Conjugation in Sulphones. Electronic Spectra and Polarographic Behaviour of Thiophen Dioxides

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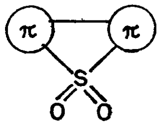
The interaction of the sulphone group with an adjacent unsaturated centre has been treated on the basis of HMO theory. The sulphur atom of the SO_2 group is assumed to form π-bonds by means of its 3*d* orbitals. Using the same set of empirical parameters [$\alpha_S(SO_2) = \alpha - 1{\cdot}4\beta$, $\alpha_O = \alpha + \beta$, $\beta_{SO} = 0{\cdot}9\beta$, and $\beta_{C-SO_2} = 0{\cdot}7\beta$], a good correlation has been obtained between the longest-wavelength absorption band and the calculated $N \rightarrow V_1$ transition energy for 18 sulphones. The energy of the lowest unoccupied molecular orbital shows a good correlation with the polarographic half-wave reduction potential. The S=O bond of sulphones is shown to be hardly affected by mesomeric interactions.

ALTHOUGH there is much conflicting evidence about the conjugative ability of the sulphone group, a distinct, albeit small, mesomeric interaction with an adjacent unsaturated centre seems well established.[1] A symmetry analysis of this interaction has been given by Koch and Moffitt,[2,3] but no calculation involving the π-system of the substituent was performed. Only in more recent studies have spin-densities in radical anions [4-6] and the effect of a methyl substituent on the polarographic half-wave reduction potential [4,7] of some sulphones been correlated with LCAO-MO calculations. In these cases however, only the lowest unoccupied MO was considered, resulting in a treatment of the SO_2 function as a group contributing one vacant 3*d* orbital to the π-system. Moreover the experimental spin-densities were equally well calculated by a model in which the sulphone group only exerts an inductive effect on the π-system of the substituent.[8]

This lack of agreement, together with the oversimplification of the p^π–d^π interactions, prompted us to develop a simple model of the sulphone group on the basis of HMO theory. On symmetry grounds thiophen dioxides were expected to show strong p^π–d^π interactions,[2,3] so sulphones of type (A) have been studied. The reliability of the model employed is illustrated by comparison with electronic spectra and polarographic half-wave reduction potentials.



(A)

RESULTS AND DISCUSSION

Molecular Orbital Calculations.—The calculations have been carried out for two extreme conformations arising from different orientations of the carbon 2*p* orbitals with respect to the C(1)–S–C(2) plane. In Moffitt's nomenclature,[2] Case I corresponds to the situation in which the carbon 2*p* orbitals are perpendicular to the C(1)–S–C(2) (*XZ*) plane, whereas in Case II they lie in the *XZ* plane (in both cases the SO_2 group lies in the *YZ* plane). The orbitals that might in principle be involved in π-bonding were selected on the basis of the following assumptions: (i) the sulphur 3*s* and 3*p* orbitals are exclusively used for σ-bonding, leaving the 3*d* orbitals available for π-bonding, (ii) the oxygen 2*p* orbitals lying in the *YZ*-plane are considered to contain a lone pair of non-bonding electrons (for a discussion of this point, see ref. 2), whereas the

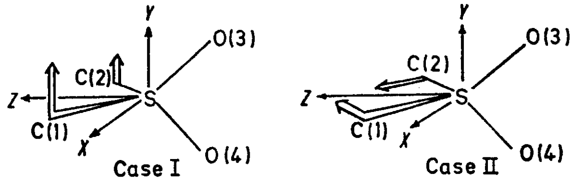


FIGURE 1

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[1] C. C. Price and S. Oae, 'Sulfur Bonding,' Ronald Press, New York, 1962.

[2] W. E. Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **200**, 409.

[3] H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 8.

[4] R. Gerdil and E. A. C. Lucken, *Mol. Phys.*, 1965, **9**, 529.

[5] G. Vincow, *J. Chem. Phys.*, 1962, **37**, 2484.

[6] E. T. Kaiser, M. M. Urberg, and D. H. Eargle, *J. Amer. Chem. Soc.*, 1966, **88**, 1037.

[7] R. Gerdil and E. A. C. Lucken, *J. Amer. Chem. Soc.*, 1966, **88**, 733.

[8] M. M. Urberg and C. Tenpas, *J. Amer. Chem. Soc.*, 1968, **90**, 5477.

$2p$ orbitals perpendicular to the YZ-plane form π-bonds with sulphur.

Although previous calculations on sulphones have dealt with compounds possessing C_{2v} symmetry, this high symmetry is not frequently encountered. Therefore to cover as wide an area as possible, no special symmetry requirement of the whole molecule has been made; any local symmetry of the sulphone group is reflected in the resonance integrals (Table 1). For the Case II type of compounds the C(1)–S–C(2) angle is assumed to be 90° (from X-ray studies values in the range of 100—105° have been reported [9,10]).

TABLE 1

Selected orbitals and resonance integrals of sulphones

	S $3d_{y^2}$	S $3d_{z^2-x^2}$	S $3d_{xy}$	S $3d_{xz}$	S $3d_{yz}$	Conformation
O_3 ($2p$)	0	0	β_{SO}	$-\beta_{SO}$	0	Case I and II
O_4 ($2p$)	0	0	$-\beta_{SO}$	$-\beta_{SO}$	0	Case I and II
C_1 ($2p$)	0	0	β_{CS}	0	β_{CS}	Case I
C_1 ($2p$)	0	β_{CS}	0	0	0	Case II
C_2 ($2p$)	0	0	$-\beta_{CS}$	0	β_{CS}	Case I
C_2 ($2p$)	0	β_{CS}	0	0	0	Case II

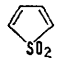
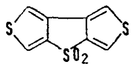
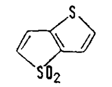
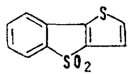
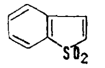
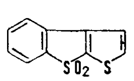
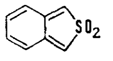
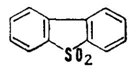
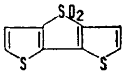
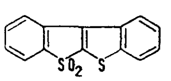
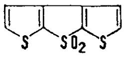
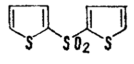
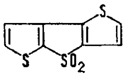
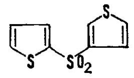
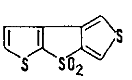
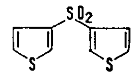
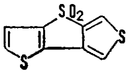
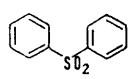
In order to reduce the number of unknown parameters, the carbon–sulphur and sulphur–oxygen resonance integrals are presumed to be independent of the kind of sulphur $3d$ orbitals used. Further, the coulomb integrals of all sulphur $3d$ orbitals have been given the same value (α_S). The inductive effect of the sulphone group was accounted for by changing the coulomb integrals of the carbon atoms C(1) and C(2).

The parameters of the thiophen-like sulphur atom were taken from the literature: [11] $\alpha_S(3p) = \alpha + \beta$, $\beta_{CS}(3p) = 0{\cdot}7\beta$. In these expressions α and β denote the carbon coulomb integral and the carbon–carbon resonance integral respectively. The parameter values of the sulphone group were varied between reasonable limits. Optimal correlation with experimental data was obtained by use of $\alpha_S(3d) = \alpha - 1{\cdot}4\beta$; $\alpha_O = \alpha + \beta$; $\alpha_{C(1)} = \alpha_{C(2)} = \alpha + 0{\cdot}2\beta$; $\beta_{CS}(3d) = 0{\cdot}7\beta$; and $\beta_{SO}(3d) = 0{\cdot}9\beta$. The calculated molecular quantities are compiled in Table 2.

Electronic Spectra.—The u.v. spectra of the sulphones studied display a longest-wavelength absorption band of moderate intensity (Table 3). It has been assumed that this band corresponds to the $N \longrightarrow V_1$ transition, except for diphenyl sulphone. From LCAO-MO calculations on aromatic hydrocarbons [21] the p-band (207 nm) and not the α-band (264 nm) was shown to be related to the $N \longrightarrow V_1$ transition. The p-band in benzene is shifted to 235 nm in diphenyl sulphone,[20] so this band is obviously related to the $N \longrightarrow V_1$ transition.

Table 2

Calculated molecular quantities for Case I [(1)—(14)] and Case II [(15—(18)] type of sulphones

	Compound	ΔE^a	$-k_{-1}{}^b$		Compound	ΔE^a	$-k_{-1}{}^b$
1		0·870	0·040	10		1·199	0·778
2		0·828	0·236	11		0·944	0·403
3		1·049	0·239	12		1·064	0·398
4		0·336	−0·175	13		1·146	0·398
5		0·828	0·408	14		0·876	0·332
6		0·990	0·398	15		1·315	0·623
7		0·898	0·404	16		1·336	0·686
8		1·100	0·565	17		1·433	0·790
9		1·055	0·618	18		1·607	0·607

[a] Energy of the $N \longrightarrow V_1$ transition in β units. [b] Coefficient of the energy expression for the lowest unoccupied molecular orbital ($\varepsilon = \alpha + k_{-1}\beta$).

TABLE 3

Position and intensity of the longest-wavelength absorption band in ethanol

Compd.	$\lambda_{max.}$/nm (log ε)	Ref.	Compd.	$\lambda_{max.}$/nm (log ε)	Ref.
1	289 (3·09)	12, 13	10	294 (3·69)	16
2 [a]	340 (3·62)	c	11	326 (3·68)	c
3	305 (3·35)	14	12	318 (3·30)	c
4 [b]	550 (2·65)	15	13	322 (3·26)	18
5	354 (3·78)	16	14	347 (3·59)	c
6	335 (2·99)	17	15	276 (3·83)	19
7	342 (3·53)	18	16	264 (3·98)	19
8	303 (3·08)	19	17	245 (4·21)	19
9	315 (3·65)	20	18	235 (4·19)	20

[a] 2,5-Dimethyl substituted. [b] 1,6-Diphenyl substituted, in benzene solution. [c] This work.

The energies of the longest-wavelength absorption bands (Table 3) and the calculated transition energies (Table 2) show a good linear correlation (1) (Figure 2).

$$E_{exp}/\text{eV} = 2{\cdot}33\Delta E(\beta) + 1{\cdot}51 \qquad \text{(correlation coefficient 0·982)} \quad (1)$$

Only thiophen dioxide (1) does not fit the correlation.

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[9] J. Toussaint, *Bull. Soc. chim. belges*, 1945, **54**, 319.

[10] C. Dickenson, *Chem. Comm.*, 1970, 920.

[11] R. Zahradnik in ' Advances in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, vol. 5, 1965, p. 1.

[12] W. J. Baily and E. W. Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1932.

[13] M. Prochazka, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1158.

[14] G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 1956, 3438.

[15] M. P. Cava, *Chem. Comm.*, 1968, 1648.

[16] F. de Jong and M. J. Janssen, *J. Org. Chem.*, 1971, **36**, 1645.

[17] F. de Jong and M. J. Janssen, *J. Org. Chem.*, 1971, **36**, 1998.

[18] A. Mangini and R. Passerini, *Gazzetta*, 1954, **84**, 606.

[19] E. Jones and I. M. Moodie, *Tetrahedron*, 1965, **21**, 2413.

[20] G. Leandri, A. Mangini, and R. Passerini, *Gazzetta*, 1954, **84**, 73.

[21] J. Koutecký, J. Paldus, and R. Zahradnik, *J. Chem. Phys.*, 1962, **36**, 3129.

Most probably this is due to the fact that in compound (1) the conjugated π-system is a polyene while for all other compounds in this series the π-system consists of aromatic units. This is supported by the fact that thiophen dioxide fits more closely on the regression line obtained for polyenes [21] (broken line in Figure 2).

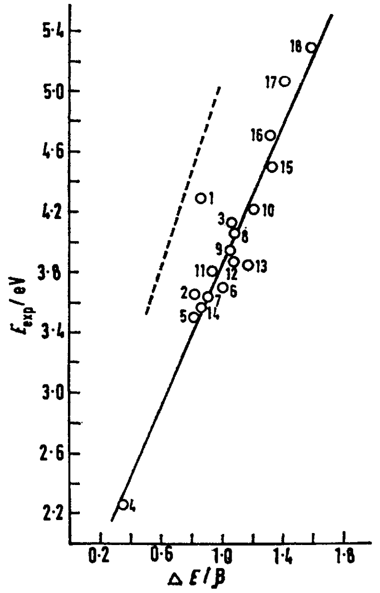
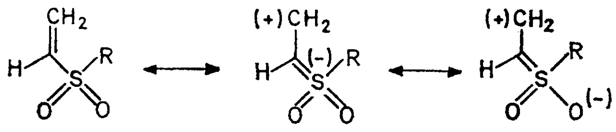


FIGURE 2 Dependence of the longest-wavelength absorption band on the calculated $N \longrightarrow V_1$ transition energies

The regression line obtained for the sulphones almost coincides with the one reported for some of the corresponding unoxidized parent compounds.[22] This enables us to discuss the changes in the u.v. spectrum of the parent compound brought about by the oxidation. For that purpose the SO_2 function of the sulphones was replaced by a thiophen-like sulphur atom and an analogous HMO calculation was carried out for the unoxidized parent compounds. As far as the $N \longrightarrow V_1$ transition is concerned, the energy of the highest occupied molecular orbital of the sulphur compound is lowered on oxidation by an almost constant value throughout the whole series of sulphones. On the other hand, the decrease in energy of the lowest unoccupied molecular orbital strongly depends on structure. It follows then that the blue or red shift of the $N \longrightarrow V_1$ transition upon oxidation is chiefly determined by the energy change of the excited state.

From symmetry consideration of Case II type of sulphones (Table 1), it follows that the mesomeric interaction between the conjugated π-system and the sulphur group does not affect the S=O bonds, neither in the ground state nor in the excited state. The sulphone group acts as an electron-acceptor site using the vacant sulphur $3d_{z^2-x^2}$ orbital [resonance structure (IV)]; structure (V) does not contribute to the resonance hybrid. The same type of interaction is also possible in Case I type of sulphones, now the vacant sulphur $3d_{yz}$ orbital is used in the resonance structure (IV). Further, in



(III) (IV) (V)

Case I type of compounds a direct mesomeric interaction between the S=O bonds and the π-system of the substituent is in principle possible [resonance structure (V)] by the use of the sulphur $3d_{xy}$ orbital. The contribution of (V) will result in a decrease of the S=O bond-order. From Table 4 it follows that the calculated bond-orders are indeed somewhat lower for Case I than for Case II type of sulphones, but the small difference suggests that the contribution of structure (V) in the former compounds is only of minor importance.

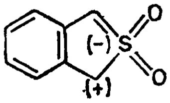
TABLE 4

Calculated S=O bond-orders for the compounds of Table 2

Conformation	Ground state	First excited state
Case I	0·983 ± 0·011	0·993 ± 0·008
Case II	1·028	1·028

The same conclusion can be drawn from the fact that the S=O bond-orders for the whole series of Case I compounds are within a very narrow range, indicating that the S=O bonds are nearly independent of the π-system of the substituent.

As far as the $N \longrightarrow V_1$ transition is concerned, the π-electrons in the sulphur–oxygen bonds are clearly not involved, since the S=O bond-order is practically unaffected by the excitation. The resonance structure (IV) [and not (V)] is found to make an important contribution to the first excited state of all sulphones studied. This conclusion contradicts the assertion of Montaudo and co-workers [23,24] that the large red shift (54 nm) observed on oxidation of thiophen was due to the stabilizing contribution of resonance structure (V) to the excited state of thiophen dioxides. Our results indicate that oxidation of the parent compound results in a red shift of the longest-wavelength absorption band whenever structure (IV) is stabilized. This can be illustrated by the unusual large red shift of 167 nm observed by Cava [15] on oxidation of benzo[*c*]thiophen. In this case resonance structure (IV) is relatively very stable in the form (VI).



(VI)

Polarographic Reduction.—The polarographic half-wave reduction potentials were determined in anhydrous

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[22] R. Zahradnik, C. Parkanyi, V. Horák, and J. Koutecký, *Coll. Czech. Chem. Comm.*, 1963, **28**, 776.

[23] N. Marziano and G. Montaudo, *Gazzetta*, 1961, **91**, 587.

[24] L. Fortina and G. Montaudo, *Gazzetta*, 1960, **90**, 987.

dimethylformamide; tetra-n-butylammonium iodide (0·15M) was used as the supporting electrolyte. The potentials were measured against the Hg-pool as internal electrode, which is known to be —0·55 V *versus* S.C.E.[25]

The $E_{\frac{1}{2}}$ values and the diffusion current constants I obtained for the first reduction wave under these conditions are summarized in Table 5. For most of the sulphones a second wave was observed with a somewhat lower intensity (I = 1·4—1·8), but for comparison with theory the study has been restricted to the properties of the first reduction wave.

TABLE 5

Characteristics of the first reduction wave

Compd.	$-E_{\frac{1}{2}}$/V	I [a]	Compd.	$-E_{\frac{1}{2}}$/V	I [a]
3	1·00	1·78	11	1·11	1·89
5	1·00	1·81	12	1·11	1·93
6	1·02	1·95	13	1·21	1·88
7	1·05	1·82	15	1·38	2·34
8	1·32	2·15	16	1·49	2·40
9	1·41	2·36	17	1·69	2·42
10	1·50	2·49	18	1·57	2·02

[a] In μA l mmol^{-1} mg$^{-\frac{2}{3}}$ s$^{\frac{1}{2}}$.

From the linear dependence of the diffusion current on the square root of the corrected height of the mercury column, it was concluded that the limiting current of the first reduction wave was diffusion-controlled.[26] When anthracene was reduced under identical conditions almost the same I value (1·93) was observed for its first reduction wave. If it is assumed that the diffusion constants of anthracene and the sulphones are of comparable magnitude, it follows then that the reduction step involves the addition of one electron, since in dry dimethylformamide the first wave of anthracene is known to correspond with a reversible one-electron process.[27] On the basis of e.s.r. experiments Gerdil and Lucken [4] also concluded that radical-anions were formed in the first reduction step. The reversibility of the electrode process was demonstrated by plotting E_{dme} against $\log i/(i_{\text{D}} - i)$. For each compound a straight line was obtained and the slopes observed (60—70 mV) were close to the value of 59 mV expected for a reversible one-electron addition.[28]

The mechanism of the electrochemical reduction of conjugated sulphones may be the same as suggested for aromatic hydrocarbons, since it has been shown that the sulphone group itself is not reduced.[29] The first reduction wave of aromatic hydrocarbons has been attributed to an *ECE* type of mechanism [30] (2)—(4). The polarographic behaviour of sulphones is easily explained by reactions (2)—(4). In anhydrous dimethylformamide the reversible one-electron addition corresponds to step (2). In aqueous media the formation of the radical-anion is followed by protonation (3) and subsequent reduction to the anion RH$^-$ [step (4)]. This offers a good explanation for the irreversible two-electron addition observed for the reduction of dibenzothiophen dioxide [31] and benzothiophen dioxide [32] in protic solvents. The reduction of diphenyl sulphones and methyl phenyl sulphones in protic solvents probably takes a different course, since sulphinic acids have been found [33-35] as the main reaction product.

$$\mathrm{R} + \mathrm{e} \rightleftharpoons \mathrm{R}^{-\bullet} \qquad (2)$$

$$\mathrm{R}^{-\bullet} + \mathrm{HX} \longrightarrow \mathrm{RH}^{\bullet} + \mathrm{X}^{-} \qquad (3)$$

$$\mathrm{RH}^{\bullet} + \mathrm{e} \rightleftharpoons \mathrm{RH}^{-} \qquad (4)$$

Since the potential-determining step appears to be the addition of one electron to the molecule, we may expect a correlation between the polarographic half-wave reduction potentials and the energy of the lowest unoccupied molecular orbital.[36] A plot of $E_{\frac{1}{2}}$ (Table 5) against k_{-1} (Table 2) gave a poor correlation (correlation coefficient 0·922). It appears, however, that most of the scatter results from combining benzenoid hydrocarbons and heteroaromatic compounds in the same correlation. Much better agreement with theory is obtained by treating the benzenoid, monohetero-, and dihetero-aromatic compounds separately. In that case, the regression lines (5) and (6) were obtained by the least-squares method (Figure 3). There were too few monohetero-

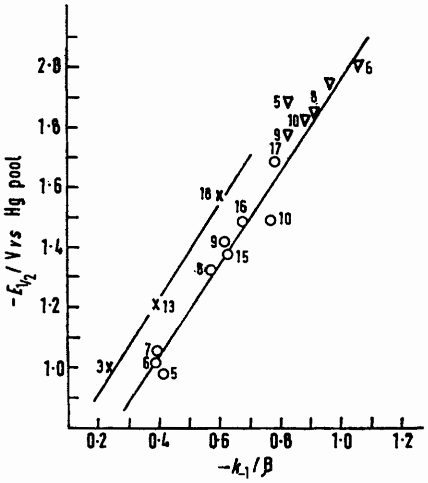

FIGURE 3 Half-wave reduction potential as a function of the energy of the lowest unoccupied molecular orbital; ○, dihetero-sulphones; ×, benzenoid sulphones; △, unoxidized parent compounds

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[25] A. Streitwieser, jun., and I. Schwager, *J. Phys. Chem.*, 1962, **66**, 2316.

[26] L. Meites, 'Polarographic Techniques,' John Wiley, New York, 1964.

[27] P. H. Given, *J. Chem. Soc.*, 1958, 2684.

[28] J. Tomes, *Coll. Czech. Chem. Comm.*, 1937, **9**, 12.

[29] C. W. Johnson, C. G. Overberger, and W. J. Seagers, *J. Amer. Chem. Soc.*, 1953, **75**, 1495.

[30] G. J. Hoytink, J. van Schooten, E. de Boer, and W. Y. Aalbersberg, *Rec. Trav. chim.*, 1954, **73**, 355.

[31] H. V. Drushel and J. F. Miller, *Analyt. Chem.*, 1958, **30**, 1271.

[32] P. Smith, *Analyt. Chem.*, 1953, **25**, 793.

[33] R. C. Bowers and H. D. Russell, *Analyt. Chem.*, 1960, **32**, 405.

[34] G. Jeminet and J. Simonet, *Compt. rend.*, 1971, **272**, 661.

[35] J. Simonet and G. Jeminet, *Bull. Soc. chim. France*, 1971, 2754.

[36] A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' John Wiley, New York, 1961, ch. 7.

compounds studied to determine the regression line for those compounds too, but the $E_{\frac{1}{2}}$ values of the sulphones (11) and (12) suggest that it lies between the two given lines.

Benzenoid: $E_{\frac{1}{2}} = 1{\cdot}56k_{-1} - 0{\cdot}61$
(correlation coefficient 0·999) (5)

Dihetero: $E_{\frac{1}{2}} = 1{\cdot}53k_{-1} - 0{\cdot}42$
(correlation coefficient 0·975) (6)

In the section concerning the u.v. spectra it was concluded that oxidation of the parent sulphur compound drastically changed the energy of the lowest vacant molecular orbital. This conclusion is strongly supported by the polarographic data for some of the unoxidized parent compounds, which are included in Figure 3 for comparison. For all these compounds the absolute value of the half-wave reduction potentials shift to more positive values on oxidation, but the amount strongly depends on structure [0·34 V for (10) and 1·00 V for (6)]. The fact that the unoxidized sulphur compounds and the corresponding sulphones fit the same regression line may serve as an additional indication of the reliability of the theoretical model for the SO_2 group suggested in this study.

EXPERIMENTAL

The u.v. absorption spectra were measured in spectral grade 95% ethanol (Merck) on a Zeiss PMQ II spectrophotometer. I.r. and ^1H n.m.r. spectra were taken on a Unicam SP 200 and a Varian A-60 instrument respectively. The polarographic data were obtained at 25·0 ± 0·1 °C on a Polariter Radiometer, type PO 4 (Copenhagen). The $m^{\frac{2}{3}}t^{\frac{1}{6}}$ value of the dropping mercury electrode was 1·66 mg$^{\frac{2}{3}}$ s$^{-\frac{1}{2}}$ (open circuit). The half-wave reduction potentials were obtained from 10^{-3}M solutions and were not corrected for the *IR* drop. The dimethylformamide (Baker Chemicals) was dried over anhydrous calcium oxide, distilled through a column, and stored under N_2 over molecular sieves A_4.

Materials.—The synthesis of the dithienothiophen dioxides has been reported.[16,17] The following sulphones were prepared by standard procedures (m.p.s are uncorrected): benzothiophen dioxide (3), m.p. 141—142° (lit.,[37] 142—143°); thieno[3,2-*b*][1]benzothiophen 4,4-dioxide (11), m.p. 204—206° (lit.,[38] 208—209°); thieno[2,3-*b*][1]benzothiophen 8,8-dioxide (12), m.p. 184—185° (lit.,[38] 186—187°); dibenzothiophen dioxide (13), m.p. 232—234° (lit.,[39] 232°); [1]benzothieno[2,3-*b*][1]benzothiophen 5,5-dioxide (14), m.p. 233—235° (lit.,[40] 234—235°); 2,2′-dithienyl sulphone (15), m.p. 129—131° (lit.,[19] 130·5—131·5°); 2,3′-dithienyl sulphone (16), m.p. 132—133° (lit.,[19] 133—134°); 3,3′-dithienyl sulphone (17), m.p. 163—164° (lit.,[19] 165°); diphenyl sulphone (18), m.p. 125—126° (lit.,[41] 128°).

2,5-*Dimethylthieno*[3,2-b]*thiophen* 1,1-*Dioxide* (2).—To a solution of 2,5-dimethylthieno[3,2-*b*]thiophen[42] (150 mg, 0·9 mmol) in dichloromethane (50 ml) cooled to −20 °C was added a cooled solution of *m*-chloroperbenzoic acid (345 mg, 2·0 mmol) in dichloromethane (20 ml). After standing for 14 h at −20 °C the solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent and recrystallization from methanol afforded 40 mg (22%) of the *dioxide* (2), m.p. 137—139°; $\nu_{max.}$ (KBr) 1290 and 1130 cm^{-1} (SO_2); $\lambda_{max.}$ (EtOH) 234 nm (log ε 3·78) and 340 (3·62); δ (CD_3·CO·CD_3) 2·15 (3H, d, *J* 1·9 Hz), 2·50 (3H, d, *J* 0·7 Hz), 6·58 (1H, broad), and 6·85 p.p.m. (1H, broad) (Found: C, 48·0; H, 4·0; S, 32·2. $C_8H_8O_2S_2$ requires C, 48·0; H, 4·0; S, 32·0%).

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[37] F. G. Bordwell, B. B. Lampert, and W. H. McKellin, *J. Amer. Chem. Soc.*, 1949, **71**, 1702.

[38] N. B. Chapman, C. G. Hughes, and R. M. Scrowston, *J. Chem. Soc.* (*C*), 1970, 2431.

[39] H. Gilman, A. L. Jacoby, and H. A. Pacivitz, *J. Org. Chem.*, 1938, **3**, 120.

[40] S. Dayagi, I. Goldberg, and U. Shmueli, *Tetrahedron*, 1970, **26**, 411.

[41] G. Holt and B. Pagdin, *J. Chem. Soc.*, 1960, 2508.

[42] J. Teste and N. Lozac'h, *Bull. Soc. chim. France*, 1955, 442.