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Photoelectric Emission from Donor–Acceptor Solids and Donor Molecules[†]

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Introduction

This paper examines the difference between the ionization energies of various organic molecules both in the vapour and in various crystal lattices. Photoelectric emission thresholds of organic crystals, as well as being of intrinsic interest, provide information on the energies of the ionized states of such crystals. In particular the difference between the ionization energy of a molecule in the gas (I_G) and in a molecular crystal (I_c) measures[1] the calculable polarization energy P of the crystal, a key quantity in the donor–acceptor theory of organic semiconductors.

So far the donor–acceptor theory is supported, e.g. by calculations[2] of I_c for aromatic hydrocarbons, by a semiquantitative explanation[3] of the change in semiconduction with high pressure, and by a determination[4] of the energy gap for intrinsic photoconduction in anthracene. None the less, information to test the calculations of P has not been extensive. This paper reports the first I_c values for solid molecular complexes as well as extending the study of one-component crystals. In addition, values of I_G are

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reported in several cases where there was no previous information and where a comparison with I_c required them.

Chemicals

Anthracene: zone refined; 1,2-benzanthracene, coronene, rubrene, pyrene, perylene: as from Light and Co.; *o*-chloranil: as from Aldrich Chemical Co. Ltd; *p*-bromanil: recrystallized twice from benzene; *p*-chloranil: recrystallized from benzene; *p*-fluoranil: as from K and K Laboratories, Inc.; trinitrobenzene; technical grade recrystallized three times from aqueous acetic acid; tetracyanoethylene (TCNE) generously supplied by E. I. Dupont de Nemours & Co. as was the TCNQ: vacuum sublimed, m.p. 196–198°C with slight decomposition in a sealed tube, cf. 198–200°C.[5] tetracyanoquinodimethane (TCNQ): recrystallized from acetonitrile freed from acetamide by distilling twice over phosphorus pentoxide, stored over calcium chloride; pyromellitic dianhydride: prepared from the corresponding acid by sublimation under nitrogen at a pressure of 10 mm (Hg); dicyanomethylenetrinitrofluorene: prepared by the method of Mukherjee and Levasseur[6] and recrystallized three times from purified acetonitrile (m.p. 249–251°C, decomp.); benzidine: vacuum sublimed; 1,6-diaminopyrene: material supplied by Koch-Light Laboratories Ltd., repeatedly vacuum sublimed; *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD): from the hydrochloride by ammonium hydroxide in aqueous solution, filtered, washed, vacuum dried and then twice vacuum sublimed; tetramethylbenzidine (TMB): vacuum sublimed; polycopperphthalocyanine: kindly supplied by Dr. A. Epstein.

Solvents Used in the Preparation of Complexes

Perylene complexes with (i) TCNE: boiling carbon tetrachloride; (ii) *o*-chloranil, *p*-chloranil or 1,3,5-trinitrobenzene: thiophene-free benzene; (iii) TCNQ: acetonitrile; (iv) pyromellitic dianhydride: A. R. glacial acetic acid. The complex was vacuum dried for three days and then heated to 50°C at 10^{-3} mm (Hg) for five hours to remove the last traces of solvent; (v) dicyanomethylene trinitrofluorene: boiling acetonitrile. Pyrene complexes with (i) TCNE: ethyl acetate; (ii) TCNQ: dichloromethane; (iii) trinitrobenzene: benzene. Anthracene complexes with (i) TCNQ: acetonitrile; (ii) trinitrobenzene: ethylene dichloride; (iii) pyromellitic dianhydride: methyl ethyl ketone. 1,2-benzanthracene and benzidine complexes with TCNQ, chrysene–trinitrobenzene, TMPD (or diaminopyrene)–*p*-chloranil (or *p*-bromanil), TMPD–*o*-chloranil, diaminopyrene–TCNQ: benzene. TNB–trinitrobenzene: single crystal (2 mm × 2 mm × 5 mm) by slow evaporation of a benzene solution. TMPD–TCNQ: A. R. glacial acetic acid or *p*-xylene.

Ionic and Non-ionic Complexes

Previous work[7, 8, 9] has shown that the following complexes are non-ionic: perylene–TCNQ, 1:1,; perylene–*p*-chloranil or *o*-chloranil; perylene–trinitrobenzene, pyrene–TCNE, or trinitrobenzene; TMB–trinitrobenzene,[9] a result confirmed by an absence of an e.s.r. signal in our sample.

Perylene–dicyanomethylenetrinitrofluorene: The infrared spectrum of the complex was measured and indicated that it was non-ionic.

The anthracene–TCNQ complex had an infrared spectrum showing bands in the same position as those of the separate components, although some were of different intensities. E.s.r. absorption was barely detectable and was attributed to impurities. The complex was therefore not appreciably ionic at room temperature.

Ionic complexes have been shown[10, 11, 12] to be formed from TMPD with *p*-chloranil, *p*-bromanil or TCNQ. Similarly the corresponding diaminopyrene complexes have been reported[13, 14] to have ionic properties.

Form of Sample

A single crystal was obtained of the TMB–trinitrobenzene complex, but crystals of the other complexes were too small to be studied singly. In general, the polycrystalline layer produced by solvent evaporation was not composed of pure complex crystals: crystals of the separate components were often seen under the microscope to be deposited along with crystals of the complex. Sublimation of a complex was successful with anthracene–pyromellitic dianhydride but generally failed to produce satisfactory crystals of a complex. Most complexes were therefore studied as pressed discs.

Experimental

Photoemission from solids was studied by measuring the photoelectric yield as a function of photon energy and also in some cases by measuring the kinetic energy distribution of the emitted electrons. The sample was mounted at the centre of a spherical cavity 10 cm in diameter and the electrons collected by a conductive coating of colloidal graphite or colloidal silver painted onto the inside of the glass sphere. The measuring electrode was guarded, the cell electrostatically shielded and surrounded by dry nitrogen. Currents were measured with an E.I.L. 33c electrometer and a recorder. An Osram XBO 150 xenon arc supplied radiation through a 0.5 metre Seya-Namioka type monochromator, the intensity of which was measured, via fluorescence from sodium salicylate, by a photomultiplier of known response. The sample, if obtained from a pressed disc, was attached to a nickel wire by colloidal graphite in isopropanol. These pressed samples were 8 mm long, 3 to 4 mm wide and approximately 0.5 mm thick. In other cases the sample was sublimed or evaporated from solution onto a 3 mm diameter wire. All measurements of kinetic energy distribution were made using film samples. Single crystals could be irradiated simultaneously with low energy light to discharge space charges as well as with ionizing radiation.

Light was not allowed to fall other than on the sample. Light scattering from the sample had no observable effect.

The determination of the shape of photoemission yield curves from many organic solids is hampered by their electrical conductivity being low. In extreme cases the emission current decreases with time and then there is also a slow decay of the recorded current after the light is switched off. The voltage V_s for which all emitted electrons are just collected is sharply defined only in the absence of a space charge in the sample, and this provides a test for the presence of space charge. Because space charges distort the yield curve most when the emission current is high, all experiments were done only after the sample showed steady behaviour when irradiated just below the threshold and with the direction of scan from low photon energies to high. Space charge, e.g. in perylene single crystals, was reduced to a minimum by simultaneous irradiation with the total light from a 100 W tungsten lamp, or else by coating the wire holding the crystal with hole-injecting *o*-chloranil. Perylene in pressed discs showed no evidence of space charge.

Photoionization of gases was observed in a heated pyrex cell with two parallel electrodes at a potential difference of 45 V. S.T.C. hermetic seals around the electrodes provided guard rings. The seals were cemented into the cell with Araldite epoxy resin and were satisfactory up to 120°C. Leybold metal–ceramic–metal seals having a resistance of 5×10^{15} ohms at 20°C and 5×10^{11} ohms at 400°C were suitable for the higher temperatures needed. Electrostatic shielding and rigid co-axial leads of 0.5 in. copper tube with a heavy copper wire supported by two 0.25 in. long perspex spacers were used, ordinary co-axial cable being unsuitable above 100°C. The current was measured as a function of photon energy. The light source was a Wilkinson type microwave-excited xenon discharge (Jarrell-Ash) using power from a Techtron 200 W microwave generator and a Broida cavity. The monochromator was that used for the work on solids. Mercury and hydrogen were used to calibrate the wavelength scale.

Lithium fluoride windows sealed against an annulus of teflon by the external pressure held a vacuum of 10^{-5} mm (Hg) at 250°C.

The photoionization yield $P = N_i/I_0 = \sigma_i(I_0 - I)/\sigma I_0$ where N_i is the number of ions formed per second; $I_0(I)$ the incident (transmitted) light intensity; σ_i the ionization cross-section; σ the absorption cross-section defined by $I = I_0 \exp(-nx\sigma)$ where n is the number of molecules cm^{-3}; x, the absorption path length.

A plot of P against $h\nu$ is within 4% of the ionization cross-section plot provided absorption does not exceed 10%.

Results

Figure 1 shows the photoelectric yield (electrons/photon) for a single crystal of perylene as a function of the energy of the photons.

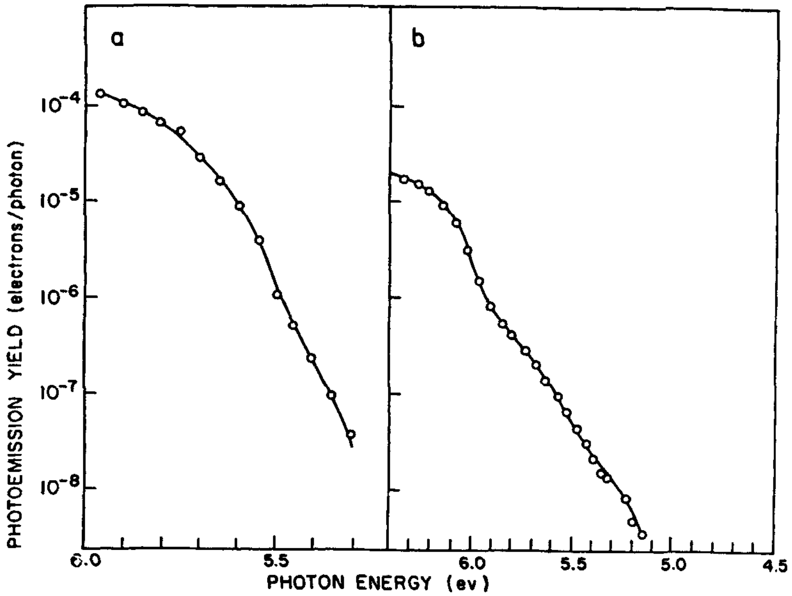

Figure 1. Photoemission from (a) a single crystal of perylene, (b) a single crystal of anthracene doped with naphthacene.

The threshold I_c of photo-emission for the present purposes was taken as the energy of the light quanta which gave rise to the lowest detectable currents. Such thresholds were reproducible to ±0.03 eV and corresponded to a photoemission yield of 10^{-8} electrons/quantum.

The value of I_c so determined agreed, to within ± 0.1 eV, with the value obtained by subtracting the measured maximum kinetic energy (Fig. 2) of the emitted electrons from the energy of the

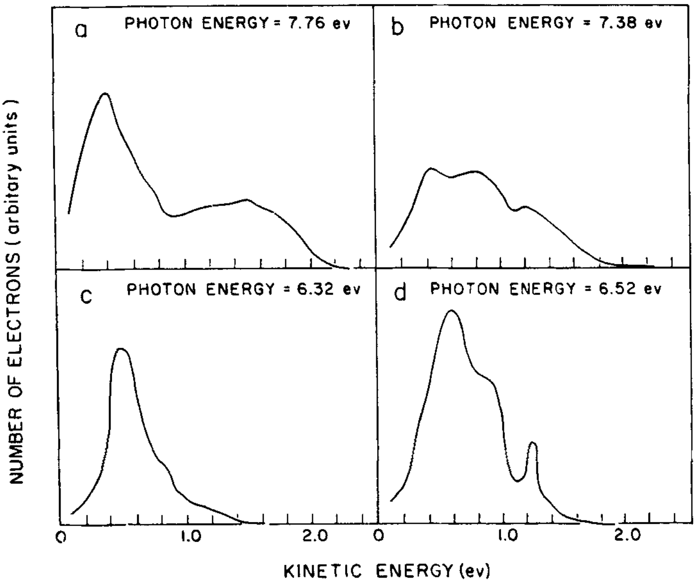

Figure 2. Kinetic energy distribution of the electrons emitted from molecular solids: (a) perylene, (b) coronene, (c) 1,6-diaminopyrene, (d) *N*,*N*,*N*′,*N*′-tetramethylbenzidine.

TABLE 1 Photoemission Thresholds for Non-ionic Complexes

Complex	Photoemission threshold (eV)
Perylene–TCNQ[a]	5.50[b]
Perylene–1,3,5-trinitrobenzene	5.54[b]
Perylene–*p*-chloranil	5.40
Perylene–*o*-chloranil	5.35
Perylene–dicyanomethylenetrinitro-fluorene	5.23
Perylene–pyromellitic dianhydride	5.16
Pyrene–TCNQ	5.70
Pyrene–1,3,5-trinitrobenzene	5.60
Anthracene–1,3,5-trinitrobenzene	5.88[b]
Anthracene–pyromellitic dianhydride	5.26
Anthracene–TCNQ	5.03
1,2-Benzanthracene–TCNQ	5.00
Benzidine–TCNQ	5.03
N,*N*,*N*′,*N*′-Tetramethylbenzidine–1,3,5-trinitrobenzene	4.72
Chrysene–1,3,5-trinitrobenzene	5.50[b]

[a] TCNQ ≡ tetracyanoquinodimethane.

[b] Space charge effects were large in this sample.

photons, for perylene, coronene, diaminopyrene and tetramethylbenzidine.

Because the peaks observed for the diamines showed poorly resolved structure and the ionization cross-section was low, the accuracy was ± 0.03 eV. For the other molecules it was ± 0.02 eV.

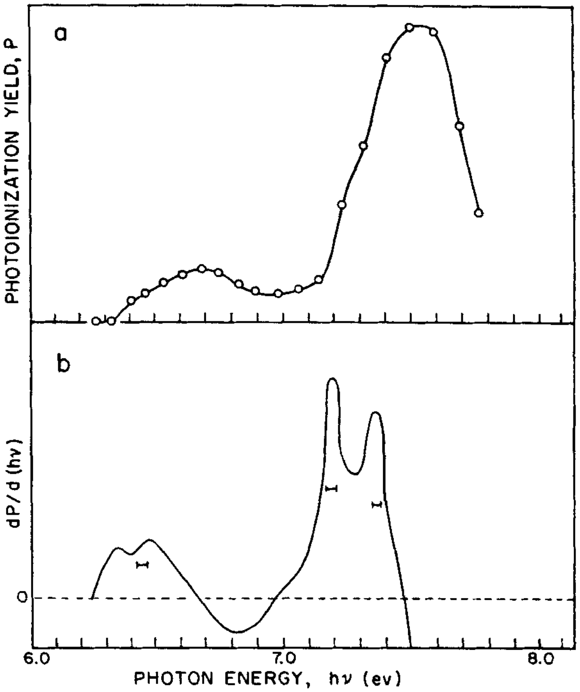

Figure 3. Gas-phase photoionization of tetramethyl-*p*-phenylenediamine: (a) yield *vs* photon energy; (b) derivative of the yield with respect to photon energy *vs* photon energy.

Figure 3 records the gas phase photoionization of tetramethyl-*p*-phenylenediamine. The experimentally measured bandwith of the light at half height is indicated on the diagram.

Thresholds are listed in Table 1 for non-ionic complexes, in Table 2 for ionic complexes, and in Table 3 for some compounds of only one component. Table 4 lists photoionization results for some

TABLE 2 Photoemission Thresholds for Ionic Complexes

Complex	Photoemission Threshold (eV)
1,6-Diaminopyrene–*p*-chloranil	4.39
1,6-Diaminopyrene–*o*-chloranil	4.88
1,6-Diaminopyrene–*p*-bromanil	4.65[a]
1,6-Diaminopyrene–TCNQ	4.58
TMPD[b]–*p*-chloranil	4.88
TMPD–*p*-bromanil	4.87
TMPD–TCNQ (crystallized from *p*-xylene)	4.86
TMPD–TCNQ (from glacial acetic acid)	4.72

[a] Space charge effects were large in this sample.

[b] TMPD ≡ *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.

TABLE 3 Photoemission Thresholds for Compounds of a Single Component

Compound	Photoemission threshold (eV)
Pyrene	5.6–5.8
Perylene	5.40
Naphthacene	5.31
Coronene	5.15
Metal-free phthalocyanine	5.12
Poly-copper phthalocyanine	5.10
Rubrene	5.10
Benzidine	5.10
1,6-Diaminopyrene	4.71
N,*N*,*N*′,*N*′-Tetramethylbenzidine	4.71
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	4.63

TABLE 4 Gas Phase Ionization Energies

Compound	Vertical ionization energy (eV)	Adiabatic ionization energy (eV)
Anthracene	7.42	7.42
Phenothiazine	7.38	<7.0
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	6.47; $\geqslant 7.35$	$\leqslant 6.25$; $\leqslant 7.00$
N,*N*,*N*′,*N*′-Tetramethylbenzidine	6.55; $\geqslant 7.36$	$\leqslant 6.40$; $\leqslant 7.04$
Perylene	7.12	6.92

of the donor molecules in the gas phase. The figures are the means of several results.

Observations on lamellar systems are discussed in the next section.

Discussion

PHOTOIONIZATION IN THE GAS PHASE

If the ionization cross-section is a step function for perfectly monochromatic radiation, then the derivative of the experimental curve obtained with a finite bandwidth should be of the same form as the distribution of light energy across the band.[15] The derivative curve should therefore show one or more peaks, possibly overlapping. If the onset of ionization is sharp it is assumed to correspond to the adiabatic ionization energy, while the vertical ionization energy is taken as the point of steepest slope of the ionization curve. In some cases, e.g. the aliphatic amines,[15] the adiabatic ionization energy may not be reached by this method. Asymmetry and broadening of a peak in the derivative curve may indicate[16] that autoionization is occurring.

For anthracene the photoionization cross-section was concluded to be approximately a step-function at 7.42 ± 0.02 eV, with another step at 7.53 ± 0.03 eV. The first peak was sharp and marked both the vertical and adiabatic energies. In energy it agreed with Vilessov's result[17] of 7.38 ± 0.03 eV but exceeded that of Angus and Morris[18] (7.12) from Rydberg spectra. The second step possibly is associated with an excited vibrational level of the positive ion.

The onset of ionization of phenothiazine is more gradual than that of anthracene. Either the adiabatic and vertical energies differ considerably, possibly because of a change of shape[19] of the molecule upon ionization, or else there are two ionization levels detected, of which the first, at about 7.2 eV, has a lower cross-section than the second.

For perylene, it was difficult to decide whether the vertical transition was at 7.12 or at the adiabatic value of 6.92 eV. Charge-transfer spectra yielded[20] a value of 7.06 eV.

The two diamines behaved similarly: (i) both ionized very easily (ii) both showed two ionization levels, in agreement with charge-transfer spectra (iii) in neither case was the adiabatic energy reached (iv) the width of the peaks was greater than the bandwidth of the light.

For TMPD, ionization energies calculated from charge-transfer spectra[10] are 6.5 and 7.3 eV, in reasonable agreement with the results of Table 4. From Fig. 3 the second vertical transition occurs at 7.15 or > 7.35 eV.

For tetramethylbenzidine, Foster and Thomson[10] record charge transfer spectra from which ionization energies of 6.6 and 7.7 eV can be expected. Table 4 shows that the first of these values agrees with the first vertical transition by photoionization. The value of 7.7 eV possibly would not have been recorded by us because of instrumental effects above 7.5 eV. Alternatively different configurations of the charge transfer complex might have been responsible for the two charge transfer bands (cf. *N,N*-dimethylaniline-iodine[21]), in which case the photoionization result is to be preferred.

PHOTOIONIZATION OF SOLIDS

That the threshold I_c was independent of the method of preparing the sample was shown by experiments on perylene: single crystals, sublimed in nitrogen and mounted in nitrogen or in air, single crystals crystallized from benzene, a film sublimed onto glass, a film sublimed onto a layer of *o*-chloranil on nickel wire, powder recrystallized from thiophene-free benzene compacted into a disc: for all of these I_c was similar (± 0.03 eV), unless space-charge effects were ignored. The photon energy necessary to dissipate the space-charge was 2.6 eV, close to the reported photoconduction threshold.[22]

Although I_c was independent of the state of the sample, the shape of the yield curve was not. In general, as the photon energy ν increased above the threshold ν_t the logarithm of the yield tended to level off at a value of about -3. This saturation value was reached at 1 to 1.5 eV above ν_t. When ν is great enough, the electrons emitted from the absorption centre presumably have enough energy to reach and penetrate through the crystal surface, despite losses of energy on the way caused by inelastic scattering. The scattering effect is expected to be greater in e.g. a pressed disc than in a simple crystal. The effect can be seen also in plots of the kinetic energy distribution of the emitted electrons, e.g. in Fig. 2. In perylene crystal the kinetic energy distribution is markedly different from the typical corresponding plot for gaseous ionization: starting from the maximum kinetic energy the curve in the solid increases relatively slowly in height, compared with the curve for a gas.[23] We attribute this difference to scattering in the solid: In the solid the emitted electrons have lost by scattering an energy of the order of 1 eV, in a distance of perhaps 10^{-4} cm. Superposed upon inelastic scattering at higher photon energies is the possibility of the ejection of an electron from an orbital of higher ionization energy. In perylene the occurrence of two peaks in the kinetic energy distribution is consistent with the ionization of electrons in two different molecular orbitals, separated, in energy, by about 1 eV. In 1,6-diaminopyrene, there is only one orbital involved, presumably centred on the amino groups.

With tetramethylbenzidine the separation in energy of 0.65 eV between the peaks in the kinetic energy distribution matches very nearly the separation of 0.64 eV., observed (Fig. 2) between the two low ionization energies thus supporting this interpretation of the kinetic energy distribution.

The maximum yield of electrons per photon appears to be much less in a solid than in a gas,[24] a difference possibly associated with an increased recombination of electrons with positive ions in the solid.

Three substances previously examined were measured again in view of discrepancies in the literature and to provide a firmer basis of comparison with the two-component systems studied. For naphthacene I_c was close to values previously reported (5.26 eV[25], 5.25[26], 5.24[27], 5.28[28]) and to the value of 5.38 eV reported by Kearns and Calvin[29] for the so-called "surface" ionization potential, but greatly exceeded the 4.75 eV of the latter authors "bulk" potential. Similar differences with Kearns and Calvin occurred for perylene and for phthalocyanine. The difference was not associated with a variation in the extrapolation procedure used to find the threshold because examination of the photon energies at which a given yield of electrons was obtained showed that Kearns and Calvin's energy was always lower than ours by 0.4 to 0.5 eV. Whilst failure to remove the effects of space charge can apparently change the threshold, it is not clear whether this is the explanation of Kearns and Calvin's results.

For perylene and phthalocyanine our results agreed with those of others,[27, 30] while for the other substances there were no previous figures.

As was expected[2] I_c for the molecular crystals was in every case lower than I_G for the corresponding molecule (Table 3). The difference $I_G - I_c$ is equated to the polarization energy P_+ of a positively charged ion in the crystal lattice.

Since P_+ depends upon the structure and nature of the lattice surrounding the ion, P_+ in a (weak) molecular complex should differ from P_+ in a lattice composed of only donor molecules; I_c therefore should differ also. One of the aims of the present work was to test this expectation which was indeed confirmed by the figures in Table 1, e.g. for perylene complexes I_c ranged from 5.16 to 5.50 eV; for anthracene complexes from 5.03 to 5.88, compared with 5.65 eV for anthracene[25] itself. For the other complexes I_c differed from I_c for the crystalline donor.

The perylene–TCNE complex showed emission at 5.15 eV (cf. perylene, $I_c = 5.40$ eV), but the TCNE evaporated from the complex during the measurement. A sample of perylene containing 10^{-2} moles of TCNE to 1 mole of perylene also showed emission at 5.15 eV. Until more is known about the structure of perylene containing TCNE the interpretation of this result as emission from perylene must be uncertain. The effect may be related to the lowering of the photoemission threshold of anthracene that has been observed[31] in the presence of oxygen. Evaporation of the acceptor occurred also with pyrene–TCNE and perylene–*p*-fluoranil, for which emission was observed at 4.1 eV. Pyrene doped with TCNE gave emission at the same energy as the pyrene–TCNE complex.

The effect on I_c of doping the host lattice with a small quantity of a guest was studied with a single crystal of anthracene doped with 500 ppm of naphthacene (Fig. 1). At photon energies greater than 6.0 eV the yields were similar to those of undoped anthracene, but at lower photon energies the yields were greater than with anthracene. The threshold of 5.10 eV was 0.5 eV lower than that of anthracene and slightly lower than that of naphthacene crystals. Whether the emission near the threshold is from naphthacene, as seems more likely, or from anthracene, changing the crystal environment around the emitting centre is again seen to affect I_c.

This observation raises the possibility that impurities may produce low values for I_c. Of the compounds that were studied the aromatic diamines are the most likely to contain impurities. Although the photoemission yield curves, which rise smoothly from the threshold and reach relatively high quantum yields, do not suggest that impurity emission is important, the possibility cannot be excluded.

Emission from ionic complexes occurred at relatively low energies (Table 2). The 1,6-diaminopyrene complex with *p*-chloranil has the lowest threshold of any purely organic compound so far measured, including graphite. The interpretation of I_c in these cases requires a different theory from that applied to crystals of one molecular species and non-ionic complexes. In ionic complexes, which are formed only when the donor has a low I_G and the acceptor a high electron affinity, the emission is presumably from the negative ion. In this case, and because the bandwidth in the crystal is taken to be small, I_c is given by the equation[32]

$$I_c = W_L - e\phi/z + A_G$$

where A_G is the electron affinity of the neutral acceptor molecule; W_L, the lattice energy per ion pair; ϕ, the electrostatic potential at the point from which the electron has been removed. When W_L and ϕ are known, a value of A_G can be used to calculate I_c, or vice versa. No calculation has been published for an ionic lattice of an organic material: the crystal structures are mostly unknown and data on polarizabilities are lacking.

The TMPD–TCNQ complex showed two values of I_c, depending on the solvent used in its preparation. The infrared and e.s.r. absorption spectra were therefore studied to learn whether the crystals differed in molecular structure or only in the state of subdivision. A sample prepared from acetic acid recrystallized from xylene in the typical xylene-form, and vice versa. The complex was slightly soluble in benzene and a comparison of optical densities at 403 nm and 304 nm gave for the ratio of TMPD to TCNQ: (1.0 ± 0.1): 1 for the xylene form and (0.8 ± 0.1): 1 for the acetic acid form. Since Hanson[33] has shown that the acetic acid complex is 1:1, the discrepancy is attributed to errors arising from the poor solubility of the complex. The infrared spectra in potassium bromide discs and Nujol mulls indicated that the complex from acetic acid was ionic. The spectra of the xylene form agreed with those of Kinoshita and Akamatu,[12] whose complex had been prepared from ethanol.

E.s.r. spectra of polycrystalline samples were similar for both forms. In some cases four lines were observed, but when the samples were finely ground, to produce random orientation of the crystallites, one line was obtained, of width 1.3 gauss, the same as the mean width for the unground samples. E.s.r. spectra of single crystals differed for the two forms. Rotation of the crystals in the cavity could be done only crudely. The crystals were rotated about each of their three axes in turn and the data treated by the method of Weil and Anderson,[34] to obtain the g-tensor. Diagonalization of this tensor gave the principal g-values and the orientation of the principal axes relative to DPPH (Table 5). It is clear that, although both complexes have a 1:1 (approximately) ratio of TMPD–TCNQ and both are ionic, the orientations of the paramagnetic species in the two forms are different. (The possibility of solvent inclusion was not removed completely.) This was confirmed by the temperature dependence of the e.s.r. signals from single crystals: for the acetic acid form the signal decreased with increasing temperature but for the xylene form, the signal increased with an activation energy of 0.067 eV at room temperature, increasing to 0.10 eV at lower temperatures (cf. ref. 35). The different values of I_c are therefore attributed to different structures of the complexes, although impurity emission cannot be eliminated as a possibility.

TABLE 5 g-Tensors for TMPD–TCNQ Complexes

Solvent used to prepare sample	Principal g-values relative to DPPH	Direction cosines of principal axes relative to external crystal axes		
		x	y	z
Acetic acid	$+0.000007 \pm 0.000005$	0	0.95	0.31
	-0.000068	1	0	0
	-0.000115	0	-0.31	0.95
p-Xylene	-0.00003 ± 0.00001	0.95	-0.10	0.30
	-0.00017	0.28	0.94	-0.20
	-0.00032	-0.28	0.30	0.92

The external crystal axes are chosen so that x is the long axis, y second longest axis and z is mutually perpendicular to x and y.

LAMELLAR SYSTEMS

The reported[29] photoemission of electrons which had been transferred from a layer of an electron donor solid to an adjacent layer of an electron acceptor solid seemed to offer the possibility of studying the electron affinity of the acceptor solid. Accordingly the attempt was made to reproduce the earlier results before studying other acceptors. We found no evidence of emission from o-chloranil layers of different thicknesses sublimed onto various substrates; e.g. onto perylene single crystals or films.

The sublimed layers reduced the emission from the perylene to as low as 1% of the original, but made little if any change in the threshold. Phthalocyanine, coronene and naphthacene single crystals, used as substrates, all gave results similar to those with perylene. We did not study alkali metal substrates, for which there is definite evidence of emission from negative ions.[36] Sublimation of tetramethyl-*p*-phenylenediamine onto chloranil gave immediately a blue colour, presumably of the TMPD cation, but TMPD was too volatile to be used as a substrate. Tetracyanoethylene, deposited on perylene or pyrene single crystals by evaporation of an ethyl acetate solution, was also volatile, and the results consequently ambiguous.

One system only showed photoemission with a threshold different from that of the donor. This was a single crystal of anthracene containing 500 ppm of naphthacene and coated with a layer of TCNQ by evaporation of an acetonitrile solution. The green coloration of the surface indicated that some of the anthracene had dissolved and redeposited as the TCNQ complex. I_c was found to be 4.68 ± 0.04 eV, which is lower than I_c for anthracene–TCNQ. It is possible that the emission is from a naphthacene–TCNQ complex, but attempts to prepare such a complex from its two components were unsuccessful. Alternatively the emission was from TCNQ anions, in which case the system was of the same type as those discussed by Kearns and Calvin.[29]

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