Association and Orientation of Copper(II) Tetra-t-butylphthalocyaninate in Multilayer Langmuir–Blodgett Films as determined by Electron Paramagnetic Resonance Spectroscopy†

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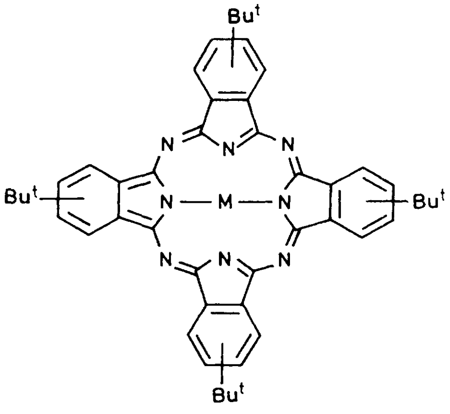
E.s.r. spectra obtained at 20 or 25 K, electronic absorption spectra measured at ambient temperature, and vapour-phase osmometry show that copper tetra-t-butylphthalocyaninate (**1**) is associated in dilute solutions in dichloromethane but unassociated in toluene. The corresponding spectra within single- and multi-component Langmuir–Blodgett films on silica slides are also reported. Films containing complex (**1**) either alone or admixed with eicosanoic acid gave spectra characteristic of the associated material. However, a three-component film containing (**1**), tetra-t-butylphthalocyanine (**2**), and eicosanoic acid (ratio 5:50:400) gave an e.s.r. spectrum showing hyperfine and superhyperfine structure. The orientational dependence of the e.s.r. spectrum was investigated and reveals that the molecules of (**1**) are aligned with the plane of the ring at 80 ± 10° to the substrate surface. Some orientational disorder is also present and can be detected in the $g_{\parallel}$ region.

There is a growing interest in the electrical and optical properties of molecular layers prepared by the Langmuir–Blodgett (L–B) technique.[1] It has been shown that phthalocyanine dyes can be spread from an organic solvent onto an air–water interface to form monolayers which can then be transferred to a solid substrate by dipping.[2,3] This constituted an important advance since the dyes were not known to be surface active but were known to possess high thermal and optical stability. However, it is clearly of crucial importance to know the structure of such phthalocyanine films and to establish the degree of molecular order within a film. For example, if the films are completely disordered then the L–B technique of spreading is unlikely to confer any properties on a film different from those of an evaporated thin film. There has been rather slow progress in the development of methods which establish order in L–B films of phthalocyanines. The first attempts at a study of a monolayer were made using electron microscopy (e.m.) of an L–B monolayer of copper tetra-t-butylphthalocyaninate, (**1**), deposited on an electron microscope grid.[4] Electron-diffraction patterns and the e.m. image indicated that small, highly disordered arrangements of domains were present, but with good crystallographic order within the domains. The molecules appeared to be lying in columns in the plane of the film with an intermolecular spacing of 0.33 nm and an intercolumnar separation of 1.9 nm. An optical study of the metal-free tetra-t-butylphthalocyanine, (**2**), spread as a monolayer onto glass suggested that a well ordered film was being obtained.[5]

We have been investigating the use of electron paramagnetic resonance (e.s.r.) spectroscopy for the determination of order and molecular orientation within L–B films containing copper phthalocyaninate pigments. The e.s.r. properties of copper phthalocyaninate, [Cu(pc)], have been thoroughly investigated in single crystals diluted in metal-free or zinc phthalocyanine,[6–9] as the tetrasulphonated derivatives in water,[10] and as the unsubstituted form in concentrated sulphuric acid.[11] When [Cu(pc)] is magnetically dilute the e.s.r. spectrum is characterized by an axial g tensor, $g_{\parallel} = 2.179$ and $g_{\perp} = 2.050$, where the principal axis of $g_{\parallel}$ is known to be perpendicular to the phthalocyanine plane. The spectrum contains a wealth of lines arising from nuclear hyperfine coupling both to copper ($I_N = \frac{3}{2}$) and to the four in-plane nitrogen atoms liganded to the metal ion. The copper hyperfine is highly anisotropic with $A_{\parallel} = 0.0202\ \text{cm}^{-1}$ and $A_{\perp} = 0.0019\ \text{cm}^{-1}$. These properties provide an excellent probe of the degree of aggregation within a film and the orientation of the phthalocyanine molecule relative to a substrate plane. The approach has been used recently in a study of the orientation of the porphyrin ring system in an L–B film,[12] and concurrent with the present work,[13] Pace *et al.*[14] have investigated tetrakis[(1-methyl-1-phenylethyl)phenoxy]-phthalocyanine films spin labelled with Cu^{II} and Co^{II}.



M
(**1**) Cu
(**2**) H,H

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† *Non-S.I. units employed:* mmHg ≈ 133 Pa, G = 10^{-4} T.

In this paper we report an investigation of the e.s.r. properties of complex (**1**) in solutions of organic solvents and spread as L–B films in concentrated and diluted forms. It is necessary to obtain a magnetically dilute film of (**1**) in order that the g-value anisotropy will be visible and that the nuclear hyperfine structure will be well resolved. Having established conditions to obtain such spectra from L–B films with a good signal-to-noise ratio, it has been possible to examine the orientation dependence of the e.s.r. spectrum of (**1**) in a film and hence to deduce the orientation of (**1**) relative to the substrate surface.

Experimental

Materials.—(*a*) *Copper*(II) *tetra-t-butylphthalocyaninate* (**1**). To a stirred solution of t-butylbenzene (20 g, 0.149 mol), iron(III) chloride (1.5 g, 0.009 mol), and iodine (one crystal) at −5 to −0 °C was added bromine (47.7 g, 0.298 mol) dropwise over 2 h. The solution was stirred at 0 °C for 4 h and then at room temperature (r.t.) for 12 h. Dichloromethane (25 cm^3) was added and the organic phase washed with 5% aqueous sodium hydroxide–sodium thiosulphate (250 cm^3) and dried ($MgSO_4$). The solvent was removed under vacuum to leave a black viscous oil which was distilled under vacuum to yield 1,2-dibromo-4-t-butylbenzene (20.44 g, 47%) as a colourless liquid, b.p. 88—90 °C, 0.15 mmHg (lit.,[15] b.p. 121—122 °C, 5 mmHg).

1,2-Dibromo-4-t-butylbenzene (6.5 g, 0.022 mol) and copper(I) cyanide (6.0 g, 0.066 mol) were heated under reflux in dimethylformamide (dmf) (120 cm^3) for 8 h. After cooling, the reaction mixture was stirred with concentrated ammonia solution (250 cm^3) for 12 h. The blue solution was filtered and extracted with dichloromethane (2 × 150 cm^3). The organic phases were combined and dried ($MgSO_4$). The solvent was removed under vacuum to yield a dark blue solid, from which copper tetra-t-butylphthalocyaninate was separated by elution through silica (CH_2Cl_2 as eluant) (Found: C, 71.6; H, 5.6; N, 13.9. $C_{48}H_{48}CuN_8$ requires C, 72.0; H, 6.0; N, 14.0%).

Metal-free tetra-t-butylphthalocyanine (**2**). 1,2-Dibromo-4-t-butylbenzene (10.5 g, 0.037 mol) and copper(I) cyanide (9.94 g, 0.11 mol) were heated under reflux in dmf (125 cm^3) for 5 h. After cooling, the reaction mixture was stirred in concentrated ammonia solution (300 cm^3) for 12 h. The blue solution was filtered and the solid residue washed with water (300 cm^3). The green solid was extracted with diethyl ether for 3 d (Soxhlet thimble). The ether was removed by evaporation to afford a residual brown oil which distilled to yield 1,2-dicyano-4-t-butylbenzene (1.33 g, 19%) as a colourless liquid, b.p. 124—128 °C, 0.15 mmHg (lit.,[16] 165—170 °C, 6 mmHg).

A solution of 1,2-dicyano-4-t-butylbenzene (1.3 g, 7.06×10^{-3} mol) in 2-dimethylaminoethanol (10 cm^3) was heated under reflux and a steady stream of ammonia gas was passed through the solution for 7 h. The dark blue solution was filtered hot, washed with ethanol and acetone, and chromatographed over silica gel (CH_2Cl_2 eluant) to afford compound (**2**) (0.32 g, 24%) (Found: C, 77.7; H, 6.8; N, 15.1. $C_{48}H_{50}N_8$ requires C, 78.0; H, 6.8; N, 15.2%).

Copper tetra-t-butylphthalocyaninate and metal-free tetra-t-butylphthalocyanine are expected to be formed as a mixture of four isomers (statistical ratio 4:2:1:1), the isomers differing through the relative dispositions of the t-butyl groups. Evidence for the presence of isomers is available from the 400-MHz ^{1}H n.m.r. spectrum (Bruker WH400) of the metal-free compound measured in $CDCl_3$ solvent. Signals for the t-butyl group protons appear at δ 1.869, 1.873, 1.886, 1.889, 1.920, and 1.932, *cf.* ref. 5 but contrast ref. 17.

(*b*) *Langmuir–Blodgett films.* The L–B trough was of the constant-perimeter design and sited in a clean room where the air was filtered. Purified water (*ca.* 18 MΩ cm^{-1}) was obtained using reverse osmosis, activated carbon deionization, and filters (pore diameter 0.22 μm). Toluene was used as the spreading solvent for pure complex (**1**) and a xylene–trichloroethane mixture was used to spread the mixed phthalocyanine monolayers containing (**1**), (**2**), and eicosanoic acid. A 'pure' water subphase (pH *ca.* 5.5 due to dissolved CO_2) was used for preparing films of (**1**) and a more acidic subphase (pH *ca.* 3.5) was used for the mixed films to ensure negligible ionization (< 1%) of the fatty acid component.

Silica substrates (Spectrosil^R grade B) were used in an attempt to minimize any unwanted e.s.r. background signal and their dimensions (37 × 2.5 × 1 mm) made them suitable for insertion into standard e.s.r. sample tubes. Multilayer films were built up on opposite faces of the narrow substrates to permit investigation of any structural anisotropy, deposition onto substrate edges being avoided by using guard substrates. Transfer of the pure monolayers of (**1**) was achieved only on slow (*ca.* 1 mm min^{-1}) substrate emersion, but the mixed monolayers could be prepared at much faster spreading speeds (*ca.* 5 mm s^{-1}) on both substrate emersion and immersion thereby allowing films 500 layers thick (*ca.* 1.4 mm) to be completed in < 1.5 h. All monolayers were transferred at a surface pressure of *ca.* 30 mN m^{-1}.

(*c*) *Physical and spectroscopic measurements.* A Knauer vapour-phase osmometer was used, with benzil as calibrant, to determine the extent of aggregation of the phthalocyanines in toluene and dichloromethane.

E.s.r. spectra were recorded with an *X*-band spectrometer, Bruker ER 200D, equipped with an Aspect 2000 minicomputer, and fitted with a flow-cryostat (ESR-900, Oxford Instrument Company, plc). The sample temperature can be controlled between 4 and 300 K by means of a flow of cold helium gas generated from a bath of liquid helium. The cryostat is fitted with a goniometer head. A L–B film spread onto silica is mounted into a slotted groove at the end of a Perspex rod and secured with paraffin wax. The rod passes through an O seal and is mounted in the goniometer head. Samples dissolved in organic solvents were placed in standard silica e.s.r. tubes (internal diameter 2 mm) which were lowered into the cavity.

The optical properties of the films were measured using either a Cary model 17 or a Pye-Unicam SP-400 spectrophotometer.

Results and Discussion

(*a*) *Solution-phase Results.*—The e.s.r. spectrum of complex (**1**) dissolved in toluene (3.7 mg per 10 cm^3) at 25 K is shown in Figure 1. This spectrum can be compared with that of copper phthalocyaninate enriched in the isotope ^{63}Cu, dissolved in concentrated sulphuric acid,[11] in which well resolved nuclear hyperfine structure from ^{63}Cu and the four nitrogen atoms bound directly in the plane to the copper ion is visible. As expected the two spectra are very similar. There are four regions, A—D, due to the parallel hyperfine coupling to ^{63,65}Cu, with A values close to 200 G. These four regions are split symmetrically about the $g_{\parallel}$ position of 2.179. The region of the line due to the third hyperfine transition of the copper ion is partially obscured by the hyperfine structure of the $g_{\perp}$ region. Each of the parallel copper hyperfine lines should be split into nine lines due to coupling with four equivalent ^{14}N ($I_N = 1$) nuclei. They can be observed clearly in the case of the regions A and B.

In the perpendicular direction the copper hyperfine coupling constant is a factor of ten smaller than in the parallel direction. However, the ^{14}N hyperfine coupling constant is almost the same in the parallel and perpendicular directions and comparable to $A_{\perp}$(Cu). Hence the perpendicular region comprises the superposition of the copper and nitrogen hyperfine lines, giving rise to a complex set of lines. The confirmation of this is most clearly obtained from the oriented single-crystal studies of Harrison and Assour[6] who show the

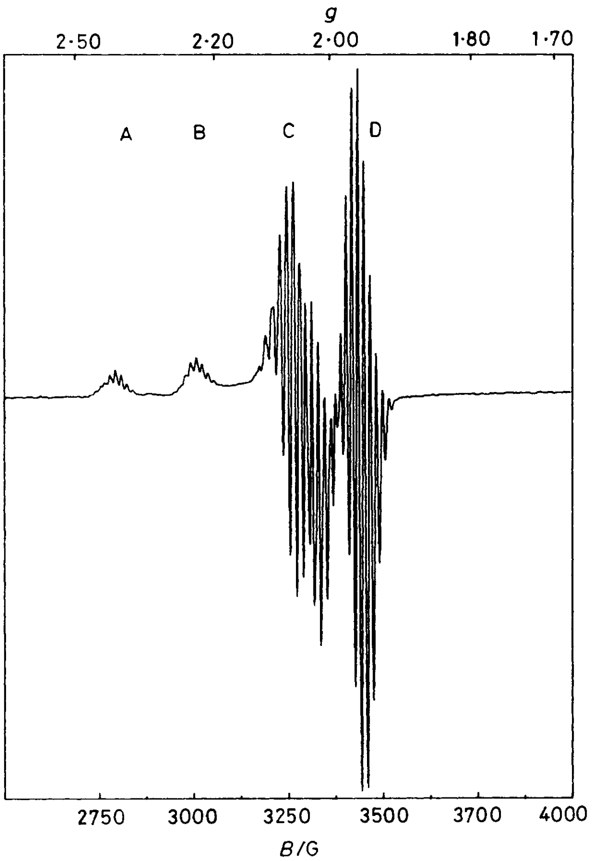

Figure 1. E.s.r. spectrum of complex (**1**) as a solution in toluene (3.7 mg per 10 cm^3 solvent) measured at 25 K. Microwave frequency 9.42 GHz; power 2.01 mW (the same values apply to Figures 4—6); gain 5 × 10^5; modulation amplitude (m.a.) 6.3 Gauss

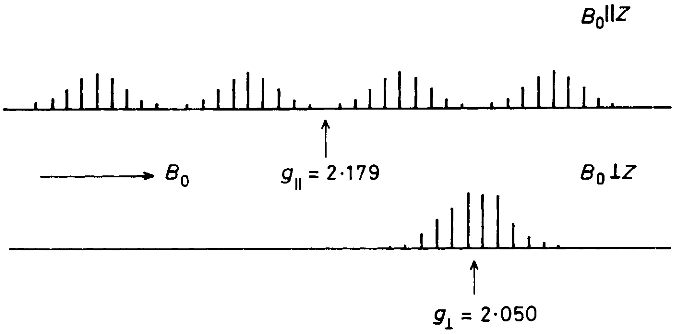

Figure 2. Stick-form representation of the absorption mode spectrum of complex (**1**) when the applied field B_0 is parallel and perpendicular to the normal to the plane of the phthalocyanine ring, *Z*

pure perpendicular spectrum as well as that with the magnetic field at 45° to the normal to the phthalocyanine plane. Figure 2 shows in stick form the absorption mode e.s.r. spectrum expected from an oriented molecule of (**1**) when the applied field B_0 is parallel and perpendicular to *Z*, the normal to the phthalocyanine plane.

It has been established that the e.s.r. spectrum of [Cu(pc)] is highly dependent upon its state of aggregation.[18,19] Since the concentration range over which oligomerization takes place will depend upon a number of factors including the nature of the substituents on the phthalocyanine ring and the polarity of the solvent, we have investigated the concentration dependence of

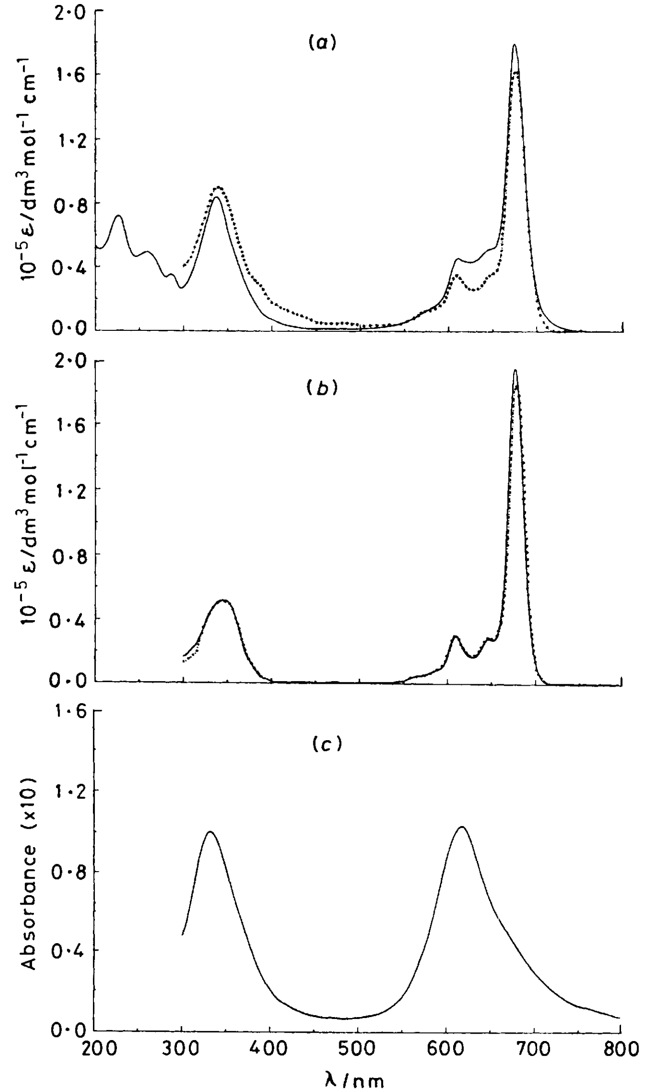

Figure 3. (*a*) The optical spectra of complex (**1**) in CH_2Cl_2 at 1 × 10^{-4} (——) and 1 × 10^{-5} mol dm^{-3} (· · · ·); (*b*) as (*a*) but with toluene as solvent. (*c*) The optical spectrum of (**1**) deposited as a L–B film (six layers) on a silica substrate

the e.s.r. and optical spectra of (**1**) in the solvents toluene and CH_2Cl_2. Figure 3 shows the optical spectra of solutions of (**1**) in toluene and CH_2Cl_2 at concentrations of 1 × 10^{-4} and 0.1 × 10^{-4} mol dm^{-3}. The spectrum in toluene is unchanged over this concentration range whereas that in CH_2Cl_2 varies. The latter effect is most clearly seen by comparing the ratios of the absorbances at the peak maxima of 677 and 610 nm. It has previously been shown[19,20] that on oligomerization of metal phthalocyaninates the most intense peak is replaced by a broader less-intense band to higher energy in the region of the subsidiary peak found at 610 nm for (**1**).

Vapour-phase osmometry (v.p.o.) confirms these findings as follows. For complex (**1**) in toluene at 65 °C the number-average molecular weight (M_n), obtained by extrapolation to zero concentration, was 841 compared with the monomer molecular weight of 801. On the other hand, M_n for (**1**) in CH_2Cl_2 at 30 °C was measured to be 1 890, giving a mean degree of association of 2.4. These results bear out the solution-phase absorption spectra. The finding that (**1**) in CH_2Cl_2 is aggregated even at infinite dilution shows that it is impossible to determine the

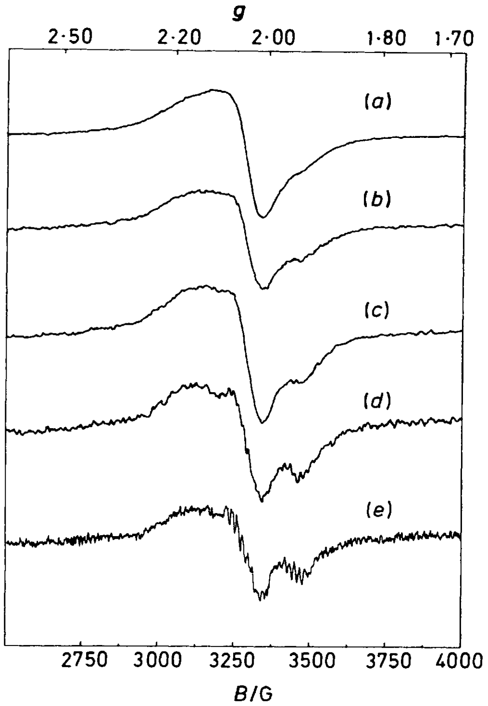

Figure 4. E.s.r. spectra of complex (**1**) measured at 25 K as solutions in CH_2Cl_2 at (*a*) 5.04 × 10^{-4} mol dm^{-3}, gain 3.2 × 10^5, m.a. 2.7 G; (*b*) 2.54 × 10^{-4} mol dm^{-3}, gain 4 × 10^5, m.a. 5.0 G; (*c*) 1.23 × 10^{-4} mol dm^{-3}, gain 4 × 10^5, m.a. 5.0 G; (*d*) 0.49 × 10^{-4} mol dm^{-3}, gain 4 × 10^5, m.a. 6.3 G; and (*e*) 0.25 × 10^{-4}, gain 5 × 10^5, m.a. 6.3 G

degree of aggregation at low number average by measurement of the absorption spectrum at a single concentration. A study of the concentration dependence of the spectrum is required.

The extent of aggregation can also be followed qualitatively by means of the e.s.r. spectrum. It has been shown that oligomerization of metal phthalocyaninates leads to loss of hyperfine structure and to development of new broad wings to the spectrum at *g ca.* 2.0.[10,20] Figure 4 shows the e.s.r. spectra, at 25 K, of complex (**1**) in CH_2Cl_2 over a range of concentration, 5.04 × 10^{-4}—0.25 × 10^{-4} mol dm^{-3}. At the highest concentration a relatively broad signal centred at $g = 2.0$ is observed with no evidence of any nuclear hyperfine splitting or *g*-value anisotropy of the same magnitude as for the monomer. On dilution, hyperfine splitting from the N nuclei begins to appear. This is evidence for a lowering of the degree of association as the concentration decreases. However, a monomer spectrum of the form seen in toluene is never observed. We use these e.s.r. properties to observe aggregation in a L–B film.

The e.s.r. spectrum of a polycrystalline sample of (**1**) at 25 K is given in Figure 5(*a*). It shows a narrow derivative line at $g =$ 2.0. Complete loss of hyperfine structure and *g*-value anisotropy has occurred presumably as a result of high exciton mobility in the crystal lattice. The lineshape is unchanged in polycrystalline samples between 300 and 25 K, suggesting that exciton mobility is not slowed sufficiently to enable the local hyperfine fields to be resolved.

(*b*) *L–B Films.*—The e.s.r. spectra of L–B films of complex (**1**) spread using a variety of conditions of electron-spin dilution have been recorded in order to define the circumstances under which a spectrum with fully resolved hyperfine structure can be obtained at a useful signal-to-noise ratio. Three different types of film have been prepared.

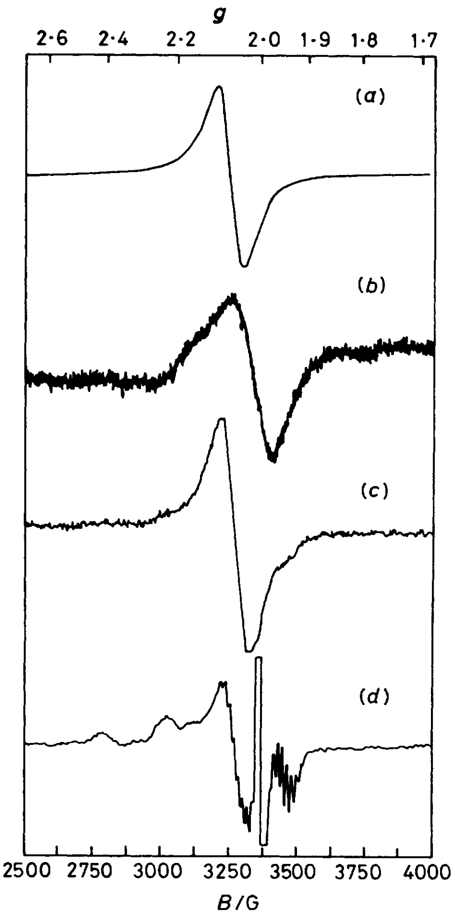

Figure 5. E.s.r. spectra of complex (**1**) measured at 25 K as: (*a*) a polycrystalline sample, gain 4 × 10^3, m.a. 0.5 G; (*b*) a L–B film (15 layers), gain 6.3 × 10^4, m.a. 8.0 G; (*c*) diluted in eicosanoic acid (5:95) and deposited as a L–B film (200 layers); (*d*) admixed with compound (**2**) and eicosanoic acid [(**1**):(**2**):C_{20} acid = 5:50:400] and spread as a L–B film (500 layers), gain 8 × 10^5, m.a. 12.5 and 6.3 G

The first consists of multilayers of pure (**1**) spread from toluene solution at a water interface. At 25 K this type of film yielded an e.s.r. spectrum, Figure 5(*b*), and an optical absorption spectrum of the aggregated type, as expected, Figure 3(*c*). The e.s.r. spectrum is similar in shape and width to that observed for the aggregated species in frozen CH_2Cl_2. It is, however, not the same as that of the polycrystalline sample. The spectrum of the film is apparently independent of the orientation of the film with respect to the applied magnetic field. The optical spectrum is similar to those reported elsewhere for L–B films of the phthalocyanine derivative (**2**),[2–5] *cf.* also ref. 21.

A second type of film was made with (**1**) diluted in the fatty acid eicosanoic acid, $CH_3(CH_2)_{18}CO_2H$, in an attempt to dilute the electron spin of (**1**) in order to obtain spectra showing anisotropic *g* values and resolved hyperfine structure. The e.s.r. spectrum of a film 200 layers thick made with 5% complex (**1**) diluted in the fatty acid is shown in Figure 5(*c*). No resolved hyperfine structure or *g*-value anisotropy is observed. The band shape is rather similar to that of polycrystalline (**1**), Figure 5(*a*). There was no orientation dependence to this spectrum. We conclude that (**1**) remains highly aggregated within the film and has not been dispersed monomolecularly by the eicosanoic acid.

A third type of film was made consisting of (**1**) diluted into the metal-free analogue (**2**) and spread with eicosanoic acid. A range of concentrations have been studied, Table, with various ratios of (**1**) to (**2**) in the film. The films were made of 500 layers

Table. E.s.r. properties of L–B films containing mixtures of compounds (**1**), (**2**), and eicosanoic acid. Each film contained 500 layers, unless otherwise stated

Ratio of components			
(**1**)	(**2**)	C_{20} acid	Comments on e.s.r. spectra
0.4	20	400	Poor signal-to-noise ratio; no parallel hyperfine observed
1	20	400	Good signal-to-noise ratio; no parallel hyperfine observed; orientation dependence of perpendicular hyperfine structure
2	20	400	Good signal-to-noise ratio; no parallel hyperfine observed
5	50	400	Good signal-to-noise ratio; parallel hyperfine structure observed
0*	5*	95*	Sharp free-radical signal; broad feature centred at *g ca.* 2.1

* Film contained 200 layers.

in order to obtain as many electron spins as possible in the spectrometer cavity and hence to give the best possible signal-to-noise ratio. We found it impossible to record useful e.s.r. spectra with any of the samples at room temperature but more satisfactory spectra were obtained at 25 K. The film containing 500 layers made up of a ratio of 5:50:400 of (**1**):(**2**):eicosanoic acid contains all the features of interest, Figure 5(*d*). It is clear that all of the major features of the solution-phase spectrum are present in addition to some other prominent peaks. The copper parallel hyperfine peaks A and B are clearly observable. At a sufficiently narrow modulation amplitude, 6.3 G peak-to-peak, the N hyperfine can be resolved although not to the same extent as in the solution-phase spectrum, Figure 1. The N hyperfine on the copper hyperfine lines B and C is evidently observable as is the perpendicular hyperfine structure. There is in addition a sharp, intense line at $g = 2.00$ and a broad background absorption between *g ca.* 2.20 and 2.00. It seems likely that these features arise from the presence in the film of the metal-free phthalocyanine and eicosanoic acid. This is suggested by the e.s.r. spectrum of a 500-layer L–B film of (**2**) (5%) in eicosanoic acid (95%); both features are present. It is not clear what is the correct assignment of these signals. However, it seems probable that the sharp signal at $g = 2.00$ arises from an organic free radical, possibly associated with the fatty acid. The broader signal centred at *g ca.* 2.10 is most likely from (**2**).[22]

The Table describes the features of the e.s.r. spectra of other three-component films investigated. Dilution of complex (**1**) either by lowering its concentration in the metal-free phthalocyanine or by increasing the concentration of the fatty acid lowered the signal-to-noise ratio so that it was no longer possible to detect the parallel-region hyperfine structure. Since it was planned to carry out a study of the orientation dependence of the features in the e.s.r. spectrum it was important to be able to observe the parallel-region features. The spectrum of each showed well resolved hyperfine structure in the perpendicular region between *g ca.* 2.10 and 1.95. In every case there was an orientation dependence to this structure which was qualitatively the same, suggesting that the gross orientational properties of all the films were similar.

(*c*) *Orientation-dependent E.S.R. Spectrum of Complex* (**1**) *in an L–B Film.*

—The film containing a ratio of 5:50:400 of (**1**):(**2**):eicosanoic acid (which gave the spectrum with the best signal-to-noise ratio) was chosen for a detailed study of the orientation dependence of the e.s.r. spectrum. In this experiment the laboratory frame, denoted by *x*, *y*, and *z*, defines the applied magnetic field direction, *z*, and the direction *y*

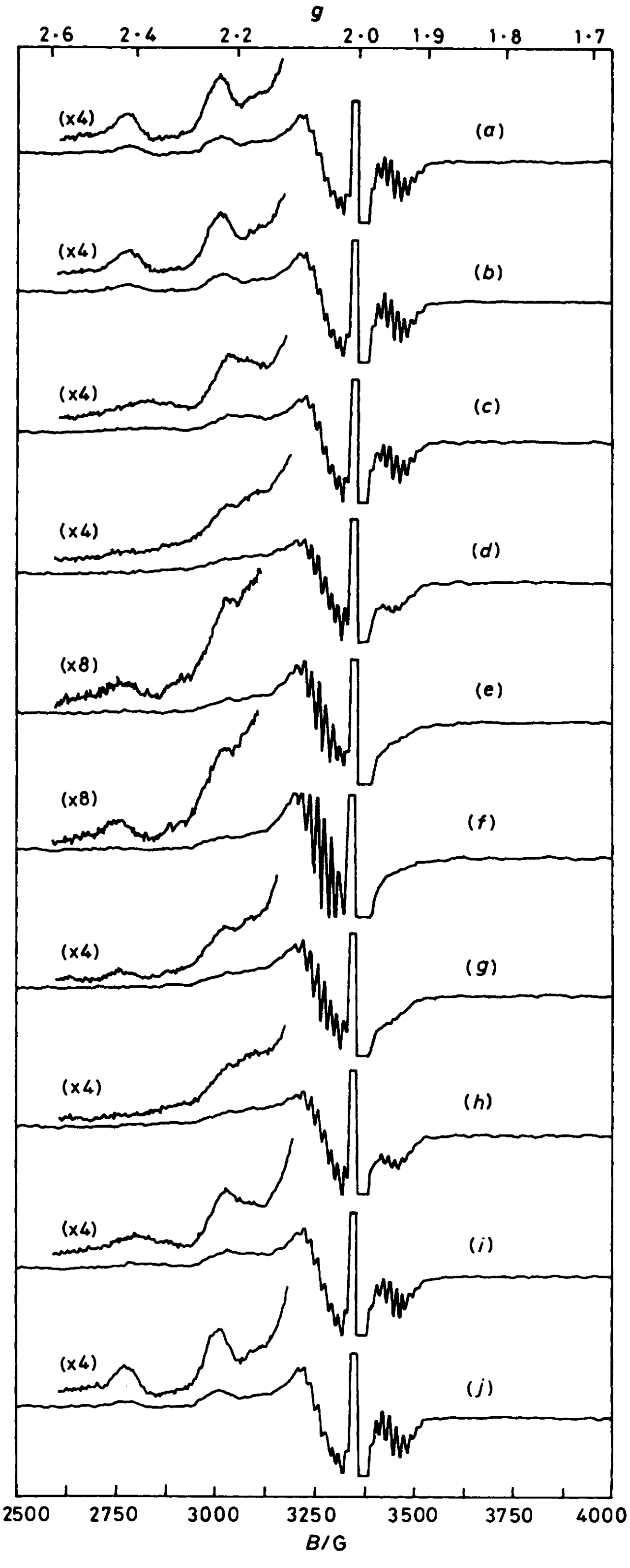

Figure 6. E.s.r. spectra measured at 25 K of a L–B film containing (**1**):(**2**):C_{20} acid in the ratio 5:50:400 as a function of θ. Gain 8 × 10^5, m.a. 12.5 G. The angle θ is defined as that between the *xz* plane and the plane of the L–B film, where the laboratory co-ordinate frame *x,y,z* is right-handed with the applied magnetic field, B_0, along *z* and the oscillating magnetic component of the microwave field parallel to *y*. The axis of rotation of the L–B film is *x*. θ = 0 (*a*), 20 (*b*), 40 (*c*), 60 (*d*), 80 (*e*), 100 (*f*), 120 (*g*), 140 (*h*), 160 (*i*), and 180° (*j*)

the oscillating magnetic field components of the microwave field. The long axis of the rectangular piece of silica lies along x and the film is rotated about this axis. The angle θ is defined as that between the xz plane and the plane of the L–B film. It is zero when the static magnetic field B_0 lies in the plane of the L–B film. Figure 6 shows the e.s.r. spectra of the L–B film recorded at intervals of 20° between $\theta = 0$ and 180°. There is a clear and pronounced dependence of the spectrum upon the orientation of the film relative to the applied static magnetic field, B_0.

At values of $\theta = 0$ and 180° the spectra are virtually identical. This relationship, namely that spectra at θ and $(\theta + 180)°$ are the same, holds for all angles of θ between 0 and 360°. The two-fold rotational symmetry is expected from a film of oriented paramagnetic molecules. The copper hyperfine lines in the parallel direction are most pronounced between $\theta = 0$ and 20° and also at 180° plus these angles. At $\theta = 40°$ these lines have lost intensity and moved to a higher field. At $\theta = 10 \pm 10°$ these lines have their maximum value and their field positions correspond closely to those of their counterparts in frozen toluene solution. Hence it can be concluded that the perpendicular to the plane containing the phthalocyanine ring, called the Z' axis, lies parallel to B_0, the applied field, when $\theta = 10 \pm 10°$. Confirmation of this angle is obtained by observing that the perpendicular hyperfine features between 3 200 and 3 350 G are at maximum intensity when $\theta = 100°$, that is, at 90° to the θ value at which the parallel features are most pronounced. These results lead to the conclusion that the perpendicular to the plane of the phthalocyanine ring lies at an angle of 10 ± 10° to the plane of the L–B film.

In order to check for anisotropy within the plane of the film an identical L–B film was prepared with the dip direction perpendicular to that of the film whose spectra are shown in Figure 6. The orientation dependence of the e.s.r. spectra was the same in both cases. This shows that the films are isotropic in the plane of the substrate.

Thus we conclude that the Z' axis of complex (**1**) lies at an angle of 10 ± 10° to the plane of the L–B film with no preferential orientation in that plane. The copper phthalocyaninate ring is lying edge on to the substrate but with a tilt angle of 10 ± 10°. Since (**1**) is diluted with the metal-free analogue this suggests that the phthalocyanine domains are also orientated in this way.

The question arises as to the degree of order or disorder within the films. This problem has been addressed by Pace *et al.*[14] There are two types of disorder to be considered. One is the extent of variation of molecular orientation about the angle θ. The second is the possibility that regions or domains of the film have quite different orientations. The first type of disorder can be investigated by means of a computer simulation of the lineshapes and the ratio of change of the parallel lines with θ. We have not carried out such an analysis. There is evidence from the spectra shown in Figure 6 of the existence of the second type of disorder within our films. At θ values of 80, 100, and 120° a weak parallel hyperfine line at *ca.* 2800 G is apparent. This must arise from a sub-population of (**1**) lying with the Z' axis almost perpendicular to the plane of the L–B film. Some phthalocyanine molecules must be lying almost flat on the surface. This may result either from failure to orient perfectly all of the molecules on the L–B trough sub-phase before transfer to the substrate, or be a consequence of the large number of layers, *viz.* 500, in the film. It could be that the stacking registration is lost as successive layers are deposited further away from the silica plate. It would be possible to distinguish between these possibilities by studying the order as a function of the number of layers in the film. However, the sensitivity of the e.s.r. technique may not be high enough to enable such a study to be carried out.

Conclusions

Copper phthalocyaninate derivatives are highly anisotropic e.s.r.-active molecules, whose spectra are sensitive to the state of aggregation and orientation relative to the applied magnetic field.

The e.s.r. spectrum of complex (**1**) is highly resolved at 25 K in the frozen solvent toluene. The g values obtained and the hyperfine coupling constants to the copper ion and to the four nitrogen atoms bonded to it are very similar in magnitude to those reported by others for solutions of unsubstituted [Cu(pc)] in concentrated sulphuric acid solutions and as oriented single crystals doped into metal-free phthalocyanine and [Zn(pc)]. In CH_2Cl_2 at 25 K, (**1**) forms aggregates and gives an e.s.r. spectrum that is almost isotropic in g value and devoid of any nuclear hyperfine structure. In the form of a polycrystalline powder the sample gives an isotropic spectrum with g value of 2.06. These aggregated forms yield spectra devoid of anisotropy and hyperfine structure because of electron exchange amongst neighbouring molecules which presumably is rapid compared with Δg and ΔA, the range of the g- and A-tensor anisotropies.

L–B Films of multilayers of complex (**1**) deposited in pure form give e.s.r. spectra characteristic of the aggregated state similar to that found in frozen CH_2Cl_2 but not as isotropic as in the crystalline powder. Dilution of (**1**) with eicosanoic acid fails to change the aggregated form of the e.s.r. spectrum. Thus it can be concluded that the phthalocyanine remains aggregated as two-dimensional domains in the eicosanoic acid L–B films.

L–B Films of complex (**1**) diluted in the metal-free phthalocyanine (**2**) and spread with eicosanoic acid show e.s.r. spectra which have incompletely resolved hyperfine structure. The spectra are strongly orientation dependent. It is concluded that the spin label (**1**) is diluted by the metal-free host (**2**), presumably in two-dimensional domains, within the L–B layer. We term these 'spin-labelled domains.' These domains are highly ordered relative to the substrate surface. The films are isotropic within the layer. An analysis of the angular dependence of the e.s.r. signal shows unequivocally that the phthalocyanine domains are oriented so that the phthalocyanine molecules are stacked like a pack of cards with the face of the ring at 80 ± 10° to the substrate surface. In other words, the normal to the plane of the ring lies close to the plane of the L–B film. The magnetic dilution is not complete. There are additional features in the spectrum due to low number aggregates of (**1**). However, there appears to be a good degree of order across the 500 layers of the multilayer L–B structures.

The evidence that the phthalocyanine molecules sit on edge almost perpendicular to the substrate surface is in contrast to the angle of 67° derived by e.s.r. spectroscopy for a copper tetraphenylporphyrinate in behenic acid (docasanoic acid).[12] It remains to be determined whether the orientation determined in the present work depends upon the presence of eicosanoic acid in the layer or is a function of the number of layers. We are in the process of investigating the ultimate sensitivity of the e.s.r. technique to determine whether it can be used to follow phthalocyanine organization within L–B monolayers. We have recently succeeded in developing a molecule substituted in such a way that L–B films of a [Cu(pc)] derivative diluted into the metal-free phthalocyanine and zinc analogue can be spread directly without the need for eicosanoic acid. The results of this work will form the basis of a later paper.

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