Radical-anions of Cyclopentadithiophenones and Dithienothiophen 7,7-Dioxides.† Electron Spin Resonance Spectra and Polarographic Half-wave Reduction Potentials

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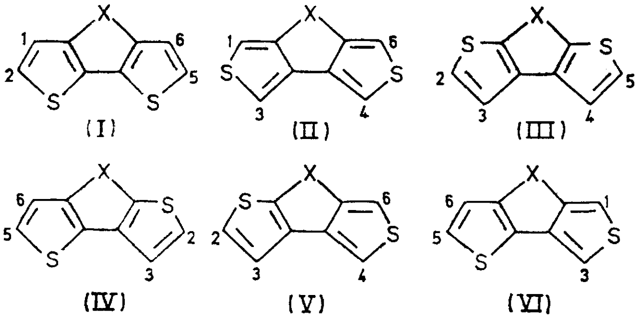
The e.s.r. spectra of the radical-anions of cyclopentadithiophenones, generated by electrolysis in acetonitrile and (or) dimethylformamide, and of three dithienothiophen 7,7-dioxides, produced by potassium reduction in dimethoxyethane, have been recorded. Assignment of the hyperfine splitting constants is based on the hyperfine splitting constants of deuteriated derivatives. The polarographic half-wave reduction potentials of cyclopentadithiophenones were determined in dimethylformamide. Cyclopentadithiophenones appear to be reduced by a reversible one-electron transfer in the first reduction step. An attempt to relate the hyperfine splitting constants to computed spin densities by Hückel–McLachlan calculations is only partially successful.

E.s.r. studies of radical-anions containing the thiophen ring have recently attracted considerable attention.[1-9] The results have been reviewed.[10,11] The emphasis has been chiefly on the possible role of sulphur $3d$ orbitals [1-5] and on conformation properties.[5-8]

Sulphur $3d$ orbitals are probably of minor importance in the ground state of thiophen [12,13] but are expected to play a more important part in excited states. Therefore, the participation of $3d$ orbitals should be most demonstrable in molecular species in which electrons occupy orbitals of higher energies. Important information may be gained from the e.s.r. spectra and polarographic half-wave reduction potentials furnishing details of, respectively, the electron spin distribution and the energy of the lowest anti-bonding orbital. The radical-anions of cyclopentadithiophenones (Ia)—(VIa) and dithienothiophen 7,7-dioxides (Ib)—(VIb) seemed suitable species for a study of possible participation of $3d$ orbitals.



(I) (II) (III)

(IV) (V) (VI)

a; X = C=O
b; X = SO_2

RESULTS AND DISCUSSION

E.s.r. Spectra of Cyclopentadithiophenones.—Radical-anions of cyclopentadithiophenones (Ia)—(VIa) were obtained by electrolytic reduction in *NN*-dimethylformamide (DMF) and acetonitrile. In order to assign the hyperfine splitting constants the e.s.r. spectra of several deuteriated ketones were recorded. On deuteriation of cyclopentadithiophenones in a mixture of deuterioacetic acid and deuterium chloride deuterium was incorporated in those thiophen rings in which the carbonyl group occupies a β-position. Thus all ketones except (IIIa) took up deuterium. The site of deuteriation always proved to be the 5-position relative to the 3-position of the carbonyl group in the thiophen portions of the molecules. This was proved by n.m.r. spectroscopy and, independently, by degradation of (IIa). No exchange was ever found of hydrogen atoms which are attached to double bonds directly conjugated with the carbonyl group. A deuteriated derivative of (IIIa) was obtained by synthesis using deuteriated starting materials. The measurement of the spectra of the radical-anions of the deuteriated ketones (IIa), (Va), and (VIa) was strongly hampered by D–H exchange during electrolysis.[14] The hyperfine splitting constants and g values of the radical-anions of cyclopentadithiophenones are compiled in Table 1.

For the symmetrical compounds (Ia)—(IIIa) the assignment of the hyperfine splitting constants follows unambiguously from the data for the deuteriated derivatives. The hyperfine splitting constants of the unsymmetrical ketones were assigned with the help of the deuteriated derivatives and by analogy with the

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† In this study the numbering of the cyclopentadithiophenones and the dithienothiophen dioxides has been chosen so that the oxo-functions are always at position 7

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symmetrical compounds. Thus, by analogy with the hyperfine splitting constants of ketones (Ia) and (IIIa), the 0·50 G hyperfine splitting constants of ketone (IVa) are assigned to 3-H and 6-H and that of 2·61 G to 2-H. Likewise, after comparison of ketone (Va) with ketones (IIa) and (IIIa), the hyperfine splitting constant of 1·19 G is assigned to 3-H. No decision, however, can be made about the assignment of the hyperfine splitting constants of 4·74 and 3·54 G to 2- or 6-H. Because of the similarity of 6-H of ketone (VIa) with 1-H in ketone (Ia) and of 1-H of (VIa) with 1-H in ketone (IIa), the hyperfine splitting constants of 0·93 and 3·94 G of (VIa) are ascribed to 6- and 1-H, respectively.

TABLE 1

Hyperfine splitting constants and *g* values of cyclopentadithiophenone and dithienothiophen 7,7-dioxide radical-anions

Compound	Solvent	*g* Value	Splitting constants (G) $\lvert a_1\rvert$	$\lvert a_2\rvert$	$\lvert a_3\rvert$	$\lvert a_4\rvert$	$\lvert a_5\rvert$	$\lvert a_6\rvert$
Ketones								
(Ia)	CH_3CN	2·0045	0·30	0·59			0·59	0·39
2,5-Dideuterio- (Ia)	CH_3CN		0·31	s			s	0·31
(IIa)	DMF	2·0040	5·77		0·51	0·51		5·77
3,4-Dideuterio- (IIa)	CH_3CN		5·78		s	s		5·78
(IIIa)	CH_3CN	2·0049		2·68	0·57	0·57	2·68	
2,5-Dideuterio- (IIIa)	CH_3CN			0·41 (d)	0·58	0·58	0·41 (d)	
(IVa)	CH_3CN	2·0037		2·61	0·50		0·19	0·50
5-Deuterio- (IVa)	CH_3CN			2·61	0·48		s	0·48
(Va)	CH_3CN	2·0040		4·74 (3·54)	1·19	0·87		3·54 (4·74)
	DMF	2·0040		4·75 (3·40)	1·16	0·82		3·40 (4·75)
4-Deuterio- (Va)	CH_3CN			4·70 (3·53)	1·20	s		3·53 (4·70)
(VIa)	CH_3CN	2·0036	3·94		1·39		0·46	0·93
3,5-Dideuterio- (VIa)	CH_3CN		~3·7		s		s	~0·8
Sulphones								
(Ib)	DMF	2·0048	0·73	2·89			2·89	0·73
2,5-Dideuterio- (Ib)	DME		0·66	0·42 (d)			0·42 (d)	0·66
(IIIb)	DME	2·0037		2·53	0·57	0·57	2·53	
2,5-Dideuterio- (IIIb)	DME			0·39 (d)	0·57	0·57	0·39 (d)	
(IVb)	DME	2·0052		2·39	0·48 (0·32)		1·63	0·32 (0·48)
2,5-Dideuterio- (IVb)	DME			0·37 (d)	0·48 (0·32)		0·25 (d)	0·32 (0·48)

s = small, d = deuterium splitting

Polarographic Reduction of Cyclopentadithiophenones.—The polarographic half-wave reduction potentials of cyclopentadithiophenones were determined in anhydrous DMF with 0·15M-tetra-n-butylammonium iodide as the supporting electrolyte. The potentials were measured with reference to an internal mercury pool anode which has a potential of —0·55 V *versus* the saturated calomel electrode.[15] Two waves were observed for each compound. Polarographic data are given in Table 2 for the first reduction waves only. A fairly good straight line was obtained plotting the square root of the corrected height of the mercury column against the diffusion current indicating a diffusion-controlled first reduction step.[16] The logarithmic analysis of the polarograms gave straight lines of slopes 66—73 mV. These slopes compare well with the values 70—90 and 60—70 mV observed for monoelectronic reduction of aromatic hydrocarbons[17] and dithienothiophen 7,7-dioxides[18] in DMF and are not too far from the value of 59 mV expected theoretically for a reversible one-electron addition.[19] Moreover, anthracene, which is known to have a reversible one-electron first reduction step in DMF,[17] gave a slope of 65·5 mV when reduced under identical conditions. Its I_d value of 1·99 μA l mmol^{-1} mg$^{-2/3}$ s$^{1/2}$ is close to those given in Table 2. Since the diffusion constants of anthracene, dithienothiophen 7,7-dioxides, and cyclopentadithiophenones are of comparable magnitude we may assume that the cyclopentadithiophenones in the first reduction step are reduced by a reversible one-electron transfer. Evidence for the formation of a radical-anion in this first step was further demonstrated by the e.s.r. spectra of the radical-anions formed by electrolysis at the top of the first wave. The division of the cyclopentadithiophenones into three groups of compounds, owing to the character of the inner ring, is well illustrated in the $E_{\frac{1}{2}}$ values of these compounds. Ketones (Ia), (IIIa), and (IVa), having a formal cyclopentadiene ring, are easily reduced. Ketones (Va) and (VIa) are reduced with more difficulty, and reduction of the least aromatic ketone (IIa), with a formal cyclopentane ring, requires the highest potential. A similar situation exists for the dithienothiophen 7,7-dioxides.[18]

E.s.r. Spectra of Dithienothiophen 7,7-Dioxides.—Dithienothiophen 7,7-dioxides can be reduced electrolytically in anhydrous DMF, their polarographic half-wave reduction potentials (*versus* the mercury pool) lying close to —1·0 V for sulphones (Ib), (IIIb), and

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(IVb) and 0·3—0·5 V more negative for the other isomers.[18] However, on electrolytic reduction, only sulphone (Ib) gave an e.s.r. signal. Chemical reduction of saturated solutions of sulphones (Ib), (IIIb), and (IVb) in 1,2-dimethoxyethane (DME) on a potassium mirror at —70° yielded the radical-anions. Attempts to obtain radical-anions from sulphones (IIb), (Vb), and (VIb) failed. Even at —100° in 2-methyltetrahydrofuran (MTHF) attempts to reduce these sulphones were not successful. E.s.r. spectra of deuteriated sulphones were recorded in order to allow assignment of the hyperfine splitting constants. The deuteriated derivatives could be obtained by deuteriation of the precursors of the sulphones, the dithienothiophens, followed by oxidation to the respective sulphones. The assignment of the splitting constants of sulphones (Ib) and (IIIb) follows unambiguously from the data for the deuteriated derivatives.

TABLE 2

Polarographic data of the first reduction wave of cyclopentadithiophenones in anhydrous DMF and the energy coefficients of the lowest vacant MO ($E = \alpha + m_{m+1}\beta$)

Compound	$-E_{\frac{1}{2}}$ (V *vs.* Hg pool)	I_d *	$-m_{m+1}$	
			p Model	*d* Model
(Ia)	0·620	2·51	0·273	0·178
(IIa)	0·965	2·40	0·569	0·317
(IIIa)	0·503	2·12	0·252	0·171
(IVa)	0·545	1·72	0·264	0·175
(Va)	0·795	1·85	0·421	0·246
(VIa)	0·903	1·95	0·464	0·254

* In μA l mmol^{-1} mg$^{-2/3}$ s$^{1/2}$.

The spectrum of dideuteriated sulphone (IVb) allows the assignment of the two smaller splitting constants to 3- and 6-H and the larger ones to 2- and 5-H. By reference to the calculated splitting constants (see later) a tentative assignment of the splitting constants of sulphone (IVb) is presented in Table 1 which summarizes the splitting constants and *g* values of the dithienothiophen 7,7-dioxide radical-anions

To investigate the possibility of sulphones being reduced to the corresponding sulphide radical-anions, some experiments have been carried out to produce radical-anions starting from dithienothiophens. E.s.r. spectra could not be obtained. Recently, Lunazzi *et al.*[20] reported the e.s.r. spectrum of dithieno[2,3-*b*:-2′,3′-*d*]thiophen, the precursor of sulphone (IVb), obtained by generating a steady concentration of the radical-anion on the surface of a sodium–potassium alloy at —100° in DME–tetrahydrofuran (1 : 2). An e.s.r. spectrum different from that of the radical-anion of sulphone (IVb) was obtained, its hyperfine splitting constants being 0·42 (2H), 2·36 (1H), and 2·98 (1H) G. Therefore, the possibility of reduction of the sulphones by potassium to the sulphide radical-anions may be excluded.

The splitting constants of the dithienothiophen 7,7-dioxides are intermediate between the corresponding values of dithienyls [7,8] and cyclopentadithiophenones. This illustrates the limited conjugative ability of the sulphone group in the first excited molecular orbital.

Molecular Orbital Calculations.—Spin density calculations were performed according to the McLachlan [21] method from the Hückel molecular orbitals. The thiophen sulphur atoms are treated using a model in which only the 3*p* orbitals participate in the π system (*p* model) and the model suggested by Longuet-Higgins [22] in which vacant 3*d* orbitals participate as well (*d* model). The sulphone group was treated in the way suggested by De Jong and Janssen.[18] The following MO parameters ($\alpha_X = \alpha_C + h_X\beta_{CC}$ and $\beta_{CX} = k_{CX}\beta_{CC}$) were used: $h_S = 1{\cdot}0$, $k_S = 0{\cdot}7$ for the *p* model [23] and $h_S = 0$, $k_{CS} = 0{\cdot}8$, and $k_{SS'} = 1{\cdot}0$ for the *d* model.[22] $\beta_{SS'}$ In this model represents the resonance integral between two of the pd^2 orbitals. Three pd^2 orbitals in the model of Longuet-Higgins are formed from the $3p_z$ orbital and the 3*d* orbitals with π symmetry ($3d_{yz}$ and $3d_{xz}$), of which two point to the adjoining carbon atoms. For the carbonyl group $h_O = 1{\cdot}5$, $k_{CO} = 1{\cdot}6$, and $h_{C(carbonyl)} = 0{\cdot}1$ and for the sulphone group [18] $h_S = -1{\cdot}4$, $h_O = 1{\cdot}0$, $h_{C(SO_2)} = 0{\cdot}2$, $k_{CS_{xy}} = k_{CS_{yz}} = \pm 0{\cdot}7$, $k_{CS_{xz}} = 0$, $k_{S_{xy}O} = k_{S_{xz}O} \pm 0{\cdot}9$, and $k_{S_{yz}O} = 0$ were used. Hyperfine splitting constants were calculated from the theoretical spin densities using the McConnell relation.[24] The typical aromatic value of —23 G has been taken for the factor *Q* throughout all the calculations. The calculated hyperfine splitting constants are given in Table 3.

TABLE 3

Calculated hyperfine splitting constants (G) of the radical-anions of cyclopentadithiophenones and dithienothiophen 7,7-dioxides ($Q = -23$)

Hyperfine splitting constants	Ketone	*p* Model	*d* Model	Sulphone	*p* Model	*d* Model
a_1	(Ia)	0·16	—0·02	(Ib)	—0·57	—0·63
a_2		0·53	1·36		1·76	2·49
a_1	(IIa)	6·57	2·05	(IIb)	7·93	0·87
a_3		—0·53	—0·46		—1·04	—0·30
a_2	(IIIa)	1·81	2·46	(IIIb)	1·74	2·66
a_3		—0·35	—0·62		—0·63	—0·72
a_2	(IVa)	1·64	2·46	(IVb)	1·83	2·76
a_3		—0·25	—0·60	(IVb)	—0·61	—0·72
a_5		0·05	1·17		1·19	2·24
a_6		0·25	0·05		—0·45	—0·55
a_2	(Va)	3·47	3·11	(Vb)	0·95	0·17
a_3		—1·18	—0·94		3·31	0·75
a_4		2·46	0·23		—1·61	—1·20
a_6		4·14	1·45		4·69	3·90
a_1	(VIa)	4·28	1·36	(VIb)	0·89	0·09
a_3		3·75	0·39		5·83	0·97
a_5		—0·41	0·87		1·20	2·20
a_6		0·15	0·16		—0·75	—0·53

With both *p* and *d* models for the thiophen sulphur atom, the general trend of the hyperfine splitting constants is reproduced.

In a reversible one-electron reduction process a linear relationship between polarographic half-wave reduction

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potentials and the energy coefficients m_{m+1} ($E = \alpha + m_{m+1}\beta$) of the lowest vacant MO is expected for a set of similar compounds.[25,26] Table 2 shows the m_{m+1} values for cyclopentadithiophenones calculated using p and d models for the sulphur atom. The following regression lines were obtained by least-squares methods: $E_{\frac{1}{2}} = 1{\cdot}445m_{m+1} - 0{\cdot}18$, correlation coefficient r 0·98 (p model) and $E_{\frac{1}{2}} = 3{\cdot}142m_{m+1} - 0{\cdot}02$, r 0·96 (d model).

A choice of the p or d model based on these calculations is not possible. More extended calculations, including electron repulsion, are now in progress.

EXPERIMENTAL

E.s.r. Spectra.—E.s.r. spectra were recorded on JES-ME-1X (JEOL), Varian E4, or Varian E3 spectrometers. Radical-anions were generated by electrolysis of 4—6 × 10^{-3}M solutions in CH_3CN or DMF at a mercury cathode at constant potential, *ca.* 0·1 mV from the polarographic half-wave reduction potential. Potentials were measured between the mercury pool cathode and a saturated calomel reference electrode. As supporting electrolyte tetra-n-butylammonium perchlorate was used in a concentration of 0·7M. Dry nitrogen gas, previously freed from oxygen, was bubbled through the solution to remove the dissolved oxygen.

The field sweep was calibrated against a solution of 2,2,6,6-tetramethylpiperidine *N*-oxide in benzene, which has a hyperfine splitting constant a_N of 15·65 G. The g values were calibrated by comparison with the g value of solid diphenylpicrylhydrazyl (g 2·0036).

Radical-anions of some of the deuteriated ketones were obtained by electrolytic reduction in a 10^{-3}M solution at a constant current of 10—25 μA (at much higher voltage). DMF (Baker Chemicals) was repeatedly distilled under N_2 *in vacuo* after drying over anhydrous CaO. Acetonitrile (Baker Chemicals) was repeatedly distilled under N_2 using an effective column. Potassium reduction of the sulphones in DME (Merck) at −70° was accomplished following a procedure described earlier.[1]

Polarography.—The polarographic data were obtained on a Polariter radiometer, type PO4 (Copenhagen) using a water-jacketted cell, thermostatted at 25·0 ± 0·1°. The dissolved oxygen was removed by bubbling dry nitrogen through the solution during 15 min. The dropping mercury electrode had an $m^{2/3}t^{1/6}$ value of 1·70 mg$^{2/3}$ s$^{1/6}$ (open circuit). Polarograms were obtained from 10^{-3}M solutions. The half-wave reduction potentials were not corrected for the IR drop. The solvent, DMF, was the same as that used for the e.s.r. experiments.

Materials.—Cyclopentadithiophenones were obtained from stock or prepared by standard methods.[27] Purification was accomplished by sublimation *in vacuo*. Samples of dithienothiophenes and dithienothiophen 7,7-dioxides were kindly provided by Dr. F. De Jong of this laboratory.

Deuteriation of Cyclopentadithiophenones.—Deuteriated derivatives of cyclopentadithiophenones were obtained by treatment with a 1 : 1 mixture of acetic anhydride and D_2O to which several drops of a solution of 20% DCl in D_2O (Merck) was added. The general procedure was as follows. To a solution of ketone (100 mg) in $(CH_3CO)_2O$–D_2O (1 : 1) (10 ml) was added DCl–D_2O (10 drops) solution. The mixture was refluxed for 16 h [(Ia), (IVa), and (Va)], 32 h [(VIa)], or 42 h [(IIa)]. The solution was extracted with ether and the ether layer was neutralized with saturated $NaHCO_3$ solution. After drying ($MgSO_4$), filtering, and removing the ether under reduced pressure, the deuteriated ketones were recrystallized from ethanol or methanol and finally sublimed *in vacuo*.

Products obtained from deuteriation were identified by analysis of the n.m.r. spectra.

The position of deuterium in *c*-annulated thiophen rings was determined unambiguously by the cleavage of dideuterio- (IIa) into 2,2′-dideuterio-3,3′-dithienyl-4-carboxylic acid using potassium t-butoxide in ether as described by Rawson and Wynberg.[28]

A deuterium derivative of ketone (IIIa) could not be prepared in this way. 2,5-Dideuterio- (IIIa) was prepared starting from bis-(3-bromo-5-deuterio-2-thienyl)methanol. To a solution of 2,3-dibromo-5-deuteriothiophen (46·6 g, 0·11 mol), prepared by methods described in the literature,[29,30] in absolute ether (40 ml) at −70°, was added 1·02N-n-butyl-lithium (108 ml, 0·11 mol) in ether. After stirring for 15 min at −70°, methyl formate (6·0 g, 0·1 mol) was added followed by stirring for another 1 h. The mixture was allowed to warm to −10° in 2·5 h and 10% aqueous ammonium chloride solution (80 ml) was added. The organic layer was washed with water and dried ($MgSO_4$). After evaporation of the ether crude bis-(3-bromo-5-deuterio-2-thienyl)methanol (27·8 g) was obtained, the identity of which was verified by comparison of the n.m.r. spectrum with that of the non-deuteriated alcohol. This product, without further purification, was oxidized and subjected to ring closure by standard methods[27] whereupon the desired 2,5-dideuterio- (IIIa) was obtained, m.p. 118—119°, $\delta(CD_3COCD_3)$ 7·05 (s). The isotopic purity of the deuteriated ketones (Ia)—(IVa) and (VIa) was >95%, that of 4-deuterio- (Va) *ca.* 60%.

Deuteriation of Dithienothiophen 7,7-*Dioxides*.—Refluxing solutions of dithienothiophen (100 mg) in $(CH_3O)_2O$–D_2O (1 : 1) (10 ml), to which 20% DCl–D_2O solution (2 drops) was added, for 6 h, followed by the general work-up for the deuteriation of cyclopentadithiophenones, afforded the deuteriated derivatives.

The oxidation of the sulphides was achieved with *m*-chloroperbenzoic acid in dichloromethane at −15°.[31] The isotopic purity of the deuteriated sulphones (Ib), (IIIb), and (IVb) was >95%. Prior to use the deuteriated sulphones were recrystallized from ethanol.

Supporting Electrolytes.—Tetra-n-butylammonium and tetraethylammonium perchlorate were obtained by reaction of their bromides (EGA-chemie K.G.) and $KClO_4$. The perchlorates were recrystallized from acetonitrile–water (4 : 1) and ethanol–water and dried *in vacuo* over P_2O_5.

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