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Electronic Spectrum and Conformational Energy of Homoconjugated molecules

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Chimica fisica. — *Electronic Spectrum and Conformational Energy of Homoconjugated molecules* (*). Nota di IGNAZIO RENATO BELLOBONO, ALDO GAMBA e MASSIMO SIMONETTA, presentata (**) dal Corrisp. M. SIMONETTA.

RIASSUNTO. — Sono stati misurati gli spettri ultravioletti dei seguenti composti: 1,3,6,8–nonatetraene, 1,3,7,9–decatetraene, 1,3,8,10–endecatetraene, 1,3,9,11–dodecatetraene, 3–vinil 1,5,7–ottatriene, 1,5–esadiene, 1,6–eptadiene, 1,7 ottadiene, 1,8 nonadiene e 1,9 decadiene, in soluzione di 2,2,4–trimetilpentano a temperatura ambiente.

Gli spettri sono stati interpretati mediante un calcolo teorico semiempirico in cui si usano combinatamente le energie di transizione ottenute con il metodo delle «Molecole nelle Molecole» e le energie conformazionali calcolate con il metodo di Westheimer.

The problem of electronic interactions between non conjugated groups and their influence on the ultraviolet spectra of homoconjugated molecules (1) has been the subject of extensive studies in recent years [2].

Certain polyenes, where two or more methylene groups are interposed between two butadienyls, represent an important example. The spectra of such tetraenes with one or four methylene groups have been previously investigated [3].

However in contrast with conjugated molecules [4, 5], no quantitative calculations for molecules of this type in which both the π–electron and conformational energy were evaluated, have appeared in literature. In the present paper experimental and theoretical results for the spectra of 1,3,6,8–nonatetraene, 1,3,7,9–decatetraene, 1,3,8,10–endecatetraene, 1,3,9,11–dodecatetraene, and 3–vinyl 1,5,7–octatriene are reported. For sake of comparison the corresponding molecules in which two ethylenic groups are the chromophores have been considered. The spectra of 1,5–hexadiene, 1,6–heptadiene, 1,7–octadiene, 1,8–nonadiene, and 1,9–decadiene are reported.

CALCULATIONS

Conformational energy.

The study of conformational energy has been performed following the classical Westheimer method [6].

In the expression for the energy, torsional energy and non-bonded interaction terms only need to be considered. The torsional energy term is given by:

$$E_t\,(\text{Kcal/mole}) = (K/2)\ (1 + \cos 3\,\omega)$$

with

$$K = 3.0\,\text{Kcal/mole} \quad \text{for } sp^3\text{–}sp^3 \text{ bonds [7]}$$
$$K = 2.0\,\text{Kcal/mole} \quad \text{for } sp^3\text{–}sp^2 \text{ bonds [8]}\,.$$

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(**) Nella seduta del 12 dicembre 1970.

(1) In the scope of the present paper homoconjugation is intended as the interaction between two groups separated by two or more bonds; see ref [1].

For non bonded interactions the following expressions were used, taken from Bartell's work [9]:

$$E_{H\ldots H}\,(\text{Kcal/mole}) = 0.659\ 10^4\ e^{-r/0.245} - 0.492\ 10^2\, r^{-6}$$

$$E_{C\ldots H}\,(\text{Kcal/mole}) = 1.2496\ 10^2\, r^{-6}\,(358.0\ e^{-r/0.49} - 1.0)$$

$$E_{C\ldots C}\,(\text{Kcal/mole}) = 2.994\ 10^5\, r^{-12} - 3.253\ 10^2\, r^{-6}.$$

Conformational energies were calculated for the following molecules: 1,4–pentadiene, 1,5–hexadiene, 1,3,6,8–nonatetraene, 1,3,7,9–decatetraene. The molecules were considered as rigid except for rotation around the "*single*" bonds between chromophores; butadiene fragments were assumed to be planar. If an interval of 60^0 for each allowed rotation is adopted, the number of conformations is 6^2 for the first and third molecules, 6^3 for the second and fourth molecules respectively.

The geometry of butadiene has been taken from published experimental data [10].

In all other situations standard trigonal and tetrahedral angles were assumed; bond lengths as given in Table I were used.

TABLE I (a).

Assumed Interatomic Distances.

Type of bond	Bond length r_e (Å)
C—C	
sp^3–sp^3	1.534 (b)
sp^3–sp^2	1.520
C=C	
sp^2–sp^2	1.334
C—H	
sp^3–H	1.108
sp^2–H	1.085

(*a*) from ref. [11] unless otherwise stated.
(*b*) from ref. [10].

Transition energies and intensities.

Two methods are commonly used for the theoretical study of spectra of systems in which two or more groups of π electrons are identifiable: that is "exciton theory" [12] and "molecules in molecules" (MIM) method [13, 14].

It has been found however [15] that while the first one is successful in the interpretation of spectra of organic crystals, the second method gives better results when applied to organic molecules. Consequently MIM method was first applied to all possible conformations of 1,4–pentadiene, 1,5–hexadiene, *trans-trans*, *trans-cis* and *cis-cis* 1,3,6,8–nonatetraene, and *trans-trans* 1,3,7,9–decatetraene.

SCF orbitals obtained in the Pople approximation [16] were used for ethylene, *cis*– and *trans*– 1,3–butadiene. The last occupied and the first nonoccupied molecular orbitals were used for each fragment. Locally excited configuration energies were obtained from spectroscopic data and are shown in Table II.

TABLE II.

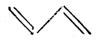
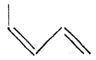
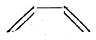
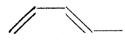
Locally Excited Configurations Energies.

Compound		$h\nu$ (eV)
1,3,6,8–nonatetraene	(*trans*)	5.472 (a)
	(*cis*)	5.484 (b)
1,3,7,9–decatetraene		5.484 (c)
1,3,8,10–endecatetraene		5.496 (c)
1,3,9,11–dodecatetraene		5.509 (a)
Ethylene		6.984 (d)

(*a*) Values taken from ultraviolet spectra of 1,3–nonadiene and 1,3–dodecadiene [3].
(*b*) Interpolated by the relation:

$$\frac{\nu_A}{\nu_C} = \frac{\nu_B}{\nu_D} = \frac{\nu_{tras}}{\nu_{cis}}$$

where subscripts A, B, C, and D refer to the following compounds [17]:

		λ (nm) calc.	λ (nm) obs.
(A)		203.2	209.4
(B)		210.0	214.8
(C)		227.0	—
(D)		235.0	—

(*c*) Values interpolated from data relative to 1,3–nonadiene and 1,3–dodecadiene.
(*d*) Taken from ultraviolet spectrum of 1–pentene [18].

Charge-transfer energies were calculated according to the usual formula:

$$T = I - A - Q$$

where I and A are ionisation potential and electron affinity of the fragment and Q is the coulomb attraction between the transferred electron and the positive hole left in the donating fragment. In absence of experimental data for I and A, empirical values were obtained from the relation [19]:

$$A\ (\mathrm{eV}) = 2.991 - 0.70\, \Delta E'$$

$$I + A = 8.14\ \mathrm{eV}$$

where $\Delta E'$ is the locally excited energy.

The electronic repulsion integrals were calculated using the point-charge approximation [16]. The resonance integral β was assumed to be proportional to the overlap integral of the relevant atomic orbitals (Slater orbitals were used throughout). The reference value of β for two parallel π orbitals 1.34 Å apart was taken as 3.00 eV.

Transition intensities were calculated according to the relation [20].

$$f = 1.085\ 10^{11}\, \nu \lambda^2$$

In this expression ν is the wave number in cm^{-1} and λ is the transition moment in cm. Empirical estimations of f were obtained by the relation [21]:

$$f = 2 \times 10^{-5}\, \varepsilon_{\max}\ .$$

When the Davydov theory was applied to 1,4–pentadiene the calculated excitation energies fell in the range 6.6–7.0 eV for all conformations, in good agreement with experiment [18], but in the case of 1,3,6,8–nonatetraene the transition energies turned out to be significantly not dependent upon conformation. This fact shows that " exciton theory " method is not reliable when interactions other than dipole-dipole are present.

Results and discussion.

The spectra obtained in 2,2,4–trimethylpentane solution are shown in figs. 1–4. The most interesting features of these spectra are also summarized in Table III. In fig. 5 the vapor spectrum of 1,4–pentadiene taken from literature [18] is also reported. It is evident from fig. 1 that all the diene spectra are very similar. The wavelengths of maximum absorption for these compounds are reported in fig. 6 together with that of the vapor phase spectrum of 1,4–pentadiene [18]: they are almost independent of the number of methylenes interposed between the two ethylene groups. In the same figure the wavelength of maximum absorption for the spectrum of 1–hexene in 3–methylpentane solution is also indicated [22] (for 1–hexene $f = 0.29$).

The intensity of diolefin absorption (cfr. Table III) is about twice that of monoolefins, as expected when no interaction occurs between the two double bonds. A limited interaction is expected when only one methylene group is present. The spectrum of 1,4–pentadiene is in fact much broader than that of 1–pentene [18]. As the literature data [18] refer to a vapor spectrum, $\lambda_{\max}$ for the same transition in solution was calculated according to a formula given by Bayliss [23].

TABLE III.

UV *Spectral data in 2,2,4-trimethylpentane solution.*

Compound	λ_{max} (nm)	$h\nu$ (eV)	ε_{max} (M^{-1} cm^{-1})	f
1,3,6,8-nonatetraene	(218)	5.685	25410	0.51
	234.8	5.279	36030	0.75
	273	4.540	1025	0.006
	294.5	4.209	214	0.001
	308.5	4.018	181	0.001
1,3,7,9-decatetraene	(221.3)	5.602	36785	1.08
	228.8	5.418	41720	
1,3,8,10-endecatetraene . .	(225)	5.509	41140	
	228.6	5.423	42060	1.14
	(235)	5.275	34600	
	(261)	4.750	473	
1,3,9,11-dodecatetraene . .	(224.5)	5.522	40670	
	228.5	5.425	41485	1.07
	(232.5)	5.332	34160	
	(260)	4.770	506	
3-vinyl 1,5,7-octatriene . .	180	6.887	16320	0.81
	223	5.559	28670	0.62
	226.5	5.473	30095	
	(231.5)	5.355	23890	
1,5-hexadiene	180.8	6.856	23710	0.58
1,6-heptadiene	180.5	6.868		
1,7-octadiene	182.0	6.811	22980	0.42
1,8-nonadiene	182.0	6.811	21390	0.39
1,9-decadiene	183.5	6.755	24190	0.66

Calculations have shown that the first two transition energies and the corresponding f values for this diolefin depend on conformation. The energy difference (ΔE) between the various conformations was obtained by adding to the difference of conformational energy (ΔE_c) the difference in the ground-state stabilisation energy (ΔE_g) as obtained by the MIM treatment. These energy differences have been used to calculate a classical Boltzmann distribution (P) among the conformations. For each conformation the product of the oscillator strength and the Boltzmann distribution value is plotted in fig. 5 at the corresponding value of transition energies. The results adequately account for the broadening of 1,4-pentadiene band respective to that of 1-pentene [18]. As an example, detailed results for this molecule are shown in Table IV.

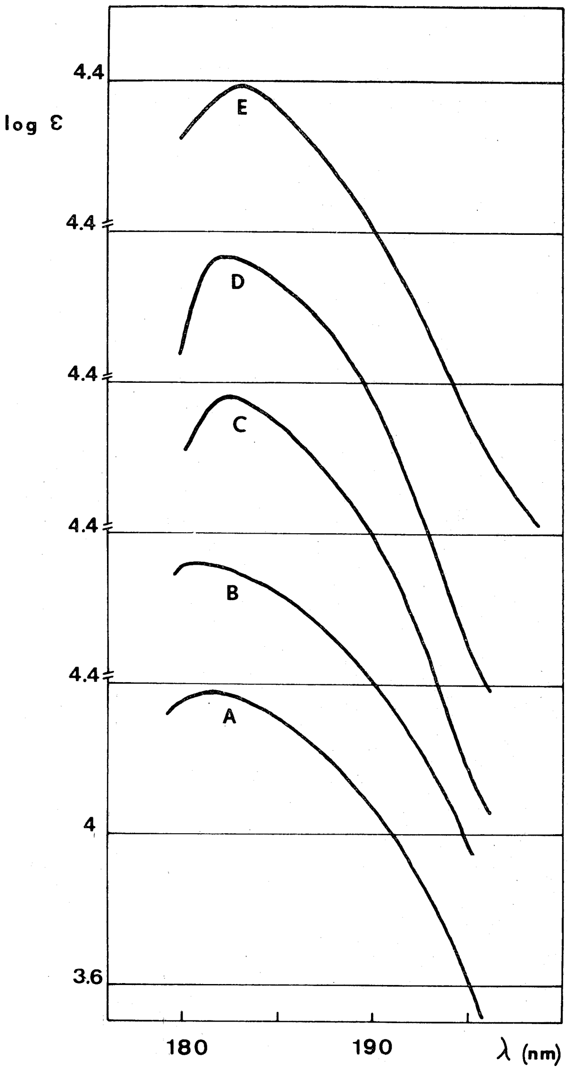


Fig. 1. – Far ultraviolet spectra in 2,2,4-trimethylpentane solution of nonconjugated diolefins:

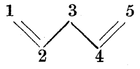
A) 1,5-hexadiene;
B) 1,6-heptadiene;
C) 1,7-octadiene;
D) 1,8-nonadiene;
E) 1,9-decadiene.

TABLE IV.

Theoretical conformational and spectral energies for 1,4–pentadiene.

Conformation (a)	ΔE (Kcal/mole)	P	1st band		2nd band	
			$h\nu$ (eV)	f	$h\nu$ (eV)	f
A1 . . .	2.463	0.0071	6.406	0.91	7.488	0.20
A2 . . .	0.720	0.5367	6.520	0.64	7.426	0.24
A3 . . .	2.359	0.0337	6.700	0.50	7.235	0.32
A4 . . .	17.682	$<10^{-4}$	6.727	0.58	7.077	0.36
B2 . . .	0.887	0.2024	6.476	0.43	7.468	0.64
B3 . . .	2.452	0.0288	6.597	0.26	7.371	0.29
B4 . . .	4.724	0.0006	6.774	0.45	7.129	0.24
B5 . . .	2.687	0.0194	6.787	0.84	7.139	0.16
B6 . . .	0.989	0.1704	6.660	0.26	7.308	0.29
C3 . . .	18.725	$<10^{-4}$	6.368	0.11	6.885	0.26
C4 . . .	12.737	$<10^{-4}$	6.468	0.12	6.710	0.28
C5 . . .	4.036	0.0010	6.849	0.27	7.119	0.28

(*a*) The following starting conformation (Al) was assumed:



with all carbon lying in the plane of the fig. By successive 60° clockwise rotations around C_2—C_3 axis, with C_2 as reference point of view, the other conformations (B, C) were obtained. By successive 60° clockwise rotations around C_3—C_4 axis, with C_3 as reference point of view, conformations 2, 3, 4, 5, and 6 were obtained.

Only the 12 non equivalent, out of all the 36 possible conformations, are reported.

The same calculations have been performed for 1,5–hexadiene and the results are shown together with the experimental spectrum in fig. 7.

In fig. 8 the maximum absorption wavelengths of tetraenes, together with values for 1,3–nonadiene and 1,3–dodecadiene, taken from the literature [3], are collected. The small differences between our spectrum of 1,3,6,8–nonatetraene and that previously reported [3], may be due to a slightly different ratio of *trans-trans* and *trans-cis* isomers (an absorption maximum was observed by Butler and Raymond at 237 nm).

The data of fig. 8 confirm that one methylene group is not a sufficient condition to isolate the two chromophores and this fact is more evident for tetraenes than for dienes. The same calculations carried out for 1,4–pentadiene and 1,5–hexadiene were extended to 1,3,6,8–nonatetraene and 1,3,7,9–decatetraene: results are shown in figs. 2 and 3. An energy difference of 0.27 Kcal, corresponding to destabilisation of the π electron system of *trans* respectively to that of *cis* 1,3–butadiene, was included in the calculation of ΔE; overall stabilisation of *trans* isomer was accounted for by non-bonded interactions. The value of 0.27 Kcal/mole was obtained applying the MIM method to *cis* and *trans* butadiene considered as built from two ethylenic fragments. The calculations for the remaining tetraenes have been skipped because of the high number of conformations and for the fact that, owing to the distance between two chromophores, no significant interaction and hence no significant dependence on conformations is to be expected. Experimental spectra shown in fig. 3 confirm this view.

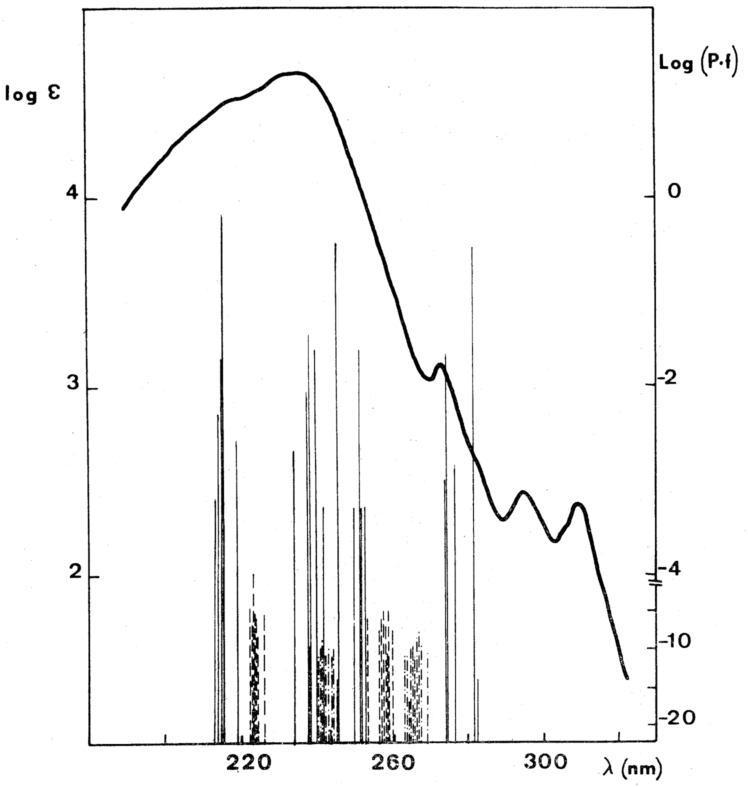


Fig. 2. – Molar absorptivities, ε (M^{-1} cm^{-1}), in 2,2,4–trimethylpentane solution and calculated values (vertical lines) of theoretical oscillator strength (*f*), multiplied by Boltzmann classical distribution (*P*), of 1,3,6,8–nonatetraene.

——— *trans–trans* isomer – – – – – *trans–cis* –·–·–·– *cis–cis*.

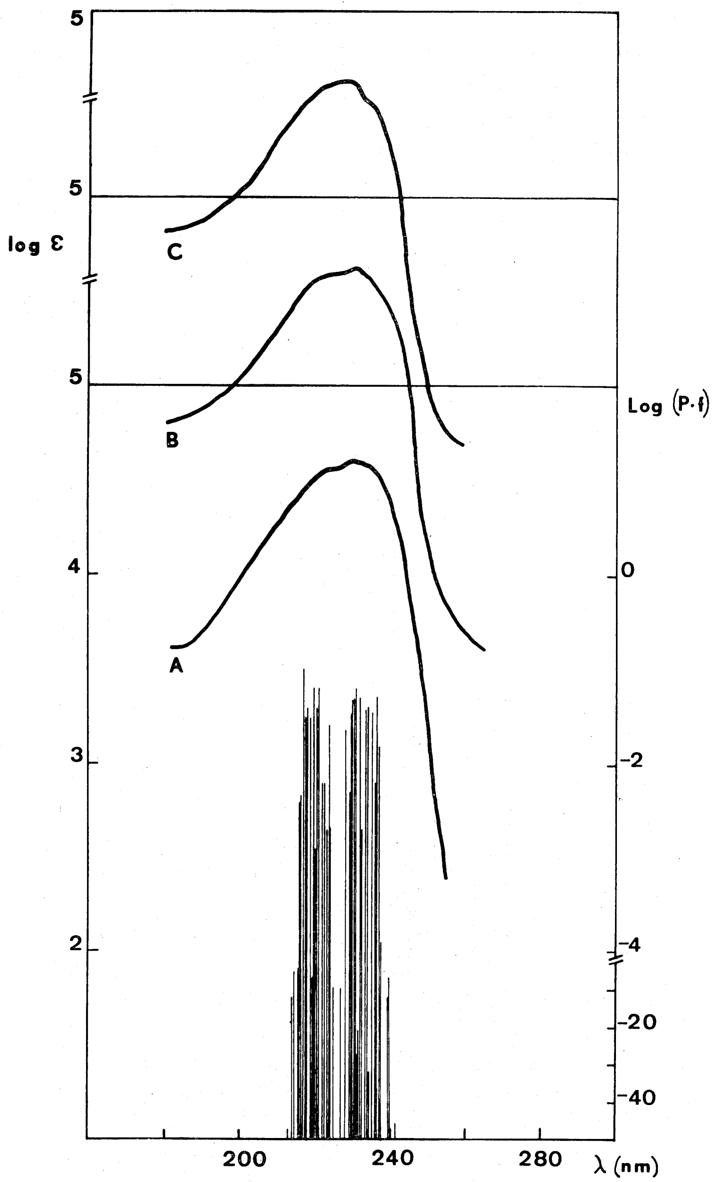


Fig. 3. – Molar absorptivities, ε (M^{-1} cm^{-1}), in 2,2,4–trimethylpentane solutions of A), 1,3,7,9–decatetraene; B) 1,3,8,10–endecatetraene, and C) 1,3,9,11–dodecatetraene. Calculated values (vertical lines) of theoretical oscillator strength (*f*), multiplied by Boltzmann classical distribution (*P*), of 1,3,7,9–decatetraene are also shown.

Our calculations refer to isolated molecules: no solvent effect has been taken into account, since this is expected to be small enough to have no influence on conclusions.

The characteristic features exhibited by 1,3,6,8–nonatetraene as compared with those of other tetraenes are thus well evidenced by theoretical calculations.

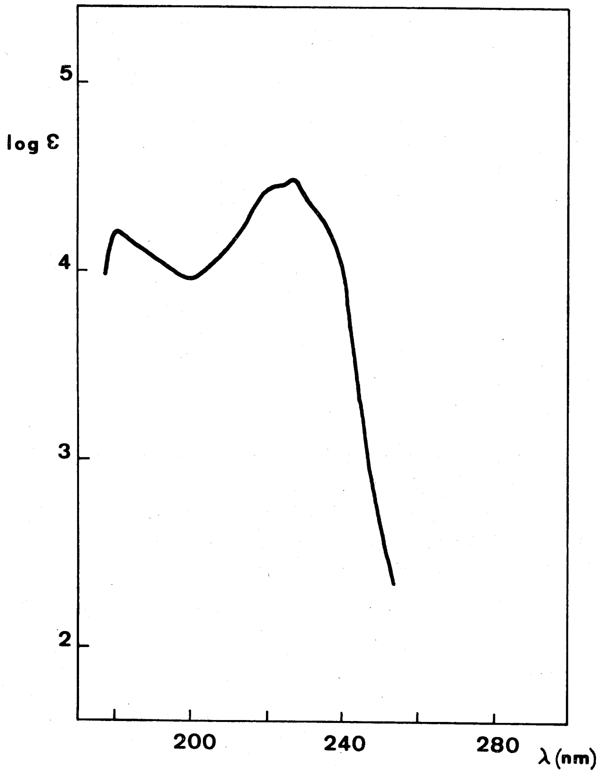


Fig. 4. – Molar absorptivities ε (M^{-1} cm^{-1}), in 2,2,4-trimethylpentane solution of 3,vinyl 1,5,7-octatriene.

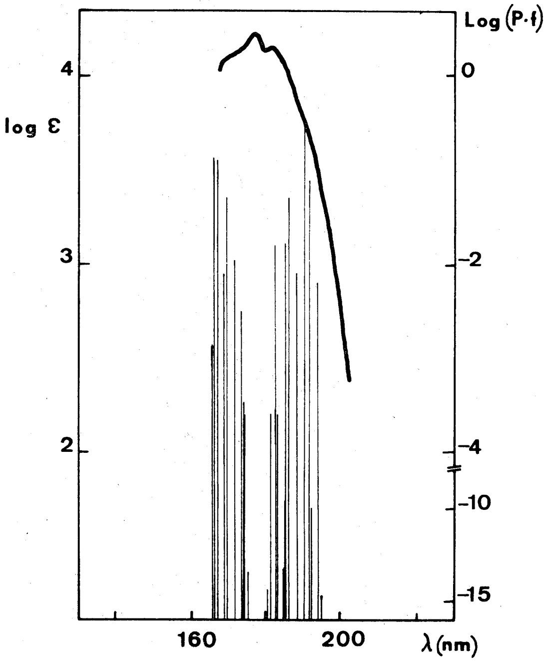


Fig. 5. – Molar absorptivities ε(M^{-1} cm^{-1}) and calculated values (vertical lines) of theoretical oscillator strength (f) multiplied by Boltzmann classical distribution (P), of 1,4-pentadiene vapor spectrum.

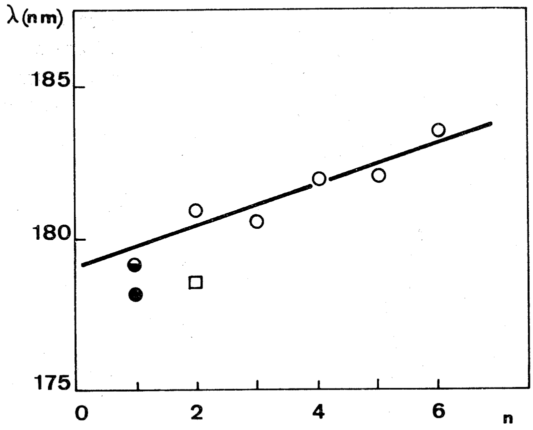


Fig. 6. – Wavelengths λ (nm) of maximum absorption of experimental (○, present work) or calculated (◒, (Bayliss formula [23])) solution spectra (2,2,4-trimethylpentane as solvent), and vapor spectrum (●, ref. 18)) of nonconjugated diolefins $CH_2{=}CH{-}(CH_2)_n{-}CH{=}CH_2$ as a function of n. The value of 1-hexene (□, ref. 22) is also plotted.

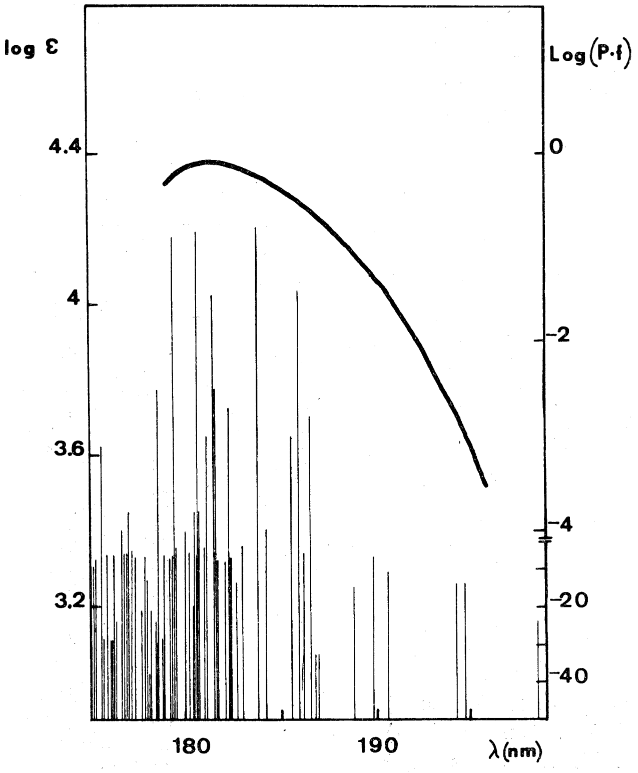


Fig. 7. – Molar absorptivities ε (M^{-1} cm^{-1}), in 2,2,4-trimethylpentane solution and calculated values (vertical lines) of theoretical oscillator strength (f), multiplied by classical Boltzmann distribution (P), of 1,5-hexadiene.

The spectrum of 3–vinyl 1,5,7–octatriene (fig. 4) constitutes a further demonstration that two methylene groups can isolate two chromophores. This spectrum can be considered a superposition of those of 1,4–pentadiene and 1,3–pentadiene [18], especially if the wavelengths of maximum absorption of vapor are corrected for a solvent effect (see also, for comparison, the spectra of 1,4–pentadiene in fig. 5 and of 1,3,7,9–decatetraene in fig. 3).

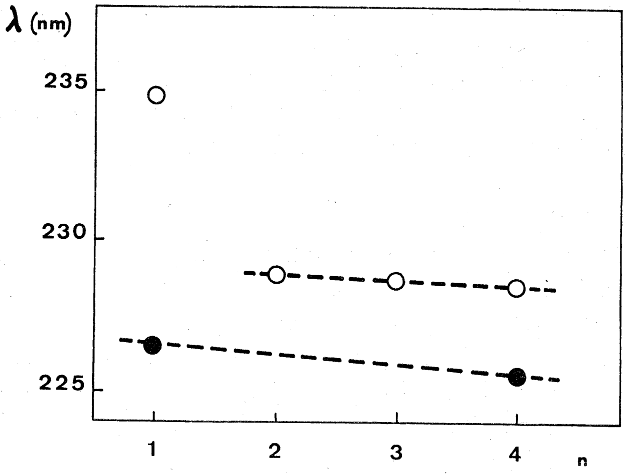


Fig. 8. – Wavelengths λ (nm) of maximum absorption of experimental (○, present work) solution spectra (2,2,4–trimethylpentane as solvent) of tetraenes $CH_2{=}CH{-}CH{=}CH{-}(CH_2)_n{-}CH{=}CH{-}CH{=}CH_2$ and dienes $CH_2{=}CH{-}CH{=}CH{-}(CH_2)_{n+3}{-}CH_3$ (●, ref. [3]) as a function of n.

The results shown in figs. 2, 3, 5 and 7 suggest that a combined use of the MIM and " molecular mechanics " calculations can lead successfully to the interpretation of spectra of homoconjugated molecules.

EXPERIMENTAL

Analyses and Materials.

Gas-liquid chromatographic analyses were made with a Wilkens Aerograph Model 600 C gas chromatographic instrument, using nitrogen and hydrogen as the eluent gas. G.l.c. analyses were made on a 2–m column, packed with 25 % squalane or diethylene glycol succinate on 42/60 mesh firebrick or 60/80 mesh Chromosorb P (Perkin-Elmer).

Unless otherwise stated, preparatory g.l.c. was carried out by a Carlo Erba Chromatograph Model C, on a 2–m column, packed with 15–25 % fluorinated silicone, on firebrick.

Infrared data were obtained with a Perkin-Elmer Model 21 double-beam infrared recording spectrometer with NaCl optics.

Purity of prepared polyolefins was checked by comparison of their infrared spectra with literature data, as well as by g.l.c. and elemental analysis.

Nmr data were obtained with a Varian A–60 spectrometer at 60 M*cps*, in 5 % (*w*/*v*) $CDCl_3$ solution containing tetramethylsilane as an internal standard, at the operating temperature of the instrument (about 35° C).

Acrolein, triphenylphosphine, and 20–25 % solution of *n*–butyllithium in hexane were obtained from Fluka (Switzerland). Dibromoalkanes $BrCH_2(CH_2)_nCH_2Br$ ($n = 0, 1, 3, 4$) were furnished by BDH (England). Dienes $CH_2{=}CH(CH_2)_nCH{=}CH_2$ ($n = 2, 3, 4, 5, 6$), kindly supplied by Prof. R. Trave and coworkers, were purified gas-chromatographically.

For ultraviolet absorption measurements, spectrograde solvents were used.

1,3,6,8–nonatetraene.

This compound was prepared *via* the Wittig reaction [24], according to the procedure of Hauser *et al.* [25, 3].

The fractionally distilled reaction product was still a mixture of compounds, and it had to be purified by preparative g.l.c. This latter was carried out succesfully on a 3,3′–oxydipropionitrile column. Purity was checked by g.l.c. analysis (98–99 %).

Anal. Calcd. for C_9H_{12}: C, 89.93; H, 10.07. Found: C, 90.0; H, 10.0.

1,3,7,9–decatetraene and *3–vinyl,1,5,7–octatriene.*

They were prepared essentially by the method of Miginiac [26]. Isolation of pure 1,3,7,9–decatetraene could be achieved by fractional distillation. By g.l.c. analysis on a squalane column, which showed a high selectivity for isomers, decatetraene was found to have impurities to the extent of approximately 0.5 %, while the vinyloctatriene fraction was less pure (maximum impurities content about 4 %). Pure vinyloctatriene (g.l.c. analysis 99 %) was obtained by preparative g.l.c. on a diethylene glycol succinate polyester column.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.55; H, 10.45. Found for decatetraene C, 89.75; H, 10.0. Found for vinyloctatriene: C, 89.4; H, 10.5.

1,3,8,10–endecatetraene. A) *Pentamethylene bis(triphenyl phosphonium bromide).*

This salt was prepared in 74 % yield by the Wittig reaction. A mixture of 35.5 g of pentamethylene dibromide and 100 g of triphenylphosphine (about 18 % excess) was heated under a nitrogen atmosphere to 190° C in an oil bath. The wet paste formed into a viscous liquid at about 150° C. Then, after 15 min, slowly solidified. Heating was prolonged for 30 min. The salt was allowed to cool to room temperature and dissolved in hot chloroform. The product was precipitated by pouring the chloroform solution into 1.8 volumes of ethyl acetate. The crystalline product was filtered and dried overnight at 60° C and 2 mm Hg. A yield of 80.5 g of the diphosphonium salt, mp 264–267° C, was obtained.

Anal. Calcd. for $C_{40}H_{38}P_2Br_2$: C, 64.88; H, 5.17; Br, 21.58. Found C, 64.6; H, 5.3; Br, 20.2.

B) *1,3,8,10-endecatetraene.*

To a stirred suspension of 75.4 g of pentamethylene bis(triphenylphosphonium bromide) in 500 ml of dry ether under a nitrogen atmosphere 100 ml of 22.5 % *n*-butyllithium in hexane was added. The hexane solution was feeded under nitrogen pressure. The mixture was cooled to — 5° C and a solution of 35 ml acrolein in 100 ml of dry ether was added over a 20-min period, while maintaining a temperature slightly below 0° C. A cream-colored suspension resulted, which after stirring for 10 min, was decomposed by addition of 250 ml of water. The solid was separated from liquid (aqueous and ethereal) phases by filtration and the aqueous layer extracted once with 150 ml of ether. The combined ethereal fractions were dried over anhydrous sodium sulphate and most of the solvent distilled away in a rotating evaporator. The resulting oil, after standing, separated in two layers: the lower one consisted mainly of triphenylphosphine oxide, which slowly crystallized (*mp* 148–150° C) (lit. *mp* 152.5–154° C). The supernatant liquid was fractionated *in vacuo.*

The fraction distilling at 70° C (1.5 mm Hg) consisted of 92–93 % endecatetraene (g.l.c. analysis), which was further purified (chromatographic purity > 99 %) by preparative g.l.c. on a 3–3′–oxydipropionitrile column. The pure compound showed bands at: 3100 (*m*), 3050 (*m*), 2970 (*s*), 2880 (*m*), 2240 (*w*), 1810 (*m*), 1650 (*m*), 1645 (*m*), 1600 (*m*), 1595 (*w*), 1450 (*w*), 1435 (*m*), 1415 (*w*), 1370 (*w*), 1290 (*w*), 1250 (*w*), 1005 (*s*), 965 (*m*), 950 (*m*), 904 (*s*), 785 (*m*) (all wave numbers are quoted in cm^{-1}).

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.9; H, 10.8.

1,3,9,11–dodecatetraene.

It was prepared by the cited procedure of Hauser *et al.* [25]. The crude product was purified by preparative g.l.c., first on a 3–3′–oxydipropionitrile column, and subsequently on a fluorinated silicone column (g.l.c. analysis 99.7 %). The *nmr* spectrum gave an integrated peak area ratio for *sp*^{2} to *sp*^{3} hydrogens of 10 : 8. It showed multiplets centered at 103 *cps* (four protons at C 6 and 7), 151 *cps* (four protons at C 5 and 8), and a series of signals between 325 and 456 *cps* (ten protons of the two butadiene moieties) (chemical shifts are quoted as *cps* downfield from tetramethylsilane).

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.1; H, 11.1.

Ultraviolet spectra.

Ultraviolet absorption spectra in the wavelength region of 1750–3500 Å were measured at room temperature by a recording ultraviolet spectrophotometer Beckman DK–2 A. In the far ultraviolet region, short–path cells with suprasil silica windows were employed: their optical path was fixed at 0.02 cm. Recording was carried out in a purified nitrogen stream (oxygen content ≤ 0.2 *ppm*). In the near ultraviolet region standard cells with optical path of 1 cm were used. Spectra were recorded in 2,2,4–trimethylpentane solution. Results are shown in Table II and in figs 1–6. Some spectra were also measured in 95 % ethanol or cyclohexane solution: they were so close to the spectra recorded in 2,2,4–trimethylpentane solution, that results are not reported here: apparently the influence of the solvent is not relevant.

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