

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

ESR studies of radical cations produced on doping discotic liquid crystals with Lewis acids

N. Boden^a; R. Borner^a; D. R. Brown^a; R. J. Bushby^a; J. Clements^a

^a School of Chemistry, The University, Leeds, England

To cite this Article Boden, N. , Borner, R. , Brown, D. R. , Bushby, R. J. and Clements, J.(1992) 'ESR studies of radical cations produced on doping discotic liquid crystals with Lewis acids', *Liquid Crystals*, 11: 3, 325 – 334

To link to this Article: DOI: 10.1080/02678299208028992

URL: <http://dx.doi.org/10.1080/02678299208028992>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ESR studies of radical cations produced on doping discotic liquid crystals with Lewis acids

by N. BODEN*, R. BORNER, D. R. BROWN,
R. J. BUSHBY* and J. CLEMENTS

School of Chemistry, The University, Leeds LS2 9JT, England

(Received 4 July 1991; accepted 19 October 1991)

We have shown previously that doping the D_{hd} phase of 2,3,6,7,10,11-hexahydroxytriphenylene (HAT6) with 1-5 mole per cent of a Lewis acid converts it from an insulator to a p-type semiconductor. Herein, ESR spectroscopic studies establish that this and related oxidation reactions produce radical cations, but that these radical cations can be of several types. For instance, oxidation of the parent hydrocarbon triphenylene (TP) with aluminium trichloride in carbon disulphide solution gives a non-covalently bonded dimer $(TP)_2^+$ in which the charge is delocalized over two aromatic nuclei. Oxidation of HAT6 in solution gives either charged aggregates $(HAT6)_n^+$ or the monomeric radical cation $(HAT6)^+$. Formation of $(TP)_2^+$, $(HAT6)_n^+$, or $(HAT6)^+$ involves removal of an electron from a π -orbital. An alternative reaction is revealed by studies of 2,3,6,7,10,11-hexahexylthiotriphenylene (HTT6): removal of an electron from a σ -orbital. In this case a cation with a novel two-centre, three-electron, sulphur-sulphur bond is formed. Electronic conduction in doped neat HAT6 involves a mechanism in which the charge carrier hops between localized states. These localized states may be discrete $(HAT6)^+$ ions but are more probably $(HAT6)_n^+$ aggregates or polarons.

1. Introduction

Future applications of discotic liquid crystals are likely to stem from the opportunities they offer for building functional properties into their supramolecular organization. The preferred strategy for doing this must be to build the functionality directly into the molecular structure of the mesogen. The seminal example to date is the attempt to prepare one dimensional conductors from discotic organometallic mesogens [1, 2]. The conductivities of the D_h phases of these mesogens are, however, disappointingly low: the highest reported conductivity being $8.2 \times 10^{-10} \text{ S m}^{-1}$ at 10^4 Hz , for $[(C_{18}H_{37}OCH_2)_8Pc]_2Lu$ [2]; hence these materials are essentially insulators. The alternative strategy is to introduce the functionality using an appropriate dopant. This may seem less attractive, but discotics are very amenable to such doping and high concentrations of dopant can be incorporated into either the columns or side chains without destroying the structure of the mesophase [3-6]. For example, in a previous publication [4], we have described how doping the D_{hd} phase of 2,3,6,7,10,11-hexahydroxytriphenylene (HAT6, 1) with 1 mole per cent of the Lewis acid aluminium trichloride converts it from an insulator (conductivity $< 10^{-9} \text{ S m}^{-1}$) to an anisotropic semiconductor in which the preferred direction of conduction is parallel to the long axes of the columns (zero frequency conductivities at 365 K are $\sigma_{\parallel} = 2.8 \times 10^{-2} \text{ S m}^{-1}$ and $\sigma_{\perp} = 3.5 \times 10^{-5} \text{ S m}^{-1}$ [7]). Since it is known that aluminium trichloride can oxidize aromatic hydrocarbons to generate radical cations [8], it

* Authors for correspondence.

was argued [4] that it acts by generating positive holes in the aromatic core of the mesogen [9]. The molecular columns in the D_{hd} phase then act like molecular wires in which the conducting aromatic core is insulated by a surrounding sheath of alkyloxy chains (see figure 1). The temperature dependence and frequency dependence of the conductivity show a mechanism in which the charge carrier hops between localized sites [7]. However, the electronic structure of these localized sites remains unclear. The simplest view would be that they are discrete $HAT6^+$ ions, but the possibility that $(HAT6)_n^+$ aggregates are involved must also be considered. Previous ESR studies on neat $HAT6/AlCl_3$ showed a single broad spectral line [4] giving little structural information. To gain some insight into the nature of the radical cations formed we have investigated these reactions in solution. Studies of the reactions of Lewis acids with triphenylene (TP, see figure 2), HAT6 (see figure 5), and the sulphur containing analogue of HAT6, HTT6 (see figure 7) show that such oxidations can produce a surprisingly diverse range of radical cation types.

2. Materials and methods

The discotic mesogen 2,3,6,7,10,11-hexahydroxytriphenylene (HAT6, **1**) was prepared by oxidative trimerization of veratrole using chloranil, demethylation using hydrogen bromide, and finally alkylation of the hexaphenol [3,4]. It was purified by column chromatography and repeated recrystallization from ethanol (C 343 K– D_{hd} 374 K–I).

Triphenylene was prepared by oxidative photocyclization of ortho-terphenyl [10] and converted to 2,3,6,7,10,11-hexahexylthiotriphenylene (HTT6, **2a**) by bromination and reaction of the hexabromide with the sodium salt of hexane thiol [11]. This was purified by repeated low temperature recrystallizations from acetone/light petroleum (C 339.9 K– D_{ho} 347.4 K– D_{hd} 366.6 K–I). The hexadeuteriated HTT6 **2b** (see figure 6) was prepared by reducing hexanal to 1-deuteriohexanol with lithium aluminium deuteride, converting this to the thiol by the method of Heweihi [12] and completing the synthesis in the same manner as that used for the undeuteriated material [11]. All other materials were obtained from commercial sources.

HAT6 and HTT6 were doped by heating the pure mesogen with the Lewis acid under vacuum to a temperature just above the D–I transition. The tube was then

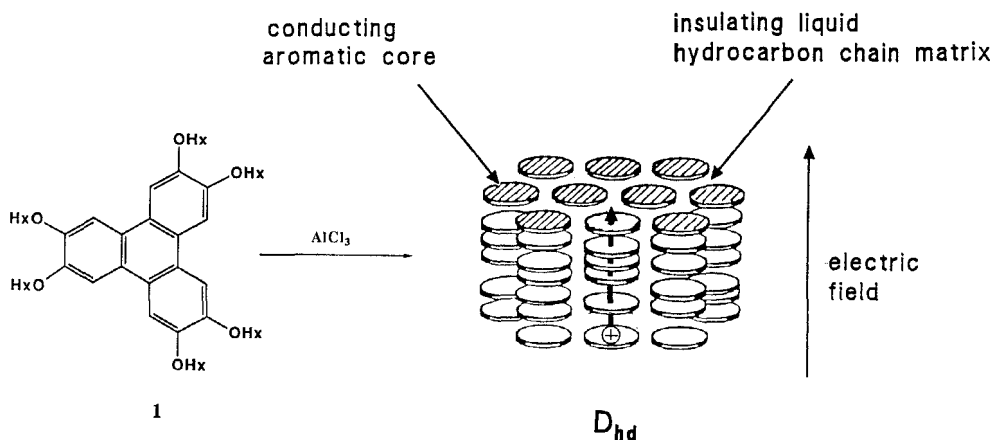


Figure 1. HAT6, **1**, and a schematic representation of the doped conducting D_{hd} phase.

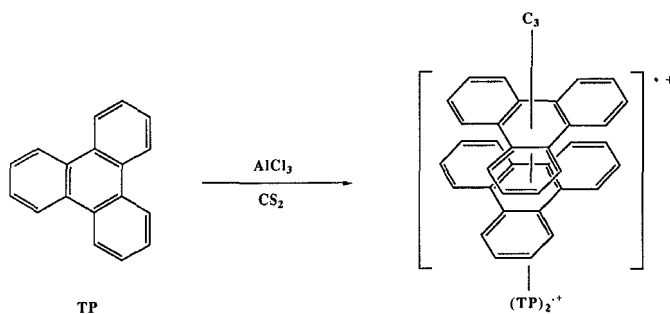


Figure 2. The oxidation of triphenylene (TP) with aluminium trichloride in carbon disulphide and the most probable structure for the dimer $(TP)_2^{\bullet+}$.

cooled, opened, solvent added, and the ESR spectrum recorded. In most cases the same spectrum was also obtained by adding the Lewis acid to a dilute solution of the mesogen as we shall see. In other cases, particularly when dilute solutions were required, a sealed two chamber cell with a breakseal was employed so that the solvent could be distilled on to the doped mesogen and the resultant solution progressively diluted under vacuum [13].

ESR spectra were obtained using a Bruker ER200 X-band or Varian X-band spectrometer.

3. The oxidation of triphenylene

The ESR spectrum obtained by treating a solution of triphenylene (TP) in dichloromethane with antimony pentachloride [14] or aluminium trichloride [15] can be analysed in terms of hyperfine coupling to two sets of twelve protons: $a(12\text{ H}) 9.12 \times 10^{-5}\text{ T}$ and $a(12\text{ H}) 5.88 \times 10^{-5}\text{ T}$. This is attributed to the non-covalent dimeric species $(TP)_2^{\bullet+}$ [14–18] in which the positive charge is delocalized equally over two TP molecules. The observed spectrum is consistent with several symmetrical structures, but the most probable geometry is that shown in figure 2 [18]. Dimeric radical cations of this type are well known. In the simplest dimeric aromatic system $(C_6H_6)_2^{\bullet+}$, the majority of the bonding energy arises from the resonance term $\{(C_6H_6)^+(C_6H_6) \leftrightarrow (C_6H_6)(C_6H_6)^+\}$ and from polarization (ion-induced dipole interactions). In polynuclear aromatics such as triphenylene, however, these bonding terms are relatively small and it is van der Waals dispersive interactions that account for most of the bonding energy [17]. It is important to note that dispersive interactions in charged aggregates like this are much larger than in their neutral counterparts. The enthalpy for the association reaction $ArH^{\bullet+} + ArH \rightarrow (ArH)_2^{\bullet+}$ can be up to 39 kJ mol^{-1} in solution and 100 kJ mol^{-1} in the vapour phase [17]. Formation of such cation-molecule non-covalent complexes is common to almost all polynuclear aromatic compounds [16] and in some cases higher aggregates result, in which a single charge stabilizes a cluster of three, four or more molecules [19].

4. The oxidation of HAT6

When neat HAT6 is oxidized with 1–5 mole per cent of $AlBr_3$, I_2 , $SbCl_5$, or $NO^+PF_6^-$ a blue–green solid is obtained which shows (see figure 3) essentially the same ESR behaviour as that reported for HAT6/ $AlCl_3$ [4]. The lineshape changes from

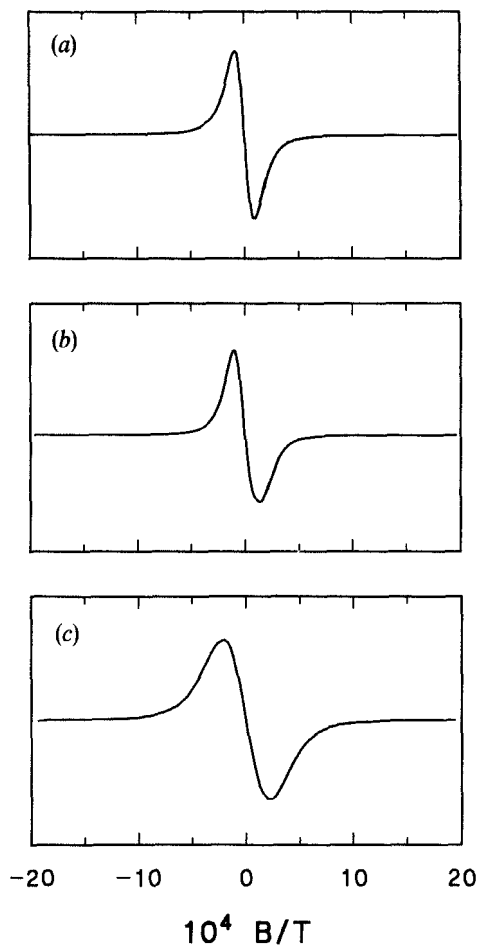


Figure 3. ESR spectra of neat HAT6 doped with 1 mole per cent aluminium tribromide: (a) isotropic liquid phase at 383 K, (b) D_{hd} phase at 368 K, (c) crystalline solid phase at 298 K. Spectra were recorded on a Bruker ER200 X-band spectrometer with a field modulation of 1.25×10^{-5} T.

symmetrical/lorentzian in the crystalline solid, to unsymmetrical/dysonian (characteristic of resonance absorption by conduction electrons) in the D_{hd} phase, to symmetrical/lorentzian in the isotropic melt. For $AlCl_3$ (1 mole per cent)/HAT6 the width of the signal at half height drops from 3.5×10^{-4} to 2.3×10^{-4} T at the C- D_{hd} transition (340 K) and then falls linearly to 1.6×10^{-4} T at 400 K with no discernible discontinuity at the D_{hd} -I transition (370 K), despite the change in lineshape [4]. In most cases, when solvent is added to doped HAT6 or when HAT6 is oxidized in solution, a blue-green solution is formed whose ESR spectrum shows a symmetrical singlet whose width at half height is similar to that found in the isotropic melt (1.6 – 2.0×10^{-4} T). (For example, when HAT6/NOPF₆ is diluted with methylene chloride or carbon disulphide, or HAT6 in carbon disulphide or methylene chloride is oxidized with NOPF₆, or when HAT6 is oxidized with trifluoroacetic or triflic acid [20] either neat or in methylene chloride solution.) It is also found that the shape and linewidth are essentially unaltered by dilution (for example, when HAT6/NOPF₆ is

diluted with carbon disulphide under vacuum to the limit of signal detection). In doped neat HAT6, as in concentrated solutions, the failure to observe the hyperfine structure expected for a $(\text{HAT6})^{\cdot+}$ ion could be attributed to rapid $\text{HAT6}^{\cdot+}/\text{HAT6}$ electron exchange. Typically, rate constants for these electron-exchange reactions are $c. 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ [21]. Exchange will, therefore, be rapid in concentrated solutions, but in very dilute solutions it will be slow on the ESR time scale. Electron exchange would, therefore, not seem to be consistent with the experimental observations. A more reasonable explanation, consistent with the observed linewidth [15, 18, 19] and also with the effect of dilution, is that these spectra can be attributed to $(\text{HAT6})_n^{\cdot+}$ aggregates [19]. Alternatively, some unidentified factor may be causing broadening of the lines. We have only found two cases where the hyperfine structure expected for discrete $\text{HAT6}^{\cdot+}$ ions can be observed. When carbon disulphide is added to $\text{HAT6}/\text{AlBr}_3$ (1 mole per cent) the ESR spectrum shown in figure 4 is obtained. It

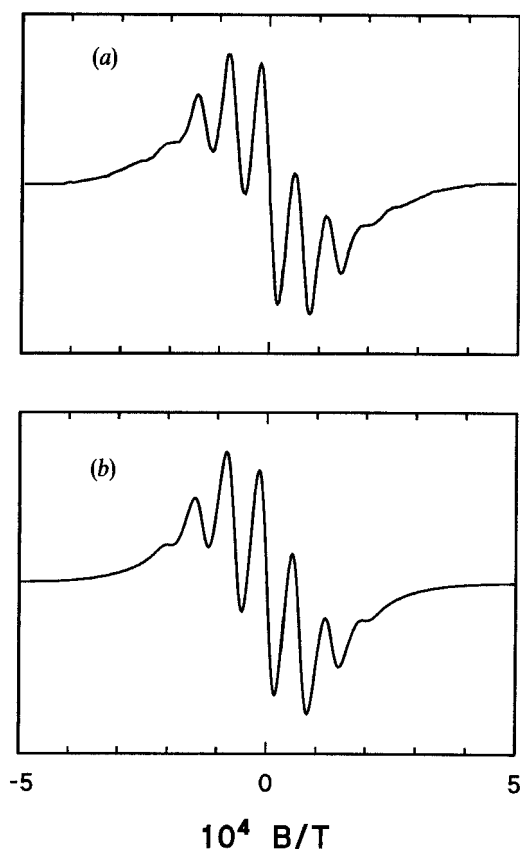


Figure 4. (a) ESR spectrum of $\text{HAT6}/\text{AlBr}_3$ diluted with carbon disulphide, recorded on a Varian X-band spectrometer at a field modulation of $5 \times 10^{-5} \text{ T}$. The simulation of the spectrum (b) assumes that a broad singlet (line width $2 \times 10^{-4} \text{ T}$) underlies the heptet, $a(6 \text{ H}) 6 \times 10^{-5} \text{ T}$. In concentrated sulphuric acid a simple heptet is observed. It is possible that the spectrum in carbon disulphide could be the central portion of a 13-line spectrum due to $(\text{HAT6})_2^{\cdot+}$ and that in concentrated sulphuric acid to $\text{HAT6}^{\cdot+}$. We have, however, been unable to obtain a satisfactory simulation in this manner, and it seems inconsistent with the fact that the hyperfine splittings are identical in carbon disulphide and sulphuric acid.

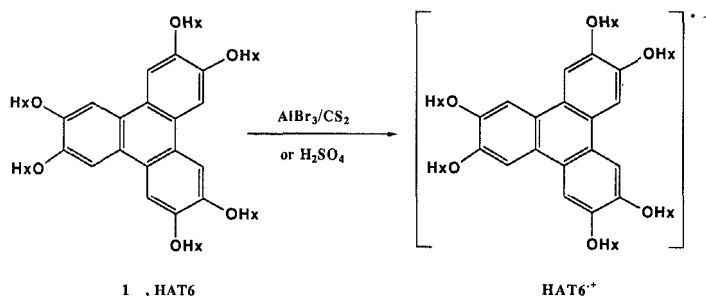


Figure 5. The oxidation of HAT6 with aluminium tribromide in carbon disulphide or concentrated sulphuric acid.

consists of a heptet with $a(6\text{H}) 6 \times 10^{-5}\text{ T}$. Using Hückel molecular orbital theory ($h_0 = 2.0$) and assuming that in the McConnell equation [22], $a_i = Q\rho_i$ the proportionality constant Q is $2.38 \times 10^{-3}\text{ T}$, gives a calculated hyperfine splitting for $\text{HAT6}^{\cdot+}$ of $8 \times 10^{-5}\text{ T}$. The same ESR spectrum can be obtained when a solution of HAT6 in carbon disulphide is treated with AlBr_3 or when HAT6 is warmed with concentrated sulphuric acid [22] (see figure 5). In the latter case it seems that HAT6 is insoluble in concentrated sulphuric acid, but that $\text{HAT6}^{\cdot+}$ ions are soluble so that reaction occurs on the surface of the solid and the ions then dissolve in the acid. The reason for the exceptional behaviour in the case of $\text{AlBr}_3/\text{CS}_2$ is less clear. It must relate in some way to the stabilities of the various possible ion pairs and perhaps to the polarizabilities of bromine containing ions, but unfortunately the structures of the counter ions in these systems are still unknown [8]. Ion pairing effects also, determine the thermal stability of these cation solutions [21]. In many cases this is limited, and when solvent is added to the doped liquid crystal, the characteristic blue–green colour is lost, and no ESR spectrum can be observed. These include $\text{HAT6}/\text{AlCl}_3$ diluted with carbon disulphide, methylene chloride, and tetrahydrofuran, and $\text{HAT6}/\text{NOPF}_6$ diluted with tetrahydrofuran. Similarly, attempts to oxidize HAT6 in various solvents with AlCl_3 failed to produce an ESR signal.

5. The oxidation of 2,3,6,7,10,11-hexahexylthiotriphenylene

Like other thio-alkyl substituted aromatics, HTT6 (also known as HHTT) is dealkylated by heating with Lewis acids [23] and doping, like that use for HAT6, has failed to produce a chemically stable system whose conductivity could be studied. However, oxidation of HTT6 in solution reveals an interesting, unexpected reaction. When HTT6 **2a** is dissolved in chlorosulphonic, or triflic acid, or a solution in dichloromethane is oxidized with aluminium trichloride, the ESR spectrum shown in figure 6(a) is obtained. It shows a splitting to four equivalent hydrogens $a(4\text{H}) 4.75 \times 10^{-4}\text{ T}$, $g = 2.0133$ and the high g factor shows that it belongs to a radical **3a** with a two-centre three-electron sulphur–sulphur bond [24]. Formation of such radicals from dialkyl thioethers is well known, but formation of a two-centre, three-electron, sulphur–sulphur bond is unusual for an aryl-alkyl thioether and the four membered ring structure proposed for **3a** is unique. In fact, the ESR spectrum obtained is consistent with either an intramolecular sulphur–sulphur bond **3a** or an intermolecular sulphur–sulphur bond **4a** (see figure 7). These possibilities were distinguished by using the hexadeuteriated derivative of HTT6 **2b**. When **2b** is dissolved in triflic acid, the ESR

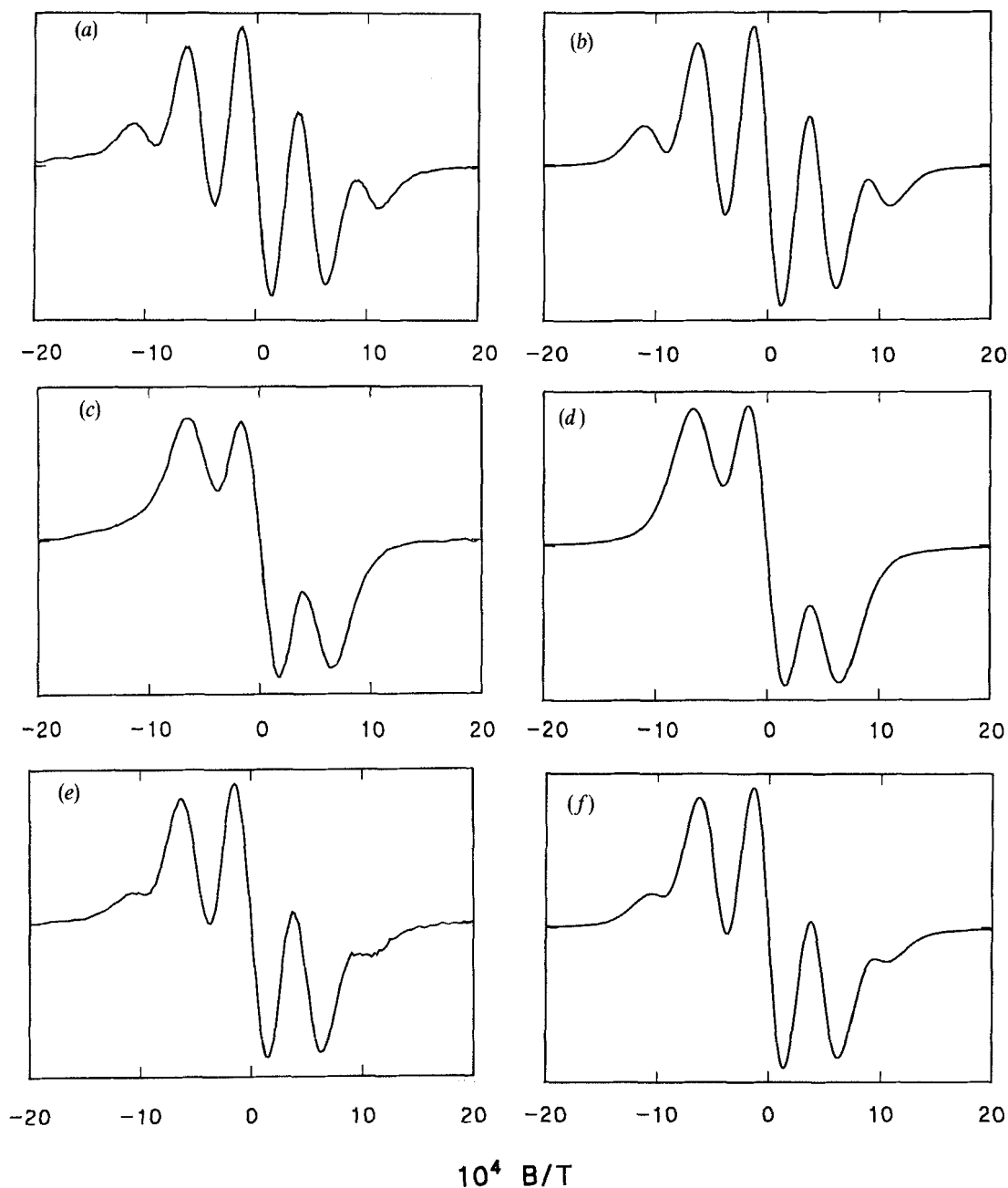


Figure 6. (a) ESR spectrum obtained when HTT6 **2a**, is dissolved in triflic acid recorded on a Varian X-band spectrometer at a field modulation of $1.25 \times 10^{-4} \text{ T}$. (b) Simulated spectrum for **3a** using a mixed gaussian/lorentzian lineshape, $a(4\text{H}) 4.75 \times 10^{-4} \text{ T}$, line width $1.70 \times 10^{-4} \text{ T}$. (c) ESR spectrum obtained when d_6 -HTT6 **2b** is dissolved in triflic acid, field modulation $2.0 \times 10^{-4} \text{ T}$. (d) Simulated spectrum for **3b**, $a(2\text{H}) 4.75 \times 10^{-4} \text{ T}$, $a(2\text{D}) 0.73 \times 10^{-4} \text{ T}$, line width $2.0 \times 10^{-4} \text{ T}$. (e) ESR spectrum obtained when a 1:1 mixture of HTT6 **2a** and d_6 -HTT6 **2b** is dissolved in the acid. (f) Simulated spectrum for a 1:1 mixture of **3a** and **3b** using the same parameters as for the simulations in (b) and (d).

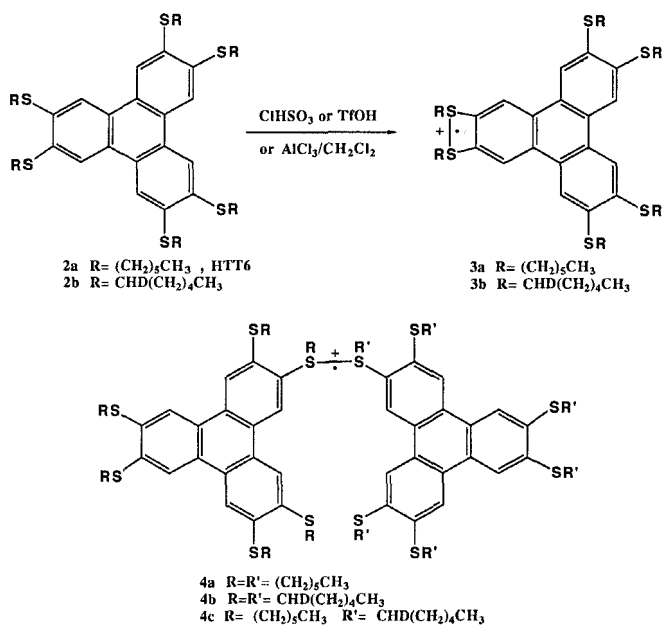


Figure 7. The oxidation of HTT6 and hexadeutero-HTT6 in chlorosulphonic acid or triflic acid or AlCl₃/CH₂Cl₂.

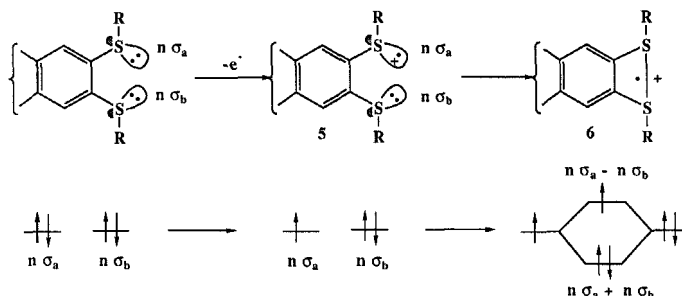
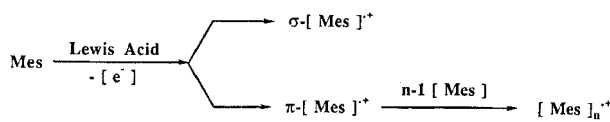


Figure 8. Formal scheme for the formation of the two-centre three-electron bond.

spectrum shown in figure 6(c) $a(2H) 4.75 \times 10^{-4} T$, is obtained. This is consistent with either the formation of **3b** or **4b**. When a 1 : 1 mixture of **2a** and **2b** is dissolved in triflic acid the ESR spectrum shown in figure 6(e) is obtained. This is only consistent with the formation of a 1 : 1 mixture of the intramolecular sulphur–sulphur bonded products **3a** and **3b** (see figure 7). If the reaction involved the formation of an intermolecular sulphur–sulphur bond, a 1 : 2 : 1 mixture of **4a** : **4c** : **4b**, showing hyperfine splittings to four, three and two hydrogens, respectively, would have been observed. Unlike the oxidation of HAT6 the oxidation of HTT6 involves removal of an electron from an orbital of σ [25] rather than of π [23] symmetry. In a formal sense, formation of this ion can be thought of in terms of the two steps shown in figure 8. In this, removal of an electron from an in-plane (σ) sulphur lone-pair orbital $n\sigma_a$ gives the localized, sulphur radical cation **5**, which is then stabilized by interaction with the degenerate, lone pair orbital $n\sigma_b$ on the neighbouring sulphur atom giving the two-centre, three-electron bond **6**.

6. Discussion



Scheme.

The ESR studies presented in this paper confirm that doping HAT6 with AlCl_3 and related oxidations of triphenylene derivatives produce radical cations [4], but there is a surprisingly diverse range of radical cation types. The scheme shows that the initial reaction may involve removal of an electron from a σ - or a π -orbital of the mesogen (Mes). HTT6 provides an example of the former type and HAT6 of the latter. The difference between these two mesogens must arise from the difference in ionization potentials of oxygen and sulphur lone-pair electrons since, in principle, formation of two-centre, three-electron bonds is more favourable for oxygen than it is for sulphur [26]. HTT6, however, appears to be unique [23]. In the vast majority of aromatic compounds, the observed reaction is removal of a π electron followed by association of the radical cation produced with neutral molecules to give aggregates $(\text{Mes})_n^+$ in the scheme). Examples of such charged aggregates are known for most types of polynuclear aromatics and their formation is well documented for the vapour phase [17], in solution [15, 17, 19, 27], and in crystalline solids [14, 16]. The argument for formation of such aggregates in the columnar phase of discotic triphenylene derivatives is further supported by the observation that both triphenylene (see figure 2) and hexamethoxy-triphenylene [28] form charged dimers and that such charge delocalized species are favoured in cyclophanes [29] which share the stacked aromatic ring motif found in the columnar phase. Further evidence consistent with the presence of these charged aggregates in doped HAT6 comes from observation that the ESR spectrum remains essentially the same between the neat isotropic phase and solution. A strong (but not yet compelling) case can, therefore, be made that the localized states in the conducting mesophase are $(\text{Mes})_n^+$, polaron-like, structures in which the charge is spread over several molecules and this possibility is being further investigated. The formation and stabilization of polarons is associated with a local distortion of the lattice structure and in this particular case it is likely that there would be local ordering of the relative orientation of neighbouring aromatic rings (see figure 2) so as to maximize intermolecular interactions [27]. For mesogens such as HTT6, where steric effects result in a strong preference for a spiral structure [30], stabilization of this type would be inhibited.

We thank the Science and Engineering Research Council for financial support for this work and for a research studentship to R.B.

References

- [1] PIECHOCKI, C., SIMON, J., SKOULIOS, A., GUILLON, D., and WEBER, P., 1982, *J. Am. chem. Soc.*, **104**, 5245; LEHN, J. M., MALTHÊTE, J., and LEVELUT, A. M., 1985, *J. chem. Soc. chem. Commun.*, 1794; OHTA, K., TAKAGI, A., MUROKI, H., YAMAMOTO, I., and MATSUZAKI, K., 1987, *Molec. Crystals liq. Crystals*, **147**, 15.
- [2] BELARBI, Z., MAITROT, M., OHTA, K., SIMON, J., ANDRÉ, J. J., and PETIT, P., 1988, *Chem. Phys. Lett.*, **143**, 400.

- [3] BODEN, N., BUSHBY, R. J., and HARDY, C., 1985, *J. Phys. Lett., Paris*, **46**, L325; BODEN, N., BUSHBY, R. J., HARDY, C., and SIXL, F., 1986, *Chem. Phys. Lett.*, **123**, 359; BODEN, N., BUSHBY, R. J., FERRIS, L., HARDY, C., and SIXL, F., 1986, *Liq. Crystals*, **1**, 109; BODEN, N., BUSHBY, R. J., JOLLEY, K. W., HOLMES, M. C., and SIXL, F., 1987, *Molec. Crystals liq. Crystals*, **152**, 37.
- [4] BODEN, N., BUSHBY, R. J., CLEMENTS, J., JESUDASON, M. V., KNOWLES, P. F., and WILLIAMS, G., 1988, *Chem. Phys. Lett.*, **152**, 94.
- [5] VAN KEULEN, J., WARMERDAM, T. W., NOLTE, R. J. M., and DRENTH, W., 1987, *Recl. Trav. chim. Pays-Bas Belg.*, **106**, 534; SLUYTERS, J. H., BAARS, A., VAN DER POL, J. F., and DRENTH, W., 1989, *J. electroanal. Chem.*, **171**, 41; SIELCKEN, O. E., NOLTE, R. J. M., and SCHOONMAN, J., 1990, *Recl. Trav. chim. Pays-Bas Belg.*, **109**, 230; VAN DER POL, J. F., NEELEMAN, E., ZWIKKER, J. W., NOLTE, R. J. M., DRENTH, W., AERTS, J., VISSER, R., and PICKEN, S. J., 1989, *Liq. Crystals*, **6**, 577.
- [6] RINGSDORF, H., and WÜSTEFELD, R., 1990, *Phil. Trans. R. Soc. A*, **330**, 95.
- [7] BODEN, N., BUSHBY, R. J., and CLEMENTS, J., *J. chem. Phys.* (in the press).
- [8] BARD, A. J., LEDWITH, A., and SHINE, H. J., 1976, *Adv. phys. org. Chem.*, **13**, 155.
- [9] VAN DER POL, J. F., DE HAAS, M. P., WARMAN, J. M., and DRENTH, W., 1990, *Molec. Crystals liq. Crystals*, **183**, 411.
- [10] SATO, T., GOTO, Y., and HATA, K., 1967, *Bull. chem. Soc. Jap.*, **40**, 1994.
- [11] KOHNE, B., POULES, W., and PRAEFCKE, K., 1984, *Chem. Z.*, **108**, 113.
- [12] EL HEWEIHI, Z., 1953, *Chem. Ber.*, **86**, 862.
- [13] BUSHBY, R. J., and FERBER, G. J., 1976, *J. chem. Soc. Perkin Trans. 2.*, 1688.
- [14] LEWIS, I. C., and SINGER, L. S., 1965, *J. chem. Phys.*, **43**, 2712.
- [15] COURTNEIDGE, J. L., DAVIES, A. G., and MCGUCHAN, D. C., 1988, *Recl. Trav. chim. Pays-Bas Belg.*, **107**, 190.
- [16] KROHNKE, C., ENKELMAN, V., and WEGNER, G., 1980, *Angew. Chem. Int. Edn. Engl.*, **19**, 912.
- [17] MEOT-NER (MAUTNER), M., 1980, *J. phys. Chem.*, **84**, 2724; 1984, *Accts Chem. Res.*, **17**, 186.
- [18] TERAHARA, A., OHYA-NISHIGUCHI, H., HIROTA, N., and OKU, A., 1986, *J. phys. Chem.*, **90**, 1564.
- [19] OHYA-NISHIGUCHI, H., IDE, H., and HIROTA, N., 1979, *Chem. Phys. Lett.*, **66**, 581.
- [20] DAVIES, A. G., and SHIELDS, C. I., 1989, *J. chem. Soc. Perkin Trans. 2.*, 1001.
- [21] SZWARC, M., 1974, *Ions and Ion Pairs in Organic Reactions*, Vol. 2, Chap. 1 (Wiley).
- [22] MCCONNELL, H. M., and CHESNUT, D. B., 1956, *J. chem. Phys.*, **28**, 107.
- [23] ALBERTI, A., PEDULLI, G. F., TIECCO, M., TESTAFERRI, L., and TINGOLI, M., 1984, *J. chem. Soc. Perkin Trans. 2.*, 975.
- [24] GILBERT, B. C., HODGEMANN, D. K. C., and NORMAN, R. O. C., 1973, *J. chem. Soc. Perkin Trans. 2.*, 1748.
- [25] MISHRA, S. P., and SYMONS, M. C. R., 1975, *J. chem. Soc. Perkin Trans. 2.*, 1492; SYMONS, M. C. R., HASEGAWA, A., and MAJ, P., 1982, *Chem. Phys. Lett.*, **89**, 254; GLIDEWELL, C., 1985, *Chem. Phys. Lett.*, **89**, 254; GLIDEWELL, C., 1985, *Chem. scripta*, **28**, 145; SAGL, D. J., and MARTIN, J. C., 1988, *J. Am. chem. Soc.*, **110**, 5827.
- [26] CLARK, T., 1988, *J. Am. chem. Soc.*, **110**, 1672.
- [27] KIRA, A., ARAI, S., and IMAMURA, M., 1972, *J. phys. Chem.*, **76**, 1119.
- [28] LE BERRE, V., ANGÉLY, L., SIMONET-GUÉGUEN, N., and SIMONET, J., 1987, *J. chem. Soc. Chem. Commun.*, 984.
- [29] OHYA-NISHIGUCHI, H., TERAHARA, A., HIROTA, N., SAKATA, Y., and MISUMI, S., 1982, *Bull. Chem. Soc. Jap.*, **55**, 1782.
- [30] HEINEY, P. A., FONTES, E., DE JEU, W. H., RIERA, A., CARROLL, P., and SMITH, A. B., 1989, *J. Phys., Paris*, **50**, 461.