$$

$$\delta(\text{H}_{2'}) \ 11.27 \ J_{2',3'} \ 4.0 \text{ Hz}$$

$$\delta(\text{H}_{3'}) \ 8.23$$

Chemical shifts and coupling constants of protonated ketone (IIIa) and thiophen

Eight protons are observed indicating that diprotonation has occurred but no CH_2 absorption appeared. The absence of this resonance fits into the negative results of the attempted deuteration in $\text{CH}_3\text{CO}_2\text{D}-\text{DCl}$.¹⁵ The deactivating influence of the carbonyl group prevents proton attack at the α -carbon atom. Double resonance showed that the doublets at δ 9.58 and 8.04 (J 4.8 Hz) belong together and must be due to H(5) and H(4) of the non-protonated ring. Irradiation at the multiplet at δ 11.01 caused the doublets at δ 7.43 (J 2.5 Hz) and 8.13 (J 4.0 Hz) to collapse to a singlet and the multiplet collapsed to a doublet (J 2.5 Hz) when irradiated at δ 8.13.

Because of the absence of a CH_2 group the extra proton must be attached to the carbocyclic ring. This causes the attacked carbon atom to become sp^b hybridized and the plane of the thiophen ring then is, as shown by study of models, bent *ca.* 30° out of the plane of the rest of the molecule. Therefore the positive charge will be localized primarily on the attacked thiophen ring which may be considered to have properties of protonated thiophen itself. In principle both positions 3a and 7a may be considered for the position of the captured proton but for reasons of charge repulsion position 7a is considered as the more likely. This assignment is supported by the similarity of the chemical shifts and coupling constants of the ring protons and the

values for the corresponding protons in protonated thiophen⁹ (see Figure).

Because of the deshielding effect of the positively charged carbonyl group the chemical shift of H(7a) is much larger than H(5') in protonated thiophen. The similarity of the coupling constants and chemical shifts of H(2), H(3), and the corresponding protons in protonated thiophen, however is striking.

Compound (IVa).—The spectral data of diprotonated ketone (IVa) show a close similarity to those of the corresponding protons of diprotonated ketones (Ia) and (IIIa). Clearly, the thiophen ring corresponding to that in ketone (Ia) is protonated.

Compound (Va).—Because of decomposition only a badly resolved spectrum of protonated ketone (Va) could be obtained. Diprotonation occurs as shown by the presence of signals for the $\overset{+}{\text{O}}\text{H}$ proton at δ 13.6 and the CH_2 group at δ 5.7. The two resonances with a coupling constant of 5 Hz show that the *c*-annulated ring is protonated.

Compound (VIa).—In the n.m.r. spectrum of ketone (VIa) in an acidic mixture with a large excess of acid five protons are observed. Irradiation at the CH_2 peak (δ 6.01) caused the multiplet at δ 9.15 to collapse to a singlet at 9.15 and a doublet at 9.16 (J 1.6 Hz). Irradiation at the multiplet shows coupling with the peak at δ 9.44 (J 1.6 Hz) and the CH_2 group (J 1.6 Hz). Position 5 is protonated; this assignment is consistent with H-D experiments showing H(5) to be exchanged before H(3). The resonance at δ 9.44 has been assigned to H(3) because of its conjugative interaction with the positively charged position 6. An $\overset{+}{\text{O}}\text{H}$ proton signal could not be observed. Probably protonation of the carbonyl group does take place but rapid exchange between this proton and the solvent prevents its observation. The large chemical shift of H(1) (δ 9.16) substantiates this idea. Using a small excess of acid, the same spectrum is obtained together with an additional absorption of the same intensity. This additional absorption consists of two doublets at δ 6.97 and 7.13 (J 5.5 Hz) and two doublets at 7.03 and 7.95 (J 1.6 Hz). These spectral data are close to those of ketone (VIa) in acetone.¹⁶ The absorption may be attributed to non-protonated ketone. The theoretical possibility of mono(carbonyl)-protonation, the absence of the $\overset{+}{\text{O}}\text{H}$ proton being ascribed to rapid exchange with solvent protons, is improbable, because if the carbonyl group were protonated, the chemical shift of H(1) (δ 7.95) is expected to be larger.

The n.m.r. spectrum of protonated fluorenone shows two $\overset{+}{\text{O}}\text{H}$ resonances at δ 14.02 and 12.47. The intensity ratio between the two peaks is *ca.* 1 : 6. The larger $\overset{+}{\text{O}}\text{H}$ resonance is assigned to mono- and the smaller to di-protonated fluorenone. The conclusions of the earlier studies of fluorenone protonated in H_2SO_4 ^{17,18} which presumed protonation of the carbonyl group, are thus confirmed. Probably ring protonation occurs on the central ring because a CH_2 group is not observed.

The pattern of the spectrum of (Ib) in $\text{CF}_3\text{CO}_2\text{H}$ at -15° is very similar to that of ketone (Ia) in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ at -60° . As in diprotonated ketone (Ia) coupling exists between H(2) and H(5) which protons absorb at higher field because of the missing positive charge of the $\overset{+}{\text{O}}\text{H}$ group. Owing to the positive charge in the dithienyl portion of the

molecule, the bridge CH_2 protons shift 0.7 p.p.m. downfield compared to the chemical shift of these protons in the neutral parent compound (solvent CCl_4). Because two α -positions are available in compound (IVb) some question may arise about the carbon atom that is protonated. Protonation at position 5 is preferred to protonation at position 2 because cyclopentadithiophen (Ib) is easily protonated and (IIIb) not (or only to a small extent) in $\text{CF}_3\text{CO}_2\text{H}$. Moreover localization energy calculations (see below) indicate the same position of attack. The downfield shift of the bridge CH_2 protons in acid compared to the chemical shift in CCl_4 is about the same (0.75 p.p.m.) as observed for (Ib). Due to low solubility, the n.m.r. spectrum of cyclopentadithiophen (VIb) is poorly resolved but the main features are identifiable. Seven protons are observed and ring protonation must have occurred at the *b*-annulated ring because the thiophen 2,3 coupling of 5.0 Hz has disappeared. The CH_2 resonance at δ 5.34 and the downfield shift of the bridge CH_2 protons compared with the chemical shift in CCl_4 are in accordance with the assumption of ring protonation. As a result of the inadequate resolution of the spectrum only a tentative assignment of the other peaks can be made. The highest field peak may be assigned to H(1) because no mesomeric structures can be drawn in which the positive charge is located at position 1. The final assignment of all protons and coupling constants is given in Table 1.

DISCUSSION

Cyclopentadithiophenones.—The observations which have been presented point to a higher basicity of the dithienyl portions of cyclopentadithiophenones than the diphenyl part of fluorenone. This follows from the relative difficulty of protonating fluorenone on a ring carbon atom. The experiments ascertain the sequence of addition of both protons to ketone (IIa) and fluorenone. These ketones are protonated first at the carbonyl group, which follows from the observed equilibria between di- and mono-(carbonyl) protonated species. Ring protonation of ketone (IIIa) is observed to occur at the carbocyclic ring even when it induces distortion of the flat π -system. Because of the loss of resonance energy due to this deformation it is reasonable to suppose that the first protonation takes place at the carbonyl group. The assignment of the spectrum of protonated ketone (VIa) is rather speculative, and only diprotonated ketones (Ia), (IVa), and (Va) have been observed. This prevents the estimation of the sequence of protonation of ketones (Ia) and (IVa)—(VIa). Factors that influence the sequence of addition of both protons are the basicity of the dithienyl portion of the molecule and the basicity of the carbonyl group. Turnbo *et al.*¹⁹ found that thiophen stabilizes positive charges better than benzene from the relative stabilities of some diarylmethyl cations. The basicity of the carbonyl group depends, among other things, on the stability of the 7-hydroxycyclopentadithiophen cations (j). 7-Hydroxycyclopentadithiophen

¹⁷ R. Stewart, M. R. Granger, R. B. Moodie, and R. J. Muenster, *Canad. J. Chem.*, 1963, **41**, 1065.

¹⁸ J. Michl, R. Zahradnik, and P. Hochmann, *J. Phys. Chem.*, 1966, **70**, 1732.

¹⁹ R. G. Turnbo, D. L. Sullivan, and R. Pettit, *J. Amer. Chem. Soc.*, 1964, **86**, 5630.

¹⁶ P. Jordens, G. Rawson, and H. Wynberg, *J. Chem. Soc. (C)*, 1970, 273.

cations (Ia; j), (IIIa; j), and (IVa; j) are expected to be energetically less favourable than (IIa; j), (Va; j), and (VIa; j). The carbocyclic rings of (Ia; j), (IIIa; j), and (IVa; j) may be considered as formal cyclopentadienyl cations which are known to be very unstable.²⁰

were derived from an X-ray study of cyclopentadithiophen (Ib).²¹ Electronic repulsion integrals were evaluated with the aid of the Nishimoto and Mataga²² approximation. The variable β modification of the PPP method was used.²³ Most of the parameters (see Table 2) used

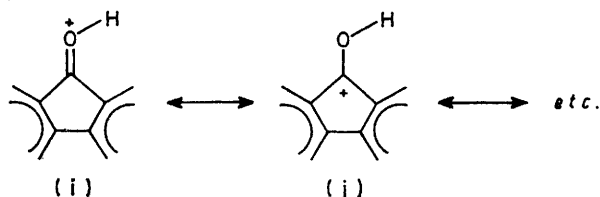
TABLE 1

Chemical shifts (δ) and coupling constants (Hz) of protonated cyclopentadithiophenones, fluorenone, and cyclopentadithiophens

Compound	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)
(Ia)	8.67(1 H) ^a	6.03(2 H) ^b	7.13(2 H) ^d	(7.13)	8.93(1 H) ^c	8.06(1 H) ^d
(IIa)	8.45(2 H) ^d 10.59(1 H) ^a		5.68(2 H) ^d 8.13(1 H) ^d	8.54(1 H) ^d 8.04(1 H) ^d		(8.45) 8.98(1 H) ^d
(IIIa)		11.01(1 H) ^b	8.13(1 H) ^d		9.58(1 H) ^d	
(IVa)		9.33(1 H) ^d	8.22(1 H) ^d		6.05(2 H) ^d	8.64(1 H) ^a
(Va)		9.1(1 H) ^d	7.7(1 H) ^d	5.7(2 H) ^f		8.9(1 H) ^f
(VIa)	7.95(1 H) ^d 9.16(1 H) ^g		7.03(1 H) ^d 9.44(1 H) ^d		7.13(1 H) ^d 6.01(2 H) ^d	6.97(1 H) ^d 9.15(1 H) ^g
Fluorenone						
(Ib)	7.98(1 H) ^a	5.44(2 H) ^h			8.91(1 H) ^c	7.63(1 H) ^d
(IVb)		7.69(1 H) ^d	7.88(1 H) ^d		5.45(2 H) ^d	8.02(1 H) ^a
(VIb)	7.50(1 H) ^f		8.93(1 H) ^f		5.34(2 H) ^f	8.10(1 H) ^f
Compound	H(7a)	CH ₂ (bridge)	C=OH ⁺	State of protonation	Coupling constants	
(Ia)			14.65(1 H) ^e	Di	$J_{1,2}$ 2.0; $J_{2,5}$ 1; $J_{5,6}$ 5.0	
(IIa)			11.49(1 H) ^e	Mono	$J_{1,3}$ $J_{4,6}$ 2.0	
(IIIa)	7.43(1 H) ^d		13.99(1 H) ^e	Di	$J_{1,3}$ 1; $J_{4,6}$ 1.5	
(IVa)			13.50(1 H) ^e	Di	$J_{2,3}$ 4.0; $J_{4,5}$ 4.8; $J_{2,7a}$ 2.5	
(Va)			13.83(1 H) ^e	Di	$J_{2,3}$ 4.7; $J_{5,6}$ 1.6	
(VIa)			13.6(1 H) ^e	Di	$J_{2,3}$ 5; $J_{4,6}$ small	
Fluorenone			12.47 ^e	Non(mono)	$J_{1,3}$ 1.6; $J_{5,6}$ 5.5	
(Ib)			14.02 ^e	Di(mono)	$J_{1,3}$ 1.6; $J_{5,6}$ 1.6	
(IVb)		4.12(2 H) ^e		Mono	$J_{1,2}$ 2.0; $J_{2,5}$ 1.0; $J_{5,6}$ 4.9	
(VIb)		4.32(2 H) ^e		Mono	$J_{2,3}$ 5.2; $J_{5,6}$ 2.0	
(VIb)		3.92(2 H) ^e		Mono	Not resolved	

^a Triplet. ^b Pair of doublets. ^c Doublet of triplets. ^d Doublet. ^e Singlet. ^f Broadened peak. ^g Doublets due to H(1) and H(6) partly coincide. ^h Broadened doublet.

Carbonium ions (IIa; j), (Va; j), and (VIa; j) are stabilized by allylic type of resonance.



In order to investigate whether the difference in behaviour of the isomeric ketones towards protonation could be explained in terms of MO theory, PPP calculations have been carried out. In these calculations, limited configurational interaction was employed by taking into account all singly excited states corresponding to excitation of an electron from the four highest occupied orbitals into the four lowest vacant orbitals. The geometry of the protonated species was considered to be the same as that of the original compounds, which in turn

²⁰ A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 269.

²¹ P. B. Koster, F. van Bolhuis, and G. J. Visser, *Acta Cryst.*, 1970, **B26**, 1932.

²² K. Nishimoto and N. Mataga, *Z. phys. Chem. (Frankfurt)*, 1957, **12**, 335.

were taken from the groups of Zahradnik^{24,25} and Nishimoto.²⁶

TABLE 2

Semiempirical parameters for the PPP calculations

Atom	I_X (eV)	γ_{XX} (eV)	β_{ex} (eV)
C	11.22	10.53	-0.51 p -1.84
C(-CH ₂)	10.76	10.53	-0.51 p -1.84
S	20.00	10.84	-1.625
S(-CH ₂)	19.54	10.84	-1.625
O	13.60	11.30	-0.56 p -2.20
O ⁺	30.88	20.03	-0.56 p -2.20

In the calculations the stability of the protonated species is presumed to be proportional to the difference in π -energy of these species and the corresponding ketone. Calculations for ring protonated ketone (IIIa) were carried out for attack at position 2. The deformation from the flat ring system after protonation of this compound at the carbocyclic ring, as has been found, prevents the calculation of a reliable value for protonation at this position. The calculated quantities, given in Table 3,

²³ K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, 1966, **4**, 155.

²⁴ J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, 1968, **72**, 3975.

²⁵ R. Zahradnik, review lecture presented at the University of Groningen, 1967.

²⁶ K. Nishimoto, *Theor. Chim. Acta*, 1967, **7**, 207.

illustrate the qualitative discussion given above. The main feature is that carbonyl protonated ketones (IIa), (Va), and (VIa) are energetically more favourable than ketones (Ia), (IIIa), and (IVa), protonated at oxygen. The calculations show clearly that position 2 of ketone (IIIa) is unfavourable for protonation.

From the calculations the preference of oxygen protonation over carbon protonation decreases in the sequence (IIa) > (VIa) > (Va) > (Ia) > (IVa). From the experimental results it cannot be decided whether

unfavourable since no mesomeric structures can be drawn in which the positive charge is spread over the other thiophen ring. This can be done for a α -protonated 2-thienyl fragment and the resonance stabilization is expected to be larger in this case. However, following these arguments compounds (IIb) and (VIb) protonated at position 3 and (Vb) protonated at position 4 should be stable. The reasons for the lack of formation of a high concentration of protonated cyclopentadithiophens (IIb) and (Vb) therefore must be sought elsewhere.

TABLE 3

Stabilities of some series of protonated ketones in eV with respect to most stable species of each series as calculated by the PPP method

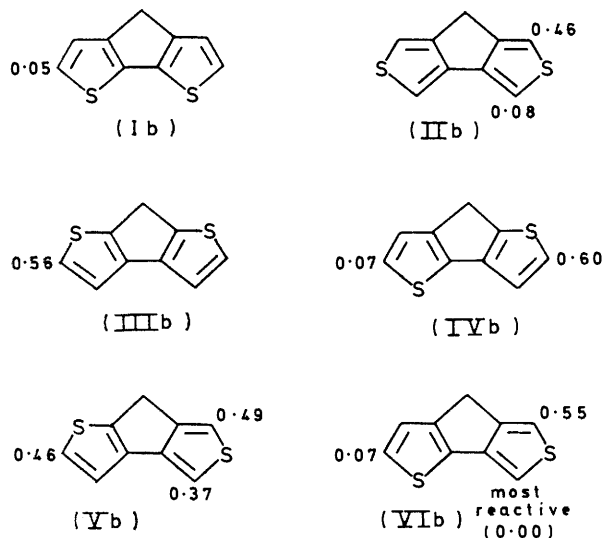
Protonated ketone (position of ring protonation)	(Ia)(2)	(IIa)(3)	(IIIa)(2)	(IVa)(5)	(Va)(4)	(VIa)(5)
O-Protonated ketone	0.295	0.000	0.423	0.367	0.097	0.036
Ring-protonated ketone	0.000	0.016	0.501	0.026	0.062	0.019

somewhere in this sequence carbon protonation will become preferred.

The extremely low field chemical shifts of the $=\overset{+}{O}H$ protons of diprotonated cyclopentadithiophenones and fluorenone are comparable with those found for protonated aliphatic ketones for which it was concluded that the C-O bond remains largely double.¹⁻³ It is therefore likely that in diprotonated ketones and fluorenone the C-O bond largely retains its double bond character as well. Delocalization of the positive charge of the oxygen atom will then take place only to a small extent. The $=\overset{+}{O}H$ proton of monoprotated ketone (IIa) is less deshielded than in the case of diprotonation. This means contribution to a greater extent of structure (IIa; j) and reduced double bond character of the C-O bond. The π -bond orders of the C-O bond of mono- and diprotonated ketone (IIa) as calculated by the PPP method differ considerably and are 0.58 and 0.90, respectively. The second protonation of ketone (IIa) takes place at a ring carbon atom and the extra positive charge gives rise to decreased delocalization of the carbonylcarbonium ion in the ring system. This is reflected in the resonance of the $=\overset{+}{O}H$ proton which is shifted 2.5 p.p.m. downfield.

Cyclopentadithiophens.—The observations presented demonstrate clearly that compounds (Ib), (IVb), and (VIb) are much stronger bases than the carbocyclic analogue fluorene because fluorene dissolves poorly in CF_3CO_2H and its saturated solution is colourless. This conclusion is consistent with the results of protonation of cyclopentadithiophenones and the observations of Turnbo *et al.*¹⁹ Cyclopentadithiophens may be considered as dithienyl derivatives. Cyclopentadithiophens (IIb), (IIIb), and (Vb) then are 3,3'-dithienyl derivatives. This indicates the basicity of a 2-thienyl group in cyclopentadithiophens to be higher than that of different annulated 3-thienyl portions of these compounds. It is reasonable that protonation at a *b*-annulated 3-thienyl portion of a cyclopentadithiophen, at positions 6 of (IIb) and (Vb) and position 1 of (VIb) is energetically

Localisation energies for proton attack at α -positions as calculated by the PPP method (for parameters, see Table 2) are shown in the Scheme. The data are given



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in eV with respect to the most reactive position of the series of compounds. Localization energies for β -positions are calculated to be much higher and are not given. The compounds which are protonated in CF_3CO_2H are calculated to be the most reactive. Moreover, (IIb) is predicted to be reactive at position 3. The localization energies thus do not explain the lack of protonation of compound (IIb). The position of protonation of (VIb) is not correctly predicted, but the difference in reactivity of positions 3 and 5 is calculated to be small.

U.v. Spectra of Protonated Cyclopentadithiophens.—The absorption spectra of cyclopentadithiophens (Ib), (IVb), and (VIb) in CF_3CO_2H at -15° , which could be taken from 270 nm (the cut-off wavelength of CF_3CO_2H) upwards, show maxima given in Table 4. The spectra did not change with time, in contrast to those of solutions of compounds (IIb), (IIIb), and (Vb) and followed the

Lambert-Beer law so that complete conversion into the conjugate acids took place in the concentration ranges applied. After diluting the acidic solutions with ethanol, cyclopentadithiophens (Ib), (IVb), and (VIb) were regenerated in 95–100% yield as indicated by their u.v. spectra. Transition energies and intensities, calculated by the PPP method, for protonated cyclopentadithiophens (Ib), (IVb), and (VIb) are shown in Table 4.

TABLE 4
Experimental and calculated transitions of
protonated cyclopentadithiophens

Protonated cyclopentadithio- phens	Experimental		Calculated	
	kk (nm)	<i>E</i>	kk (nm)	<i>f</i>
(Ib)	26.6(376)	34 590	24.7(405)	0.80
	27.8(360)(sh)	26 740	26.0(384)	0.14
	31.9(313)	7 760	29.5(339)	0.23
(IVb)	26.4(378)(sh)	14 140	23.1(433)	0.10
	29.5(339.5)	24 700	26.8(374)	0.65
	32.8(305)(sh)	8 310	30.0(333)	0.24
(VIb)	21.2(472)	11 140		
	21.9(457.5)	11 320	22.4(447)	0.06
	22.5(445)(sh)	7 825		
	27.6(362)	21 600	26.6(376)	0.77
	31.2(321)	7 060	29.9(334)	0.26

1 kk = 1 000 cm⁻¹.

Although practically all the absorption bands are calculated to be at too low energy, the main features of the spectra are nicely reproduced. The spectrum of each protonated compound consists of one very strong band and two weaker bands at energies below 37 kk (37 000 cm⁻¹). The strong absorption band of protonated compound (Ib) is the first band, whereas in protonated compounds (IVb) and (VIb) the second band is the strong one. These facts are in excellent agreement with the calculated transitions. The calculated weak absorption of (Ib) at 26.0 kk is partly hidden in the strong 26.6 kk band and found as a weak shoulder at 27.8 kk. The observed 31.9 kk band may be safely regarded as the calculated 29.5 kk transition. The calculated medium, 30.0 kk, and low intensity, 23.1 kk, bands of protonated (IVb) are found as shoulders at, respectively, 32.8 and 26.4 kk. In protonated (VIb) the first transition is calculated to be appreciably weaker than is actually found. Possibly a small amount of compound (VIb) is protonated at position 3 and thus responsible for the intensity of this band. The latter carbonium ion is predicted to have a very strong band (*F* 0.94) at 20.9 kk. In contrast to the agreement of the experimental and calculated values for protonated compounds (Ib), (IVb), and (VIb), the spectra of solutions of (IIb), (IIIb), and

(Vb) differ totally from the spectra as calculated for the protonated compounds and it is probable that these spectra are derived not from the transient protonated cyclopentadithiophens but rather from intermediates in decomposition reactions.

EXPERIMENTAL

Cyclopentadithiophenones and cyclopentadithiophens were obtained from stock or prepared by standard methods^{6,27} and purified by sublimation *in vacuo*. SbF₆ (A.C.S., Soesterberg), FSO₃H (K and K Laboratories), and CF₃CO₂H (Baker Chemicals) were distilled at low pressure under nitrogen.

N.m.r. spectra were measured on Varian A 60D, HA 100, or XL 100 spectrometers with variable temperature probes. Tetramethylsilane was used as external (cyclopentadithiophenones and fluorenone) or internal (cyclopentadithiophens) standard.

Samples of protonated cyclopentadithiophenones and fluorenone were obtained by adding very rapidly ketone (50–100 mg) to a solution of an equimolar mixture of FSO₃H and SbF₆ (0.25 ml) in SO₂ (0.75 ml) at -70°. Immediately after the mixture was made up it was shaken vigorously during a few seconds until a clear solution was obtained. Protonated cyclopentadithiophens were prepared by the same technique in CF₃CO₂H at -15°. N.m.r. spectra of the samples prepared in this manner could be recorded several times without appreciable chemical shift and intensity differences for 5–40 min after the preparation of the sample solutions. Apparently protonation is fairly rapid (complete protonation takes place before a spectrum can be recorded) and, under the experimental conditions, the ions are fairly stable. At higher temperatures the protonated compounds decomposed, probably into polymeric products.

U.v. spectra were recorded on a Cary 15 spectrophotometer equipped with a Cryoson TRL 1B variable temperature control unit. MO Calculations were performed on the Telefunken TR-4 Computer of the Computing Center of the University, Groningen. The Algol programs were based on the Householder method for the determination of eigenvalues and eigenvectors.

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²⁷ A. Kraak, A. K. Wiersema, P. Jordens, and H. Wynberg, *Tetrahedron*, 1968, **24**, 3381.