Perylene and its Monoperchlorates: Conductivities of Compounds and Mixtures

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The ionic perylenium perchlorate is prepared, electrolytically, for the first time. It has a needle-axis conductivity σ of 0.1 Ω^{-1} cm^{-1} and compacted discs showing 0.0075 Ω^{-1} cm^{-1}. Compacted (covalent) perchloratoperylene has σ 1.6 × 10^{-4} Ω^{-1} cm^{-1} but compressed-powder mixtures with the ionic species show a maximum σ at 1 : 1 composition, with σ enhanced to 0.1 Ω^{-1} cm^{-1}. The bisperylene perchlorate gives $10^7\sigma/\Omega^{-1}$ cm^{-1} 1.6 (needle axis) and 500 (transverse), *cf.* 1.7 (compressed powder); admixtures with perylenium perchlorate are studied. The electrocrystallisation processes yielding the radical salts are examined.

As π donors, polycyclic aromatic compounds form donor–acceptor complexes[1] having electrical conductivities from 10^{-9} to 10^2 Ω^{-1} cm^{-1}. The bisperylene perchlorate[2] and metal–dicyanoethylenedithiolate,[3] and the bispyrene perchlorate,[4] have been made by electrocrystallisation.[5] We have now made the new (mono) perylenium perchlorate salt $C_{20}H_{12}ClO_4$, and contrasted its properties with the covalently bonded compound perchloratoperylene $C_{20}H_{11}ClO_4$. These are abbreviated, respectively, to pery$^+ClO_4^-$ and pery-ClO_4^-. Comparison is made with bisperylene perchlorate pery^{0}pery$^+ClO_4^-$ or pery$_2^+ClO_4^-$), and physical mixtures of the ionic and covalent monospecies are also studied in a novel organic 'valence mixture' system. The species pery$^+ClO_4^-$ has been obtained in a mixed salt[6] with AgI but not hitherto as a pure compound.

Experimental

Electrochemical details are given later. Pery$_2^+ClO_4^-$ was made by a reported[2] electrolytic procedure (Found: C, 79.9; H, 4.0. Calc. for $C_{40}N_{24}ClO_4$: C, 79.5; H, 4.0%). For pery$^+ClO_4^-$, a nitrobenzene solution (100 ml) containing perylene (1 mmol) and tetrabutylammonium perchlorate (2 mmol) was electrolysed on Pt foil at 1.235 ± 0.001 V *versus* s.c.e. for 120 h at 20 °C.[5] The initial current density 267 μA cm^{-2} decreased to 102 μA cm^{-2} in the first 30 min, rose to 133 μA cm^{-2} in the next 29 h, then fell to 108 μA cm^{-2} over the following 91 h; this is one of the current sequences diagnostic of crystal formation.[5] The dark green needle-shaped crystals (2 × 0.01 × 0.01 mm), m.p. 205 °C (Found: C, 67.6; H, 3.5. Calc. for $C_{20}H_{12}ClO_4$: C, 68.3; H, 3.4%), were taken from the electrode and copiously washed with ether and then n-hexane and dried at 10^{-2} mmHg and 50 °C.

To obtain pery-ClO_4, perylene (1 mmol) in CCl_4 (300 ml) and tetrabutylammonium perchlorate (1 mmol) were mixed in an infinite pathlength photoreactor. A medium-pressure 100 W Hanovia lamp was used for 8 h irradiation, yielding a dark brown microcrystalline compound, which was filtered off and washed with acetonitrile, then ether, then vacuum dried at 40 °C for 8 h, m.p. 260—262 °C (Found: C, 68.5; N, 3.2. Calc. for $C_{20}H_{11}ClO_4$: C, 68.5; H, 3.2%).

For compaction conductivities, compounds were ground in an agate mortar for 10 min, until homogeneously powdered. Discs (diameter 5 mm, *ca.* 0.25 mm thickness) were pressed, after evacuation, to 9 000 kg for 4 min. Components of mixtures were powdered separately before mixing. Direct current conductivities at up to 10 V were obtained by two-probe or four-probe techniques.[5] Material from the same batch will have comparable conductivities but different samples can differ considerably.[5] Perylene–perchlorate mixtures (not involving pery-ClO_4) were made by mixing pery^0 with pery$^+ClO_4^-$ [for $\beta < 0.5$, in pery-$(ClO_4)_\beta$] or pery$^+ClO_4^-$ with pery$_2^+ClO_4^-$ (for $\beta > 0.5$) except where indicated.

Table 1. Near i.r. absorptions

Substance		Peak (cm^{-1})	Ref.
pery$^+ClO_4^-\cdot$AgI	(solid)	1286	7, 12
pery$^+ClO_4^-$	(solid)	1280 at low resolution	This work
		1050 } high 1400 } resolution	This work
pery$_2^+ClO_4^-$	(solid)	1420	This work
pery$^+SbCl_5^-$	(solid)		13
pery$^+SbCl_5^-$	(solution)	1280 (low resolution?)	13

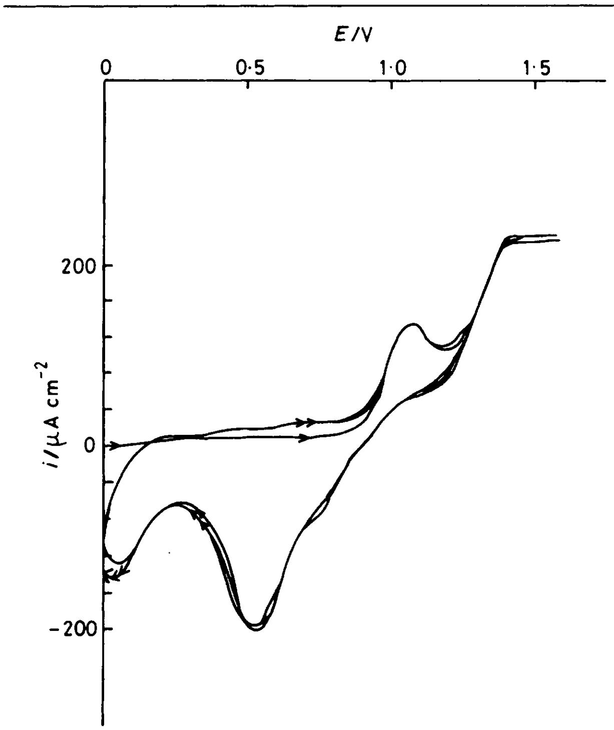

Figure 1. Cyclic voltammogram of perylene (2.2 × 10^{-3}M) in dichloromethane and 0.056M-Et_4NClO_4 at 20 °C. Scan rates 20 mV s^{-1}; 25 °C

I.r. spectra were run on a Perkin-Elmer 357 spectrophotometer. Near-i.r. spectra were measured on KBr discs using a Beckman Acta IV M spectrophotometer. The electrochemistry associated with the electrocrystallisation was examined using a Bruker E44S or Bruker E310 potentiostat.

Results and Discussion

I.r. Spectra.—The i.r. spectra show bands in all compounds clearly related to the parent perylene, the spectra of which accorded with the literature;[8] ClO_4-containing species show the

Table 2. Effects of temperature and solution composition on electrocrystallised products. Series 1, CH_2Cl_2; pery$_2^+$ClO$_4^-$ product; 1.026 V applied. Series 2: $C_6H_5NO_2$; pery$^+$ClO$_4^-$ product; 1.235 V applied. Series 3: other solvents; nil product; 1.026 V applied (except THF, 1.350 V)

Temp (°C)	$\frac{[\text{pery}]}{[\text{ClO}_4^-]}$	Product	σ/Ω^{-1} cm^{-1}
Series 1 (only pery$_2^+$ClO$_4^-$ is formed)			
23	2	Crystal[a]	1.6×10^{-7}
23	1	Crystal[a]	1.0×10^{-7}
23	0.5	Crystal[a]	1.0×10^{-7}
10	2	Powder[b]	1.8×10^{-7}
0	2	Powder[b]	2.1×10^{-7}
Series 2 (only pery$^+$ClO$_4^-$ is formed)			
23	2	Crystal[a]	0.84
23	1	Crystal[a]	0.1
23	0.5	Crystal[a]	0.25
10	0.5	Powder[b]	1.0×10^{-4}
0	0.5	Powder[b]	1.2×10^{-6}
Series 3			
23	0.5	Nil	

[a] Single-crystal conductivities at 296 K along needle axis using two probes. [b] Compacted disc conductivities at 296 K using two probes one on each face.

expected[9] 1 110 cm^{-1} feature. The near-i.r. spectra shows peaks at 1 400 and 1 050 cm^{-1} in pery$^+$ClO$_4^-$ and at 1 420 cm^{-1} for pery$_2^+$ClO$_4^-$ (Table 1). The discrepant observations for pery$^+$SbCl$_5^-$ are explained[10] as arising from the solution-phase transition 2pery$^+$ $\xrightarrow{h\nu}$ pery^{0}pery^{2+} not being possible in the solid, where the required monocation juxtaposition is precluded. Pery$_2^+$ exists in equilibrium[11] with pery$^+$ in solution as indicated by e.s.r. However, individual pery$^+$ in pery$_2^+$-ClO$_4^-$ appear to be segregated from neighbouring cation and from pery^0 by incorporation into anion–cation stacks (see below) which may account for obliteration of the 1 050 cm^{-1} transition.

Electrocrystallisation of pery$_2^+$ClO$_4^-$.—Cyclic voltammograms of perylene in dichloromethane with tetraethylammonium perchlorate (Figure 1) show an irreversible anodic peak at *ca.* 1 V *versus* s.c.e. (forming pery$^+$?) and a plateau-form peak at 1.4 V on the first scan (possibly forming pery^{2+}); succeeding scans, if at scan rate $r < 20$ mV s^{-1}, show an additional (anodic) plateau-like contribution centred about 0.75 V. For the former two peaks $i_{pa}/r^{\frac{1}{2}}c$ decreases with $r^{\frac{1}{2}}$ which implies[13] a successive reaction to each oxidation. The 0.76 V plateau at low r suggests that some pery$^+$ survives the reductive limb of the first cycle to form, by addition to pery^0, pery$_2^+$, which is possibly more readily oxidised than pery^0, the perylene molecule itself. Electrocrystallisation[5] at 1.026 V thus apparently proceeds by step (1) followed by (2) and (3).

$$\text{pery}^0 \longrightarrow \text{pery}^+ + \text{e} \tag{1}$$

$$\text{pery}^+ + \text{pery}^0 \longrightarrow \text{pery}_2^+ \tag{2}$$

$$\text{pery}_2^+ + \text{ClO}_4^- \longrightarrow \text{pery}_2^+\text{ClO}_4^-(\text{cryst}) \tag{3}$$

Table 3. Conductivity measurements (25 °C) exemplifying different configurations

Compound	Method	σ/Ω^{-1} cm^{-1}
Perylene	Disc	10^{-12}
pery$^+$ClO$_4^-$	Disc	10^{-4}
	Disc (four probe)	7.5×10^{-3}
	Single crystal, needle axis	0.1
pery-ClO$_4$	Disc	1.6×10^{-4}
pery$_2^+$ClO$_4$	Disc	1.7×10^{-7}
	Single crystal needle axis	1.7×10^{-7}
	transverse	5×10^{-5}

Table 4. Values of half-wave potentials $E_{\frac{1}{2}}$ for reductions in 2×10^{-1}M-dichloromethane solution; 25 °C, 0.056M tetrabutylammonium perchlorate

Reduction	$E_{\frac{1}{2}}$/V (against s.c.e.)
$\text{pery}^+ + \text{e} \longrightarrow \text{pery}^0$	1.01
$\text{pery}^{2+} + \text{e} \longrightarrow \text{pery}^+$	1.34
$\text{pery}^0 + \text{e} \longrightarrow \text{pery}^-$	−0.19

(Stockholm convention: $\Delta G^\circ = -nFE_{\frac{1}{2}}$)

Electrocrystallisation of pery$^+$ClO$_4^-$.—Two irreversible peaks appear in cyclic voltammograms of perylene and tetrabutylammonium perchlorate in nitrobenzene, at 1.40 and 2.07 V with $r = 20$ mV s^{-1} (Figure 2). The prediction[12] of a stable pery$^+$ ion has been confirmed[11] in nitrobenzene solution. In this solvent $i_p/r^{\frac{1}{2}}c$ is[11] constant with $r^{\frac{1}{2}}$ hence no subsequent association pery$^+$ + pery^0 is indicated. In highly polar solvents pery$^+$ solutions are found[11] to be free of pery$^+$–pery$^+$ charge-transfer absorptions found in weakly polar solvents, which implies a discreteness and stabilisation of pery$^+$ in the former. Thus the formation sequence of pery$^+$ClO$_4^-$ crystals is predicted as reactions (4) and (5).

$$\text{pery}^0 \longrightarrow \text{pery}^+ + \text{e} \tag{4}$$

$$\text{pery}^+ + \text{ClO}_4^- \longrightarrow \text{pery}^+\text{ClO}_4^-(\text{cryst}) \tag{5}$$

Variation of Conditions of Electrocrystallisation.—The effect of change of solvent on the stoicheiometric composition of electrocrystallised crystals has been noted already. In elaboration of these experiments we tried the alternative solvents tetrahydrofuran, 1:1 (v/v) trichlorobenzene–dichloromethane, nitromethane, and acetonitrile, to no effect. Variation of anion concentration showed that better looking crystals ensued with more anion present. In further experiments using the crystal-producing solvents the temperature was lowered, and, contrary to our expectation, in both cases lower temperatures produced not crystals but powders. No IO$_4^-$ adducts formed in nitrobenzene or dichloromethane. The results are summarised in Table 2, together with the electrical conductivities of the products. The latter show the probable anisotropy of conductivity in pery$^+$ClO$_4^-$, discs from powder showing low conductivities governed by the lower components, contrasting with the substantial needle-axis values. Further discussion follows below.

Formation of pery-ClO$_4$.—Photo-oxidative charge transfer (CT) occurs in halogenoalkane solutions of ferrocene, alkylamines,[14] and tetrathiafulvalene. Carbon tetrachloride forms CT complexes with benzene and substituted benzenes.[15,16] The photo-oxidations involve an initial weakly donor–halogenoalkane complex which ionises on irradiation into the CT band. For the perylene system a similar mechanism is probable with subsequent elimination of a hydrogen atom and bond formation with ClO$_4^-$ (which isomer forms was not established).

Conductivities of the Stoicheiometric Species pery^0, pery$_2^+$ClO$_4^-$, pery$^+$ClO$_4$, *and* pery-ClO$_4$.—Values of conductivity σ are given in Table 3. If the simplifying assumption is made that

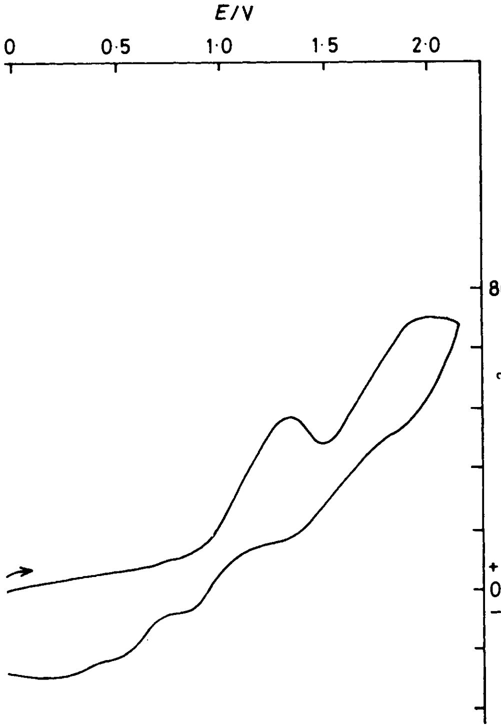

Figure 2. Cyclic voltammogram of perylene (0.01M) in nitrobenzene and 0.2M-Bu$_4$NClO$_4$ at 20 mV s^{-1}, 25 °C

mobilities μ in all the solids are approximately constant, then in the expression $\sigma = ne\mu$ (where n is the number of charge carriers per unit volume) we should examine the factors governing n in order to rationalise relative σ values of pery^0 and pery$^+$ClO$_4^-$. It has been suggested[17] that the relative extents of the disproportionations (6) and (7) in the solid state can be

$$2\text{pery}^0 \longrightarrow \text{pery}^+ + \text{pery}^- \qquad (6)$$

$$2\text{pery}^+ \longrightarrow \text{pery}^{2+} + \text{pery}^0 \qquad (7)$$

inferred from solution-phase data, and that in an electron-hopping mechanism in the solids the relative disproportionations will govern n. From the tabulated $E_{\frac{1}{2}}$ values differences $\Delta E_{\frac{1}{2}}$ in the values in Table 4 for the pairs of couples making up (6) and (7) are respectively −1.20 and −0.32 V, favouring (7), and so in accord with relative σ values, in conformity with the hypothesis. Structural factors are ignored in such analyses. Presumably pery-ClO$_4$ falls between pery^0 and pery$^+$ in ease of disproportionation, but structural assistance like head to tail dipole dispositions could be important. (Two-probe conductivities are, as illustrated, well known to represent lower limits).

The conductivity of pery$_2^+$ClO$_4^-$ is by contrast lower than that of pery$^+$ClO$_4^-$, despite incorporating (nominal) pery^0 and pery$^+$ as components and so notionally facilitating hopping. Paramagnetism studies[2] indicate that perylenium radicals pery$^+$ alternate with anion X$^-$ in stacks, pery^0 being outside the stacks, which we represent by parentheses, in (D$^+$X$^-$)D^0. This would explain the conductivity observation. (By contrast pery$_2^+$\{M(mnt)$_2$\}$^-$, the metal-dicyanoethylenedithiolate adducts,[3] with metal M as Ni or Pt, show high σ values, up to 50 Ω^{-1} cm^{-1}; here pery$^+$pery^0 are stacked[3] in a (D$^+$D^0)X$^-$ structure. In perylene nickel-dithiete adducts[18] simple (D^{0}X^0) stacks give moderate (10^{-3}—10^{-5} Ω^{-1} cm^{-1}) room-temperature conductivities. Single-crystal σ values for pery$^+$ClO$_4^-$ and pery$_2^+$ClO$_4^-$ bear out the inferences (Table 3); the latter substance unusually shows a higher σ for the transverse than the needle axis. The disc values are within 10-fold or so of the least-conductive-axis values obtained on single crystals, as has been observed before.[18]

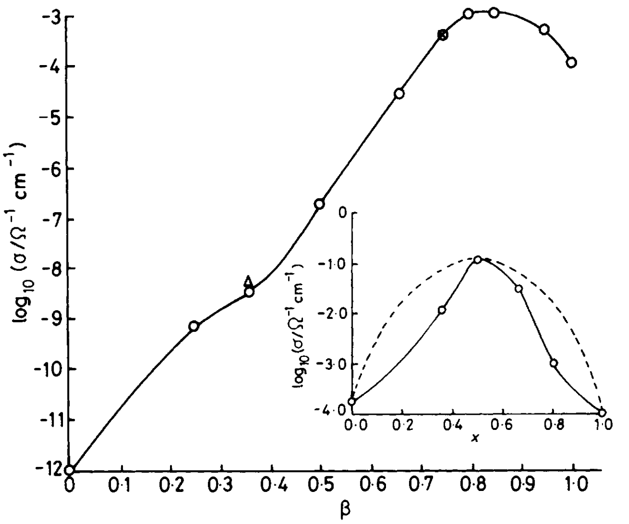

Figure 3. Conductivity σ of mixtures of pery$^+$ClO$_4^-$ and pery-ClO$_4$ with mole fraction x of pery$^+$ClO$_4^-$, and of 'pery(ClO$_4$)$_\beta$' with β. ○, for β <0.5, by mixing pery^0 and pery$_2^+$ClO$_4^-$; ○, for β >0.5, by mixing pery$_2^+$ClO$_4^-$ and pery$^+$ClO$_4^-$; △, ×, by mixing pery^0 and pery$^+$ClO$_4^-$

Conductivities of Mixtures over Continuous Composition Ranges.—Ground powders have been mixed and compacted. 'Pery(ClO$_4$)$_{0.33}$' was made by so mixing pery^0 and pery$^+$ClO$_4^-$ and also pery^0 and pery$_2^+$ClO$_4^-$, giving σ values of 5 × 10^{-9} and 3 × 10^{-9} Ω^{-1} cm^{-1}, respectively. Likewise 'pery(ClO$_4$)$_{0.75}$' from pery^0 with pery$^+$ClO$_4^-$, and from pery$^+$ClO$_4^-$ with pery$_2^+$ClO$_4^-$, have identical σ values, 5 × 10^{-4} Ω^{-1} cm^{-1}. Thus the trituration and compaction processes appear to homogenise the samples to a remarkable degree, and the σ observations on mixtures will be discussed as though for true (non-stoicheiometric) chemical compositions. (Other malleable materials have proved comparably amenable to such analysis.[19])

The 'pery(ClO$_4$)$_\beta$' conductivities with composition are depicted in Figure 3. There is a weak maximum at $\beta = 0.8$, which does not merit comment, the main feature being the fairly regular increase of 10^8-fold in σ with β.

Similar mixtures of pery$^+$ClO$_4^-$ with pery-ClO$_4$ offer more promise in being notionally of almost identical composition (one hydrogen atom different). While clearly highly polar, however, pery-ClO$_4$ has essentially molecular perylene as half the molecule, which can play the role of pery^0 in mixtures. The admixture with pery$^+$ in pery$^+$ClO$_4^-$ leads to the classical mixed-valence σ-composition profile in Figure 3. Use of $\sigma = n_0(x_1x_2)e\mu$ where the pery^0 and pery$^+$ mole fractions are given by x_1 and x_2, with a mobility μ assumed constant across the range of composition, gives the dashed line.[20] The equimolar enhancement of 10^3-fold is notable, and probably implies a new compound at this maximum (pery-ClO$_4$pery$^+$ClO$_4^-$).

Conclusions.—The greater conductivity of pery$^+$ClO$_4^-$ than of pery$_2^+$ClO$_4^-$ is unexpected and implies a structure of the latter disallowing stacks of alternating pery$^+$pery^0, a configuration yielding high σ in other compounds.[3] Pery$^+$ClO$_4^-$ and pery-ClO$_4$ have closely similar conductivities, which are enhanced by 10^3 in a 1:1 physical mixture compaction; this observation relates to the least conductive σ component in pery$^+ClO_4^-$. Preparations of the two ionic species proceed by very different mechanisms in their respective solvents.*

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* Perylenium perchlorate was found to explode on contact with nickel and the materials in this paper should also be handled with caution, in small amounts, especially in contact with metals.

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