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The Electronic Spectra of [n]-Radialenes

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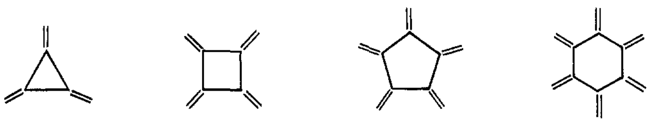
Application of Simpson's "Independent Systems Approach" to [*n*]-radialenes yields predictions for their electronic spectra which are in good qualitative agreement with observation.

Application du „Independent Systems Approach" de Simpson aux [*n*]-radialènes fournit des prédictions pour leurs spèctres éléctroniques, qui sont qualitativement en bon accord avec l'experience.

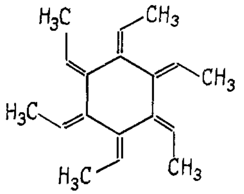
Die Anwendung von Simpsons „Independent Systems Approach" auf [*n*]-Radialene liefert Voraussagen für ihre Elektronenspektren, die in guter qualitativer Übereinstimmung mit der Beobachtung stehen.

[*n*]-Radialenes are hydrocarbons $C_{2n}H_{2n}$ of symmetry D_{nh} consisting of *n* cross-conjugated double bonds:

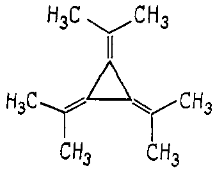


$n =$	3	4	5	6
Sym.	D_{3h}	D_{4h}	D_{5h}	D_{6h}

The electronic spectra of the first alternant member of this series ($n = 4$) [*1*] and of the hexamethyl derivative of [6]-radialene (in the following denoted by I) [*2*, *6*] have been known for some time. These spectra consist of one or more weak bands in the region $\tilde{\nu} = 35000$ to $40000\ \mathrm{cm}^{-1}$ ($\varepsilon = 5000$ to 7000), followed at shorter wavelength by an intense band at $\tilde{\nu} \approx 50000\ \mathrm{cm}^{-1}$ ($\varepsilon > 30000$), as shown in Fig. 1 and Tab. A.



I



II

Recently the electronic spectrum of the hexamethyl derivative of [3]-radialene (in the following denoted by II), that is of the first non alternant radialene, has been reported [*3*]. In contrast to the spectra of [4]-radialene and of I it shows a first intense band at $\tilde{\nu} = 33000\ \mathrm{cm}^{-1}$ ($\varepsilon = 18000$), well separated from bands which follow at $\tilde{\nu} > 50000\ \mathrm{cm}^{-1}$ and lacks therefore the characteristic low inten-

Table A

Compound	$\tilde{\nu}$ [a]	ε	$\tilde{\nu}$ [a]	ε	$\tilde{\nu}$ [a]	ε
II	32000	18000			50000	
[4]-Radialene	37000	7000			48000	50000 (?)
I	39000	6000	(43000)	(4000)[b]	49000	33000

[a] in cm^{-1}. [b] see Ref. [6].

sity transitions which preceed the strong bands in the spectra of the two alternant systems [4]-radialene and I.

As a first crude approximation we consider the [n]-radialenes as consisting of n double bonds $j = 1, 2, \ldots, n$ which do not interact in the electronic ground state of the system (Simpson's "Independent Systems Approach" [5]):

$$\Gamma = \| \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \cdots \psi_n \bar{\psi}_n \| = \| 1 \bar{1} 2 \bar{2} \ldots n \bar{n} \|$$

(ψ_j stands for the doubly occupied MO $\psi_j = (\varphi_{j1} + \varphi_{j2})/\sqrt{2}$ of the j^{th} double bond).

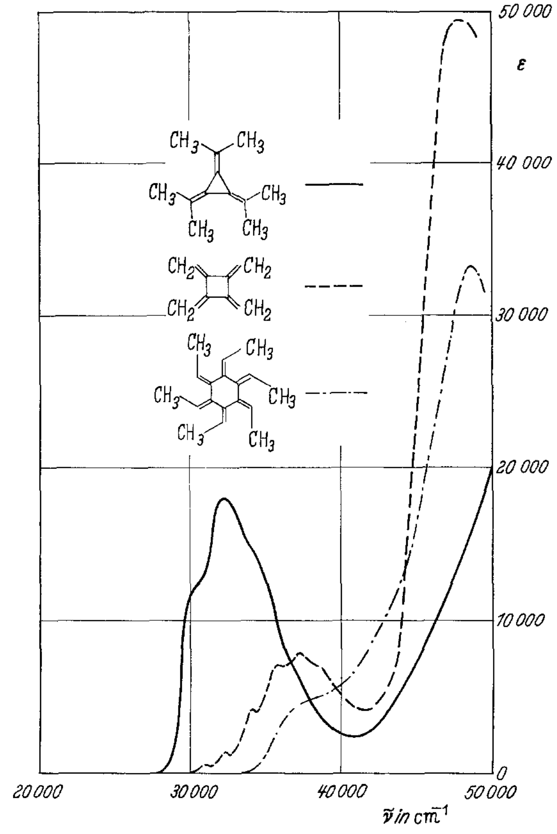


Fig. 1. Electronic Spectra of Hexamethyl-[3]-radialene (II), [4]-Radialene and of the Hexamethyl-[6]-radialene (I). The spectra (in apolar hydrocarbon solvents) are redrawn from the figures given in the following references: a) Hexamethyl-[3]-radialene II: The region $\tilde{\nu} < 40000$ cm^{-1} is taken from ref. [3]. The part $\tilde{\nu} > 40000$ cm^{-1} has been recorded using a sample of II, which was put at our disposal by Dr. KÖBRICH. b) [4]-Radialene: The spectrum for $\tilde{\nu} < 42000$ cm^{-1} has been given in ref. [1] together with the position and extinction of the high intensity band at 48000 cm^{-1}. The part of the spectrum from 42000 to 50000 cm^{-1} has been extrapolated, making use of this information. c) Hexamethyl-[6]-radialene: Spectrum taken from ref. [6]

Furthermore we assume that the gross structure of the electronic spectrum can be deduced by taking into account only the energy delocalisation in the excited states, that is the interactions between the transition moments $\vec{\mu}_j$ of the individual double bonds.

If $\psi_{-j} = (\varphi_{j1} - \varphi_{j2})/\sqrt{2}$ is the antibonding MO of the j^{th} double bond, then the transition from $\boldsymbol{\Gamma}$ to the locally excited state

$$\lambda_j = \frac{1}{\sqrt{2}}\{\|1\,\bar{1}\,\ldots\,j\,\overline{-j}\,\ldots\,n\,\bar{n}\,\| + \|1\,\bar{1}\,\ldots\,-j\,\bar{j}\,\ldots\,n\,\bar{n}\,\|\}$$

is accompanied by a transition moment $\vec{\mu}_j = \langle\,\boldsymbol{\Gamma}\,|\,\vec{\mathscr{M}}\,|\,\lambda_j\,\rangle$ which for symmetry reasons has the same absolute value μ for all j. The interaction between λ_j and λ_i $(j \neq i)$ can be approximated roughly as follows

$$\langle\,\lambda_j\,|\mathscr{H}\,|\,\lambda_i\,\rangle = \gamma_{ji} = \frac{\mu^2}{R^3}\,[\cos\,(\theta_j - \theta_i) - 3\cos\theta_j\cos\theta_i]$$

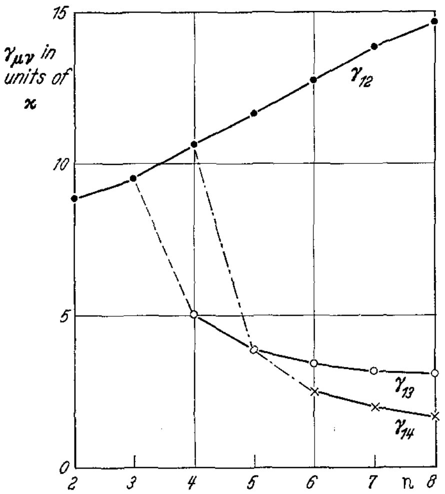


Fig. 2. Dependence of $\gamma_{\mu\nu}$ on n, According to a Dipole Dipole Interaction Approximation. Assumed symmetry in the $[n]$-radialene: D_{hn}. Bond lengths: C—C bonds: 1.43 Å, C = C bonds: 1.35 Å. Parameter $\varkappa = 50\,\mu^2$ in units of cm^{1-}, if μ in Debye-units

where R is the distance between the centers of the bonds j and i and θ_j, θ_i are the direction angles which the moments $\vec{\mu}_j$ and $\vec{\mu}_i$ make with the line joining the two corresponding bond centers. Fig. 2 shows how these interaction terms vary as a function of n, assuming the length of the single bonds to be 1.43 Å and that of the double bonds 1.35 Å.

The correct linear combinations of the locally excited states λ_j are fully determined by symmetry. For each irreducible representation $\Gamma^{(J)}$ of the group D_{nh} we have $\left(\omega = \exp\frac{2\pi i}{n}\right)$

$$\Psi_J = \frac{1}{\sqrt{n}}\sum_j \omega^{Jj}\lambda_j\,.$$

The corresponding energy

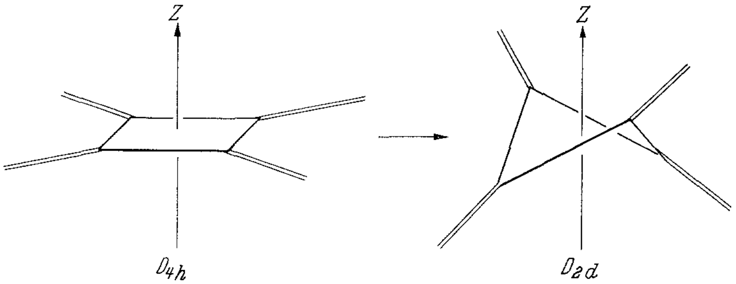
$$\mathscr{E}\,(\Gamma^{(J)}) = \langle\Psi_J\,|\mathscr{H}\,|\,\Psi_J\,\rangle$$

can be written directly in terms of the γ_{ji}, as shown in Tab. B. (If the absolute value μ of the transition moment is given in Debye units, then $\varkappa = 50\,\mu^2$ in cm^{-1}. For a double bond one finds that $\mu^2 \approx 12$ (Debye units)^2, so that $\varkappa \simeq 50 \cdot 12 \simeq 600\ \text{cm}^{-1}$).

The resulting level scheme is shown in Fig. 3. The only transitions which are electronically allowed are:

$$A_{1g} \rightarrow E_{1u} \quad \text{for } n \text{ even,}$$
$$A_1' \rightarrow E_1' \quad \text{for } n \text{ odd.}$$

These transitions are indicated by heavy arrows in Fig. 3. All other transitions are forbidden in the D_{nh} conformation. However bending modes or permanent deformations [6] of the appropriate symmetry will make these transitions allowed, so that they can be observed as weak bands in the electronic spectrum (dotted arrows in Fig. 3). In particular, a reduction from D_{nh} to $D_{\frac{n}{2}d}$ in the even radialenes, *e. g.*



for [4]-radialene activates the $A_{1g} \rightarrow B_{1g}$ transition if $n/2$ is even, or the $A_{1g} \rightarrow B_{1u}$ transition if $n/2$ is odd. The transition moment becomes parallel to the z-axis.

The predictions deduced from the independent systems model (Tab. B and Fig. 3) are seen to be in good qualitative agreement with observation (Tab. A and Fig. 1).

1. All [n]-radialenes, with the notable exception of [3]-radialene, should yield spectra in which weak bands preceed the intense band assigned to the $A_{1g} \rightarrow E_{1u}$ or the $A_2' \rightarrow E_1'$ transition. On the basis of this model there should be one such weak band in the spectrum of [4]-radialene and two in that of [6]-radialene. This seems to be indeed the case [*1*, *6*].

2. In (3)-radialene, the first absorption band of the electronic spectrum is assigned to the strongly allowed transition $A_1' \rightarrow E_1'$ and should therefore be of high intensity.

3. With increasing values of n the strongly allowed transitions $A_{1g} \rightarrow E_{1u}$ or $A_1' \rightarrow E_1'$ should shift to higher energies relative to U_λ, so that the corresponding bands are found at shorter wavelengths.

Both predictions 2. and 3. are nicely borne out by observation.

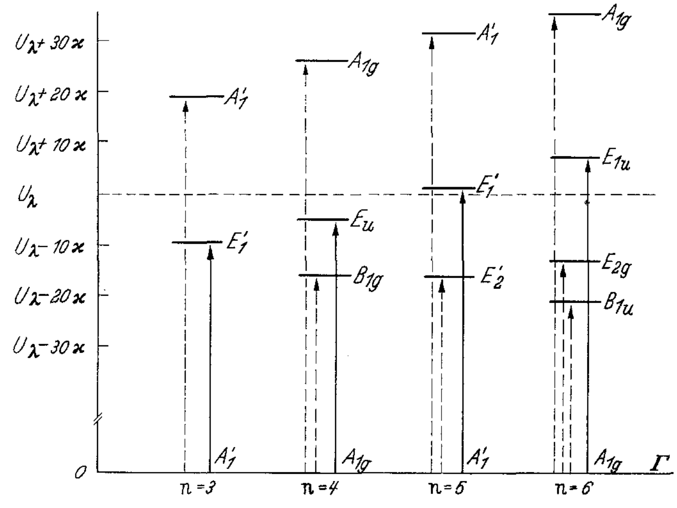


Fig. 3. Level Scheme for [n]-Radialenes, According to SIMPSON's Independent Systems Approach. Energies (in units of $\varkappa$) are given relative to U_λ (energy of a locally excited state λ_j). Note that the absolute value of U_λ is not necessarily the same for all [n]-radialenes. Full arrows: electronically allowed transitions, (for D_{nh} conformation), dotted arrows: symmetry forbidden transitions.

The following points must be taken into account, if a more quantitative correlation is desired:

a) The value U_λ for an exocyclic double bond depends on n, that is on the internal angle between two consecutive carbon-carbon bonds of the central ring. U_λ should be smallest for $n = 3$. This will shift the $A_1' \rightarrow E_1'$ transition of [3]-radialene (and therefore also of II) to longer wavelength, relative to the bands of the spectra of the higher [n]-radialenes.

b) Substitution by alkyl groups will produce a bathochromic shift of the absorption bands (WOODWARD rule). The size of the shift will be roughly proportional to the number of alkyl groups per double bond, which again contributes to the relatively longwave position of the first band in the spectrum of II.

c) It is known that the "Independent Systems Approach" as used in this note yields only part of the interaction between double bonds [*4*], accounting for about one half of the observed shift relative to U_λ. Inclusion of charge resonance states [*4*] will give rise to larger splittings and to more states. This will lower the transition energies, especially in [*3*]-radialene, which has no non-bonded pairs of exocyclic double bonds.

Table B[a]

$n = 3$	[3]-Radialene	(D_{3h})
$\mathscr{E}(A_1')$	$= U_\lambda + 2\gamma_{12}$	$= U_\lambda + 19.0\,\varkappa$
$\mathscr{E}(E_1')$	$= U_\lambda - \gamma_{12}$	$= U_\lambda - 9.5\,\varkappa$
$\mathscr{E}(A_1')$	$= 0$	$= 0$
$n = 4$	[4] – Radialene	(D_{4h})
$\mathscr{E}(A_{1g})$	$= U_\lambda + 2\gamma_{12} + \gamma_{13}$	$= U_\lambda + 26.0\,\varkappa$
$\mathscr{E}(E_u)$	$= U_\lambda - \gamma_{13}$	$= U_\lambda - 5.0\,\varkappa$
$\mathscr{E}(B_{1g})$	$= U_\lambda - 2\gamma_{12} + \gamma_{13}$	$= U_\lambda - 16.1\,\varkappa$
$\mathscr{E}(A_{1g})$	$= 0$	$= 0$
$n = 5$	[5]-Radialene	(D_{5h})
$\mathscr{E}(A_1')$	$= U_\lambda + 2\gamma_{12} - 2\gamma_{13}$	$= U_\lambda + 31.0\,\varkappa$
$\mathscr{E}(E_1')$	$= U_\lambda + \sqrt{5-1}\,\gamma_{12} - \sqrt{5+1}\,\gamma_{13}$	$= U_\lambda + 0.9\,\varkappa$
$\mathscr{E}(E_2')$	$= U_\lambda - \sqrt{5+1}\,\gamma_{12} + \sqrt{5-1}\,\gamma_{13}$	$= U_\lambda - 16.4\,\varkappa$
$\mathscr{E}(A_1')$	$= 0$	$= 0$
$n = 6$	[6]-Radialene	(D_{6h})
$\mathscr{E}(A_{1g})$	$= U_\lambda + 2\gamma_{12} + 2\gamma_{13} + \gamma_{14}$	$= U_\lambda + 34.7\,\varkappa$
$\mathscr{E}(E_{1u})$	$= U_\lambda + \gamma_{12} - \gamma_{13} - \gamma_{14}$	$= U_\lambda + 6.7\,\varkappa$
$\mathscr{E}(E_{2g})$	$= U_\lambda - \gamma_{12} - \gamma_{13} + \gamma_{14}$	$= U_\lambda - 13.6\,\varkappa$
$\mathscr{E}(B_{1u})$	$= U_\lambda - 2\gamma_{12} + 2\gamma_{13} - \gamma_{14}$	$= U_\lambda - 21.1\,\varkappa$
$\mathscr{E}(A_{1g})$	$= 0$	$= 0$

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[a] $U_\lambda = \langle \lambda_j | \mathscr{H} | \lambda_j \rangle$ is the energy of a locally excited state relative to the ground state energy ($\langle \Gamma | \mathscr{H} | \Gamma \rangle = 0$).

A more detailed treatment of the electronic spectra of [n]-radialenes will be published at a later date.

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References

[*1*] GRIFFIN, G. W., and L. I. PETERSON: J. Amer. chem. Soc. **84**, 3398 (1962).

[*2*] HOPFF, H., u. A. K. WICK: Helv. Chim. Acta **44**, 19 (1961); **43**, 1473 (1960).

[*3*] KÖBRICH, G., u. H. HEINEMANN: Angew. Chem. **77**, 590 (1965).

[*4*] MURRELL, J. N.: The Theory of Electronic Spectra of Organic Molecules. New York: John Wiley and Sons 1963.

[*5*] SIMPSON, W. T.: J. Amer. chem. Soc. **73**, 5363 (1951). – Theories of Electrons in Molecules, Prentice-Hall, Englewood Cliffs, 1962.

[*6*] WELTIN, E., F. GERSON, J. N. MURRELL, and E. HEILBRONNER: Helv. Chim. Acta **44**, 1400 (1961).

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