ductivities of (I) : DDQ and (II) : DDQ are almost equal. The infra-red spectra of (II) : DDQ and (III) : DDQ closely approximate the superposition of the spectra of their components. However, for (II) : DDQ the carbonyl band at $\approx 1,700$ cm^{-1} is appreciably reduced in intensity and there is a broad absorption from 2μ into the visible (similar to that mentioned for (I) : DDQ). Neither (II) : DDQ nor (III) : DDQ gave an electron spin resonance signal; however, Hammond[10] reports electron spin resonance absorption for complexes of DDQ with some methylbenzenes. Seebeck coefficients are negative for (II) : DDQ and (III) : DDQ, indicating majority carriers to be electrons rather than holes as found for (I) : DDQ. The hydrocarbon complexes have well-defined melting points well below 300° C as opposed to the melting behaviour of (I) : DDQ. The large difference between the resistivities of the DDQ complexes with (II) and (III) appears to be a consequence of the very large activation energy for (III) : DDQ, since the pre-exponential term, ρ_0, is quite similar for both complexes.

The resistivity of pure DDQ is strongly affected by the solvent from which it is last recrystallized. DDQ from CH_2Cl_2 yields transparent yellow needles. DDQ crystallizes from benzene as deep red platelets of the $(DDQ)_x$: (benzene)$_y$ complex from which the benzene quickly evaporates; the resulting pure DDQ is in the form of pale yellow, opaque platelets retaining the morphology of the benzene complex. X-ray powder diffraction indicates a difference in crystal structure between the two forms of DDQ, which may account for the difference in conductivity.

Table 1

1:1 Complex with DDQ	m.p. (° C)	ρ_{25} (Ω–cm)	E_c (eV)	Q (mV/° C)		ESR	Infra-red spectrum
p-Phenylene-diamine	decom-poses > 300	10^6	0·37	30° C 65° C	+ 0·24 + 0·85	yes	▲
Perylene	204	3×10^6	0·45	30° C 65° C	− 0·36 − 0·53	no	+
Pyrene	233–234	10^{12}	0·9	60° C	− 1·9	no	+
Pure DDQ (a) from benzene	214–215	5×10^8	0·6	30° C 60° C	− 1·9 − 1·9	no	
(b) from CH_2Cl_2	214–215	3×10^{10}	0·6			no	

Q = Seebeck coefficient.
+ = Infra-red spectrum obtainable by superposition of spectra of components.
▲ = Infra-red spectrum not obtainable by superposition of spectra of components.
Electron spin resonance sensitivity $\simeq 10^{13}$ spins for a 1 gauss line width.

The difference between the melting behaviours of the amine complex and the hydrocarbon complexes is indicative of a correlation between the existence of an electron spin resonance signal and the melting behaviour of a C–T complex. Complexes for which we have an electron spin resonance signal have not melted but have decomposed above 300° C. We suggest that this may be due to the increase in the number of ion-radicals with increasing temperature[6]. Using the approximate spin concentration[2b] and the spin activation energy[6] for the complex (I) : p-chloranil it is estimated that about 10 per cent of the molecules exist as ion-radicals at the m.p. of chloranil (290° C). This scarcely seems sufficient to prevent normal melting behaviour. However, there is a random fluctuation of energy distribution throughout the solid, and at those units where there is sufficient energy to expect normal melting there should also be sufficient energy to form ion-radicals, thus inhibiting normal melting. Furthermore, in view of the great difficulty of obtaining absolute values of spin concentrations by means of electron spin resonance[11] it is quite possible that the actual concentration of ion-radicals is significantly higher than 10 per cent. There is also the possibility that at the higher concentrations the reactivity of the ion-radicals leads to reactions or polymerizations which prevent normal melting.

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3-Methoxy-4,5-methylenedioxy Amphetamine, a New Psychotomimetic Agent

THE establishment of trimethoxyamphetamine (Ib, TMA)
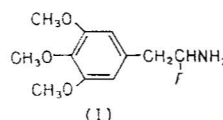
a: R = H (mescaline)
b: R = CH$_3$ (TMA)
c: R = CH$_2$CH$_3$

as being of greater psychotropic potency than either α-ethyl mescaline (Ic) (ref. 1) or mescaline itself (Ia) (ref. 2) has led to the examination of analogues which retain the three carbon chain but vary in other areas of the molecule. The presence of elemicin (3,4,5-trimethoxy allylbenzene) in the aromatic ether fraction of oil of nutmeg[3], and the proposal of a possible in vivo mechanism for its conversion to TMA (ref. 4) have afforded an explanation of the psychotropic action[5] of nutmeg. The substance myristicin (II) is the major component of this fraction, and if it were to undergo a transformation parallel to that proposed for elemicin, a second amphetamine, 3-methoxy-4,5-methylenedioxy amphetamine (MMDA, IVa), would result.
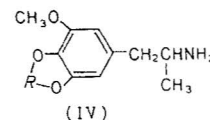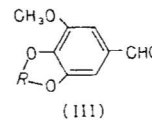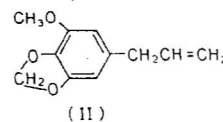
a: R = —CH$_2$—
b: R = —CH$_2$CH$_2$—
c: R = —CH$_2$CH$_2$CH$_2$—
d: R = —CH(CH$_3$)—

This latter amphetamine has been synthesized from myristicin in vitro, by a three-step process. trans-Iso-myristicin, obtained from myristicin by heating in alcoholic potassium hydroxide, is converted by means of

tetranitromethane to β-nitro isomyristicin. Reduction of this nitropropene with $LiAlH_4$ led smoothly to MMDA, which was isolated as the hydrochloride. Examination of MMDA in mice and dogs displayed a behavioural and toxicological pattern similar to that of TMA, both quantitatively and qualitatively. Preliminary human evaluation revealed initial intoxication at about 1·0 mg/kg (as free base). More extensive assay has confirmed a thoroughly effective hypnogogic dementia at less than 2·0 mg/kg. The psychotomimetic syndrome was complete at this level: increased dosages (to 3·2 mg/kg) merely prolonged the duration of the episode. Thus the potency of MMDA is somewhat greater than TMA and nearly three times greater than mescaline.

Substitution of either an ethylenedioxy or a trimethylenedioxy group for the methylenedioxy moiety (compounds IVb and IVc) resulted in a marked decrease in psychotropic effectiveness. These amphetamines were prepared from the aldehydes IIIb and IIIc by condensation with nitroethane followed by reaction with $LiAlH_4$. A prohibitively small yield of the ethylidene analogue IIId precluded further synthetic efforts.

As with TMA, the effects of MMDA are hallucinogenic and permit complete recall. They will be reported shortly, in full, with appropriate synthetic detail.

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Electronic Transitions in α-, β- and γ-Titanium Trichloride

As there is considerable interest in the electronic structure of the different modifications of titanium trichloride, we investigated the optical properties of α-, β- and γ-$TiCl_3$.

In order to throw some light on the problem, we observed the diffuse reflexion spectrum of Ti^{3+} in lithium fluoride, in which the Ti^{3+} ions are supposed to occupy sites of octahedral symmetry. The spectrum is presented in Fig. 1. Next we observed the diffuse reflexion spectrum of α- and γ-$TiCl_3$, as well as the absorption spectrum of β-$TiCl_3$. The spectra are presented in Figs. 2, 4 and 3, respectively. The band maxima are summarized in Table 1.

Table 1. OBSERVED BAND MAXIMA

Absorption	$TiCl_3$ in H_2O			20,300 (ref. 1)	
Absorption	Ti^{3+} in Al_2O_3			19,380 (ref. 2)	
Reflexion	Ti^{3+} in LiF			18,500	15,400
Reflexion	α-$TiCl_3$		27,500	19,000	14,300	(8,000 ?)
Absorption	β-$TiCl_3$	38,200	29,200	24,120	
Reflexion	γ-$TiCl_3$		27,500	19,000	14,300

Wave-lengths in cm⁻¹

At present we do not know whether an exciton is moving freely through the lattice or whether the observed phenomena must be interpreted in terms of a more localized electron model.

It may be concluded, however, from the observed spectra of α- and γ-$TiCl_3$ that the bands at 19,000 cm⁻¹ and 14,300 cm⁻¹ closely resemble the bands of Ti^{3+} in lithium fluoride, observed at 18,500 cm⁻¹ and 15 400 cm⁻¹, for which the localized electron model will hold. It appears from the absorption spectrum of β-$TiCl_3$ that the positions of the electronic levels are different from those in α- and

γ-$TiCl_3$, which may be in agreement with the quite different chemical and crystallographic properties. We did not obtain reliable results from reflexion measurements of β-$TiCl_3$.

In the crystal modifications of α-, β- and γ-$TiCl_3$, the Ti^{3+} ions occupy sites of octahedral symmetry. According to Bjerrum's rule[3] the interaction with next nearer neighbour ions will, in general, be very small and can be neglected in a first approximation. Disregarding deformations of the octahedron, we tentatively assign the bands observed at about 19,000 cm⁻¹ to a $^2T_{2g} \rightarrow {}^2E_g$ transition. Owing to the Jahn–Teller effect the excited level may now be split, which gives rise to two absorption bands, as was found by Hartmann[1] and McClure[2]. In fact McClure gives a split of 1,850 cm⁻¹. With these facts in mind, one might think that the bands at about 19,000 cm⁻¹ and about 15,000 cm⁻¹ of Ti^{3+} in lithium fluoride and α- and γ-$TiCl_3$ may be caused by the Jahn–Teller effect, but then the split must be very large.

Besides the tentative assignment of the bands to the $^2T_{2g} \rightarrow {}^2E_g$ transition, electron transfer can play an important part. However, for a straightforward and conclusive interpretation of the observed bands more experimental and theoretical work is necessary.

In this connexion additional experiments will be carried out with titanium tribromide.
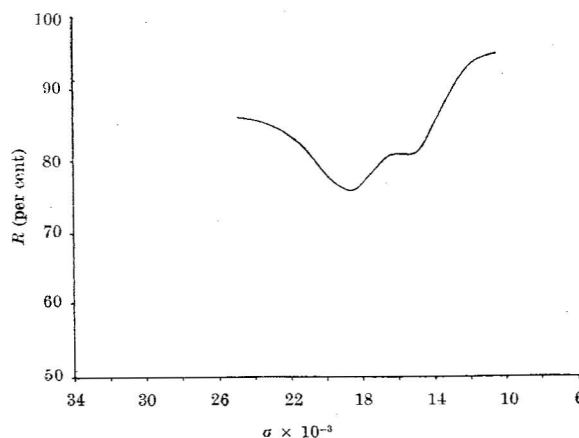

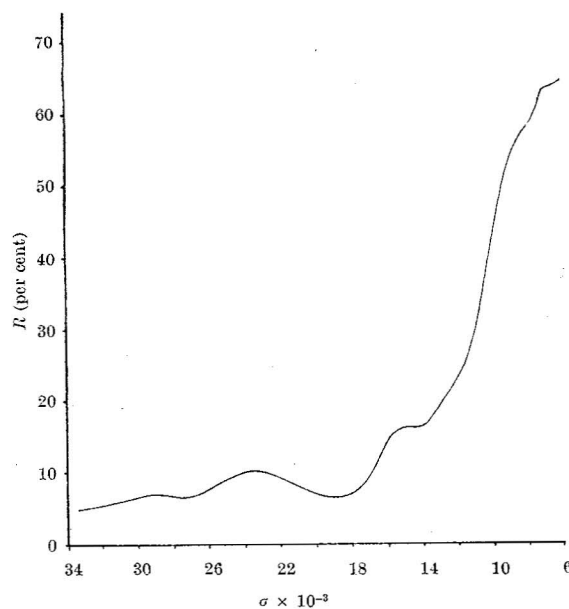Fig. 1. Reflexion spectrum of Ti^{3+} in lithium fluoride

Fig. 2. Reflexion spectrum of α-$TiCl_3$