493. *Magnetic Perturbation of Singlet–Triplet Transitions. Part VI.* Octa*-1,3,5,7-*tetraene.*

By D. F. Evans.

The singlet–triplet absorption spectrum (induced by oxygen under pressure) of octa-1,3,5,7-tetraene in chloroform solution, and the first singlet–singlet absorption of the pure vapour have been measured. A simple preparation of octa-1,3,5,7-tetraene is described.

The induced singlet–triplet absorption spectra of ethylene, butadiene, and hexa-1,3,5-triene in the presence of oxygen under pressure have been reported.[1] The present paper is concerned with the next member of the series, octa-1,3,5,7-tetraene. Although this

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* Part V, *J.*, 1961, 1987.

[1] Evans, *J.*, 1960, 1735.

very unstable compound has previously been prepared by two different routes,[2,3] a third, and in some ways more convenient, preparation was devised. The vapour-phase singlet–singlet absorption spectrum of octa-1,3,5,7-tetraene was also measured.

EXPERIMENTAL

Octa-1,3,5,7-*tetraene*.—Octa-2,4,6-trien-1-ol was prepared in good yield by reduction of octa-2,4,6-trienal with sodium borohydride in methanol; this method seems more convenient than that given in ref. 4. It was slowly distilled under *ca.* 0·1 mm. of oxygen-free nitrogen through a tube packed with aluminium oxide (desiccating agent) which was heated at 290°. The products were condensed in a trap kept at −78°. After warming to room temperature, the crude solid octa-1,3,5,7-tetraene was dissolved in isopentane, and the solution was dried (Na_2SO_4) and cooled at −78°. The resulting, almost colourless crystals were filtered on a low-temperature filter, washed with cold isopentane, and quickly dried in a stream of nitrogen (yield *ca.* 40%). The product was characterised by its infrared spectrum in carbon disulphide solution, and its ultraviolet absorption spectrum in 2,2,4-trimethylpentane solution, which were in good agreement with those reported by Woods and Schwartzman [2] and Lippincott *et al.*[3] According to the latter workers, octa-1,3,5,7-tetraene probably has an all-*trans*-structure. Since octa-1,3,5,7-tetraene polymerizes very rapidly in the solid state, solutions were prepared immediately the compound was dry, and physical measurements were made within 1—2 hr.

The vapour-phase singlet–singlet absorption spectrum was obtained by using evacuated 1-mm. or 1-cm. quartz cells attached by a graded seal to a bulb containing a few crystals of octa-1,3,5,7-tetraene.

Ultraviolet and visible spectra were measured on a Perkin–Elmer 4000 recording spectrophotometer.

RESULTS AND DISCUSSION

Singlet–Triplet Transitions.—The spectrum (Fig. 1) closely resembles those obtained[1] for butadiene and hexa-1,3,5-triene. It is clear that two transitions are present and they can similarly be assigned as involving the first and the second triplet level of octa-1,3,5,7-tetraene. The positions of the 0,0 bands (13,750, 21,550 cm.$^{-1}$) and absorption maxima (*ca.* 17,000, *ca.* 23,000 cm.$^{-1}$) for the two transitions follow the trend found with butadiene and hexa-1,3,5-triene. The separation between the 0,0 bands of the first and the second transition shows a remarkable constancy in the series (7920 cm.$^{-1}$ butadiene; 7860 cm.$^{-1}$ hexa-1,3,5-triene; 7800 cm.$^{-1}$ octa-1,3,5,7-tetraene).

Singlet–Singlet Transition.—The first singlet–singlet transition (V_1–N) of octa-1,3,5,7-tetraene in the vapour phase is shown in Fig. 2. The bands are much sharper than those observed for gaseous butadiene [5] or hexa-1,3,5-triene.[6] All the main bands can be satisfactorily accounted for by two vibrational frequencies (1640 and 1240 cm.$^{-1}$; see Table), which may be tentatively assigned as symmetrical " double- " and " single- " bond stretching frequencies of the upper singlet state. The vapour-phase spectrum of hexa-1,3,5-triene, measured photographically by Price and Walsh,[6] also shows two vibrational intervals, at 1615 and 1230 cm.$^{-1}$. Although these authors considered the possibility that two vibrational frequencies of the V_1 state were involved, they thought it more likely that two geometrical isomers of hexa-1,3,5-triene were present (no bands involving multiple quanta of the 1230 cm.$^{-1}$ vibration could be detected). The present results for octa-1,3,5,7-tetraene suggest that the first alternative is, in fact, probably correct. The absence of multiple quanta of the 1230 cm.$^{-1}$ vibration is probably due largely to the breadth of the hexa-1,3,5-triene bands, together with the difficulty of detecting weak, diffuse bands photographically.

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[2] Woods and Schwartzman, *J. Amer. Chem. Soc.*, 1949, **71**, 1396.
[3] Lippincott, Feairheller, and White, *J. Amer. Chem. Soc.*, 1959, **81**, 1316.
[4] Reichstein, Ammann, and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 261.
[5] Price and Walsh, *Proc. Roy. Soc.*, 1940, *A*, **174**, 222.
[6] Price and Walsh, *Proc. Roy. Soc.*, 1946, *A*, **185**, 182.

The absorption spectrum of octa-1,3,5,7-tetraene in 2,2,4-trimethylpentane (Fig. 2) or hexane solution [2] shows no trace of the two vibrational intervals found in the gas phase.

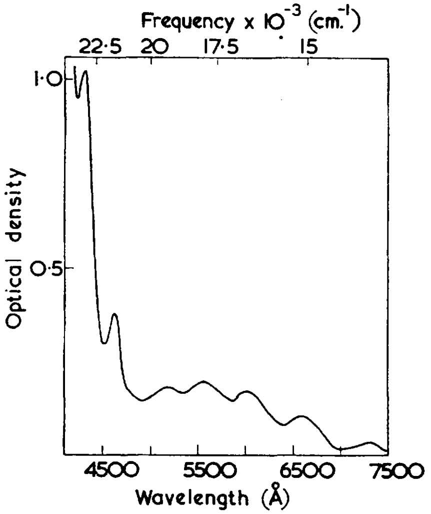
*V_1–N bands of octa-*1,3,5,7-*tetraene in the vapour phase. (The positive deviations at high frequencies may arise partly from the neglect of anharmonicity. There is evidence for a further vibrational frequency of* ca. 350 *cm.$^{-1}$.)*

Frequency (cm.$^{-1}$)	Analysis	Deviation (cm.$^{-1}$) (calc. — meas.)
35,520	0,0	
~35,860 (i)		
36,770	1240	−10
37,170	1640	−10
~37,540 (i)		
38,010	2 × 1240	−10
38,410	1640 + 1240	−10
38,820	2 × 1640	−20
~39,200 (i)		
39,660	1640 + 2 × 1240	−20
40,030	2 × 1640 + 1240	+10
40,460	3 × 1640	+20
41,270	2 × 1640 + 2 × 1240	+10
41,670	3 × 1640 + 1240	+10
42,040	4 × 1640	+40
~42,410 (i)		
42,860	3 × 1640 + 2 × 1240	+60
43,270	4 × 1640 + 1240	+50
43,670	5 × 1640	+50
~43,990 (i)		

(i) = Inflection.

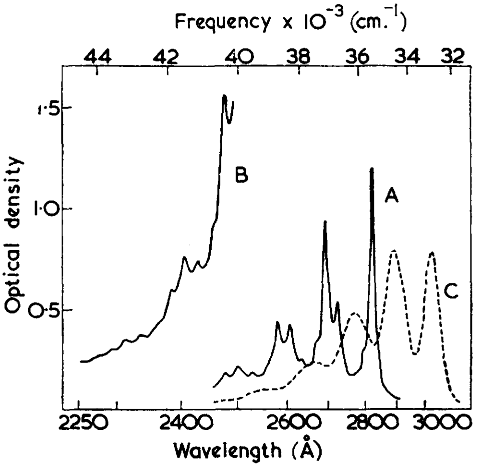
Owing to the effect of the solvent in broadening the bands, only a single interval of *ca.* 1500 cm.$^{-1}$ is observed, which is presumably composite. It seems very likely that the " characteristic " vibrational interval of 1400—1500 cm.$^{-1}$ found in the electronic spectra of all types of polyenes in solution (and in butadiene vapour [5]) also involves two vibrational frequencies. Over 25 years ago, Hausser, Kuhn, and Seitz [7] showed the presence of two vibrational intervals (1570, 1230 cm.$^{-1}$) in the absorption spectra of diphenylpolyenes, polyenecarboxylic acids, and lycopene in rigid glasses at —196°. Although the bands are

Fig. 1. *Light absorption of oxygen at* 130 *atm. dissolved in a chloroform solution of octa-*1,3,5,7-*tetraene* (5·2-*cm. cell*).



(*Owing to the rapid polymerisation of solid octa-*1,3,5,7-*tetraene, the concentration of the solution was not determined.*)

Fig. 2. *First singlet–singlet absorption spectrum of octa-*1,3,5,7-*tetraene in the vapour state and in solution.*



A, *Vapour* (*saturated vapour pressure at* 29°) (1-*mm. cell*). B, *Vapour* (*saturated vapour pressure at* 29°) (1-*cm. cell*). C, *Solution in* 2,2,4-*trimethylpentane.*

(*Owing to the rapid polymerization of solid octa-*1,3,5,7-*tetraene, the concentration of the solution was not determined. Solution max. at* 33,140, 34,680, 36,130, 37,600, *and ca.* 39,200 (i) *cm.$^{-1}$.*)

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[7] Hausser, Kuhn, and Seitz, *Z. phys. Chem.*, 1935, *B*, **29**, 391.

rather broad, two vibrational intervals (*ca.* 1600 and *ca.* 1200 cm.$^{-1}$) can be detected in the previously reported [1] induced singlet–triplet transitions of gaseous butadiene.

The 0,0 band in the spectrum of octa-1,3,5,7-tetraene shifts to lower frequency by 2380 cm.$^{-1}$ as we go from the vapour phase to solution in 2,2,4-trimethylpentane. This solvent shift is slightly greater than the solvent shifts found for butadiene (1800 cm.$^{-1}$) and hexa-1,3,5-triene (2150 cm.$^{-1}$; hexane solution [6,8]), although the increase seems smaller than would be expected from the theoretical formula for solvent shifts derived by Longuet-Higgins and Pople.[9]

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

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[8] Howton, *J. Org. Chem.*, 1949, **14**, 1.

[9] Longuet-Higgins and Pople, *J. Chem. Phys.*, 1957, **27**, 192.