

TABLE 1

Natural lifetimes τ in benzene and absorption maxima λ_{\max} for 1,3-dienes

<i>Diene</i>	τ (ns)	λ_{\max} (S-S) ^a (nm (kJ mol ⁻¹))	λ_{\max} (T-T) ^b (nm (kJ mol ⁻¹))
CPD	1600 (1700 ^c)	240 (500)	300 (400)
CHxD	5200 (4700 ^c)	259 (463)	310 (387)
CHpD	390 (410 ^c)	246 (488)	310 (387)
COD	140	227 (529)	315 (381)
TMB	80 (73 ^c)	236 (509)	310 (387)

^aIn cyclohexane.^bIn benzene.^cFrom energy transfer experiments [3, 4].

good agreement with the available calculations and correlate well with those determined for the extended polyenes.

2. Experimental details

2.1. Pulse radiolysis

The experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester, using the Vickers 10 MeV linear accelerator with pulse widths of either 10 or 20 ns. Kinetic absorption spectrometry measurements were made using the apparatus described by Keene and Hodgson [5]. The time dependences of the transient absorptions were displayed as cathode ray oscilloscope traces of voltage waveforms at the anode of an EMI 9783R photomultiplier coupled to a 56 Ω load resistance (minimum rise time, 2.5 ns). The irradiations were carried out at room temperature and the solutions were deaerated by prolonged argon bubbling.

2.2. Materials

Benzene (AnalaR) was distilled from phosphorus pentoxide after sulphuric acid-water-bicarbonate-water treatment. CPD was prepared by thermal decomposition of the dimer (Koch Light) over iron filings, and CHpD was prepared according to the published procedure [6]. Before use, these two dienes, CHxD (Fluka), COD (Fluka) and TMB (Aldrich) were distilled from lithium aluminium hydride under nitrogen through a column 4 ft long packed with steel wool.

3. Results and discussion

Energy absorption from a 10 or 20 ns pulse of high energy electrons (several mega-electronvolts) by an aromatic liquid such as benzene (B) pro-

duces significant yields of short-lived bound excited states of the matrix molecules [7] according to



After the pulse these species may decay via the normal photophysical channels or in the presence of suitable additive molecules, *e.g.* a diene (D), may pass on their electronic excitation energy. Since intersystem crossing from ${}^1D^*$ to ${}^3D^*$ will be unimportant, the formation of ${}^3D^*$ should take place only via transfer from ${}^3B^*$:



Since the latter species has a very short lifetime of 3 ns [8], the formation of ${}^3D^*$ will be complete within 50 ns. Its subsequent decay will be governed by the processes



Reaction (4) takes account of the known triplet-sensitized dimerization of some 1,3-dienes [9]. (It is not known whether k_{DD} contains contributions which do not lead to the dimer, *e.g.* classical self-quenching.) The first-order decay of ${}^3D^*$ should therefore occur with a constant k' defined by

$$k' = k_D + k_{DD}[D] \quad (5)$$

The pulse radiolysis of deaerated benzene solutions of each diene (10^{-1} mol l^{-1}) resulted in the "immediate" formation of a transient species (Fig. 1) which was quenchable by oxygen in all cases. The transient decay was first order (Fig. 1(a)) and extrapolation of the decay constant to zero diene concentration according to eqn. (5) (Fig. 1(b)) yielded natural lifetimes in benzene which are reproduced in Table 1 together with available values obtained from energy transfer experiments [3, 4]. These data clearly identify the transients as diene triplet states. In all cases the residual absorption, after the loss of the triplet, decays over several tens of microseconds and presumably is due to radical products resulting from bimolecular and possibly unimolecular decay of the diene triplet.

An inspection of Table 1 shows that, as anticipated, the triplet lifetime decreases with the increase in flexibility, and therefore the increase in the ability to relax, along the series CHxD, CHpD, COD, TMB. However, ${}^3CPD^*$, which hardly relaxes at all [3] although it is relatively long lived, decays faster than ${}^3CHxD^*$.

The triplet-triplet absorption spectra of the five dienes are reproduced in Fig. 2. They were recorded at the time of maximum transient absorption, under essentially identical conditions of concentration, radiation dose etc. The relative optical densities in Fig. 2 should therefore be some indication

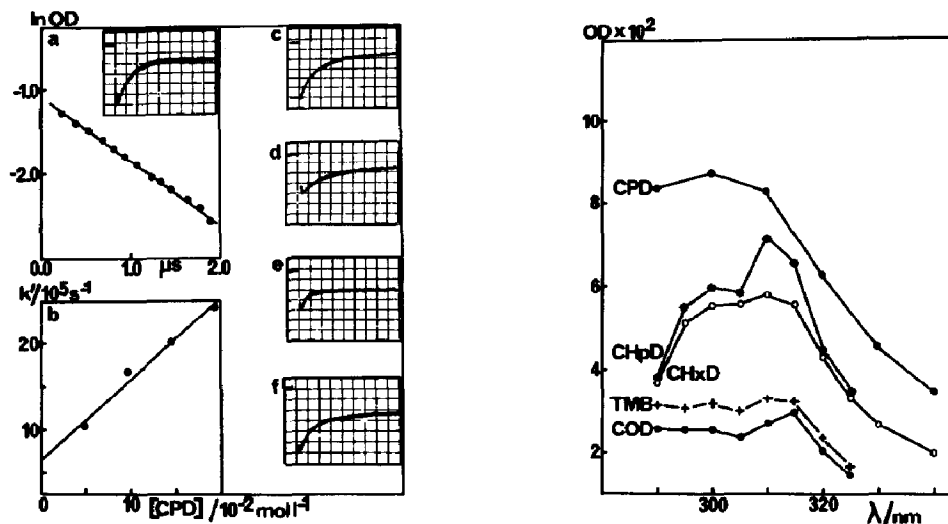


Fig. 1. (a) Semilogarithmic plot for the decay at 310 nm of the absorption of the CPD triplet formed on absorption of a 20 ns electron pulse by liquid benzene containing CPD ($10^{-1} mol l^{-1}$) (inset: time dependence of the transient absorption for the same experiment (3% absorption per division, 500 ns per division)); (b) first-order constant monitored at 300 nm for CPD triplet decay plotted against the CPD concentration; (c) time dependence of CHxD triplet absorption at 300 nm after the absorption of a 20 ns pulse by liquid benzene containing $10^{-1} mol l^{-1}$ of CHxD (2% absorption per division, 2 μs per division); (d) time dependence of CHpD triplet absorption at 300 nm after the absorption of a 20 ns pulse by liquid benzene containing $10^{-1} mol l^{-1}$ of CHpD (3% absorption per division, 200 ns per division); (e) time dependence of COD triplet absorption at 315 nm after the absorption of a 20 ns pulse by liquid benzene containing $10^{-1} mol l^{-1}$ of COD (1.5% absorption per division, 200 ns per division); (f) time dependence of TMB triplet absorption at 310 nm after the absorption of a 20 ns pulse by liquid benzene containing $10^{-1} mol l^{-1}$ of TMB (0.75% absorption per division, 100 ns per division).

Fig. 2. Absorption spectra of diene triplets formed "immediately" on absorption of a 20 ns electron pulse by liquid benzene containing $10^{-1} mol l^{-1}$ of diene.

of the relative triplet-triplet extinction coefficients. The similarity of the spectra of the CHxD-CHpD and COD-TMB pairs should be noted. Certainly the weak absorptions and the short lifetimes for the latter pair are clearly in agreement with comparable degrees of relaxation. The spectrum of $^3CPD^*$ appears to be rather different, which is possibly a further reflection of the factor(s) which makes the triplet lifetime appear slightly anomalous.

The triplet-triplet absorption maxima of the five dienes correspond to transition energies in the range 380 - 400 $kJ mol^{-1}$ (Table 1). These values are in remarkably good agreement with the results of self-consistent field-configuration interaction calculations by Simmons [10] for *s-trans*-butadiene and *s-cis*-butadiene (392 $kJ mol^{-1}$ and 375 $kJ mol^{-1}$ respectively) and with improved linear combination of atomic orbitals calculations by Bénard and Julg [11] for butadiene (404 $kJ mol^{-1}$). Previously the shortest polyene for which a triplet-triplet absorption spectrum had been

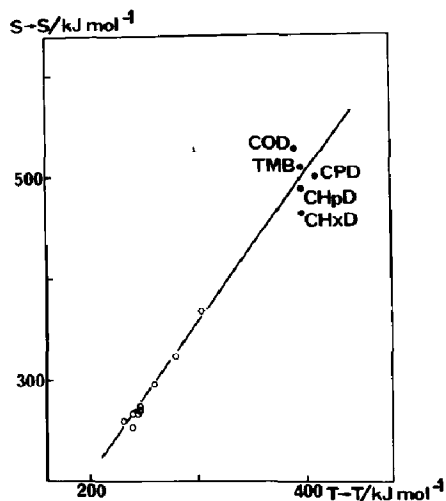


Fig. 3. Plot of singlet-singlet absorption maxima against the corresponding triplet-triplet values for retinal- and carotene-related polyenes (\circ) [2] and 1,3-dienes (\bullet).

recorded was retinol (vitamin A) [2] which contains five conjugated double bonds. In this work by Trustcott *et al.* a linear relationship was observed between the absorption maxima of the singlet-singlet and triplet-triplet transitions of retinal- and carotene-related unsaturated polyenes. In Fig. 3 the corresponding data for the five dienes (Table 1) are reproduced together with those for the polyenes [2]. The excellent correlation and the agreement with the calculations are encouraging but are presumably at least in part fortuitous when one considers (a) the likely torsional differences between the π systems of the various relaxed triplet states and (b) the necessary restriction of the published calculations to planar excited states.

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