

A THEORETICAL APPROACH TO
THE RULE OF HOMOLOGOUS LINEARITY

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Abstract: The rule of homologous linearity is an empirical^{1a} or semi-empirical^{1b} rule. We derive it here from a theoretical point of view. Starting from a particular homologous series—polyene series with arbitrary terminals we get following homologous equation

$$F(n) = a + b \sin \frac{\pi}{2(n+1)}$$

This equation is extended to other homologous series. Calculation shows that this equation is a very good representation of the rule of homologous linearity. About 600 homologous lines of the linear fitting of the above equation are carried out, some of which are given here.

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I. Introduction

For a homologous series AP_nB most of its physicochemical quantities can vary with n regularly,

$$F(n) = a + bf(n) \quad (1)$$

where $F(n)$ stands for a physicochemical quantity of the system AP_nB , $f(n)$ is a universal function of n , and a and b are constants depending on what AP_nB and $F(n)$ we deal with. Take $F(n)$ and $f(n)$ as variables eq (1) is a linear equation. This is called empirically the rule of homologous linearity¹.

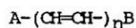
The rule of homologous linearity can be very helpful, for example in identifying the peaks of electronic spectra of homologous series². As a matter of fact for those HOMO & LUMO related properties, such as the first peaks of the electronic spectroscopy, the first ionization potential, and the half-wave potential of the redox polarography, we have

$$F(n) = a' + b'\epsilon_f \quad (2)$$

where ϵ_f is HOMO energy, LUMO energy, or their difference, and a' and b' are constants. In what follows, we want to derive eq (1) based on eq (2) in the Hückel molecular orbital (HMO) scheme.

II Theory

Consider a polyene with arbitrary terminals



where A and B are arbitrary terminals. By means of graphical method³ we

can get the characteristic polynomial in HMO scheme for this molecule,

$$P_n(x) = Y_1(x)g_n\left(\frac{Z}{\eta}\right) + Y_2(x)g_{n-1}\left(\frac{Z}{\eta}\right) \quad (3)$$

where

$$Z = x^2 - 1 - \eta^2$$

$$x = \frac{\epsilon - \alpha}{\beta}$$

$$Y_1(x) = (AB - \frac{\eta_a^2 \eta_b^2}{\eta^2} A' B^O) \eta^n \quad (4),$$

$$Y_2(x) = [\eta^2 AB - \eta_a^2 x A' B - \eta_b^2 x A B^O + \frac{\eta_a^2 \eta_b^2}{\eta^2} A' B^O (x^2 - 1)] \eta^{n-1}$$

$g_n(x)$ is the Gegenbauer polynomial with superscript 1, η is the interaction parameter between two adjacent repeated units (the parameter is 1 inside the repeated unit), η_a and η_b are interaction parameters between repeated units and terminals A and B respectively, A and B stand for the characteristic polynomials of corresponding molecular fragments, and A' and B^O have the same meaning whereas molecular fragments A' and B^O are from A and B respectively by deleting the atoms connected with the repeated units.

Letting $Z = 2\eta \cos \theta$ we get the secular equation,

$$Y_1(x) \sin(n+1)\theta + Y_2(x) \sin n\theta = 0 \quad (5)$$

or

$$\operatorname{tg}\left(n + \frac{1}{2}\right)\theta = q(x) \operatorname{tg} \frac{\theta}{2} \quad (6)$$

with

$$q(x) = \frac{Y_2(x) - Y_1(x)}{Y_2(x) + Y_1(x)} \quad (7)$$

Approaching the solution of eq (6) step by step yields

$$\theta_j = \frac{2j\pi}{2n+1+t}, \quad j = 1, \dots, n \quad (8)$$

where t satisfies

$$\operatorname{tg} \frac{tj\pi}{2n+1+t} = q(x_j) \operatorname{tg} \frac{j\pi}{2n+1+t} \quad (9)$$

with

$$x_j = \pm \sqrt{1 + \eta^2 + 2\eta \cos \theta_j} \quad (10).$$

This is an exact solution. Note that $\eta = 1 + \delta$ with $|\delta| \ll 1$. After neglecting δ^2 term we have

$$\begin{aligned} \epsilon_{\pm j} &= \alpha \pm \beta \sqrt{1 + \eta^2 + 2\eta \cos \theta_j} \\ &= \alpha \pm 2\sqrt{\eta\beta \cos} \frac{j\pi}{2n+1+t}. \end{aligned}$$

$j = n$ corresponds to the HOMO & LUMO energy,

$$\epsilon_f = \alpha \pm 2\sqrt{\eta\beta \cos} \frac{n\pi}{2n+1+t} \quad (11).$$

t is a terminal-dependent parameter, determined by eqs (4) and (7)-(10).

To get a universal function of n we approximate t by 1, so

$$\begin{aligned} \epsilon_f &= \alpha \pm 2\sqrt{\eta\beta \cos} \frac{n\pi}{2(n+1)} \\ &= \alpha \pm 2\sqrt{\eta\beta \sin} \frac{\pi}{2(n+1)} \end{aligned} \quad (12).$$

Calculation shows that this is a very good approximation. As a matter of fact eq (12) is the zeroth order approximation to eq (11). (see Appendix.)

Combination of eq (2) with eq (12) gives

$$f(n) = \sin \frac{\pi}{2(n+1)} \quad (13).$$

Hence

$$F(n) = a + b \sin \frac{\pi}{2(n+1)} \quad (14).$$

This equation is referred as the homologous equation or homologous line.

III Fitting results and discussion

Experimental data can be used to get values of a and b in eq (14) by linear fitting. The correlation coefficients (r) will be used to evaluate the validity of the homologous equation. The fitting results show that eq (14) holds very well (see TABLES 1-7). Also it can be predicted from eqs (12) and (14) that for different systems the value of a should remain more or less constant for the same property while the value of b may change. This prediction is verified in the given tables.

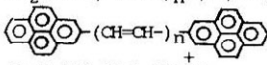




3.1 Electronic absorption spectra

The electronic absorption spectrum is a property related to the energy difference. Eq (14) holds true for the first peaks of the electronic spectroscopy. It can also be extended to other peaks. The fitting results are given in TABLES 1-6.

Terminal effect. The interactions between terminals and conjugated system are very complicated. The major interactions include inductive effect, spatial effect, conjugation, and hyperconjugation. All these interactions will affect the energy level distributions of the homologs. This can easily be seen from eqs (9) and (10). In eq (14) this will be reflected as the changes in the values of a and b.

The homologous lines of the first peaks of the electronic absorption spectra of polyene homologous series against $\sin \frac{\pi}{2(n+1)}$ are given in TABLE 1. Taking the homologous series with terminal -H as a standard compare the effects of terminals on the homologous lines. We see that the alkyl terminals have very small effect on the homologous lines, while the conjugated terminals make a larger and b smaller. The changes in the values of b can be understood as follows: the introduction of the conjugated terminals enlarges the delocalization domain of the π -electron, so the changing rate of E or ΔE with n becomes slower. This makes b smaller. The effect of alkyl terminals comes from the hyperconjugation. Although the introduction of charges make values of a and b decrease a lot, the effects of terminals on homologous lines remain the same. The same relationship between terminals and values of a and b holds true for polyacetylene homologous series, which consist of two perpendicular conjugated π -system (see TABLE 2). The terminals have the same effects even in the extended cases (see TABLE 3).

TABLE 1. Homologous lines of the first peaks in the electronic absorption spectra for polyene homologous series[†]

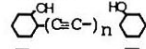
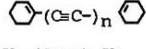
Homologs	Solvent	10 ⁻⁴ ×a	10 ⁻⁴ ×b	r	N*	ref
H-(CH=CH-) _n H	i-Oct [‡]	1.2912	6.5378	0.9992	6 (3-10)	4
Me-(CH=CH-) _n Me	Alkane	1.2624	6.3186	0.9991	3 (3-5)	5
Carotenoids		1.4338	5.5349	0.9896	4 (10-19)	6
Ph-(CH=CH-) _n H	EtOH	2.1217	2.8119	0.9991	4 (1-4)	7
Ph-(CH=CH-) _n Ph	EtOH	2.0603	1.6172	0.9936	4 (1-4)	8
Me ₂ C=CH-(CH=CH-) _n C(Me)=CH ₂	i-Oct [‡]	1.7802	2.7999	0.9984	4 (2-5)	9
 (CH=CH-) _n	THF	2.2173	0.2744	0.9976	6 (1-6)	10
Me ₂ N-(CH=CH-) _n CH=NMe ₂	CH ₂ Cl ₂	0.3000	4.1477	0.9989	6 (1-6)	11
Ph-N(Me)-(CH=CH-) _n CH=N ⁺ (Me)-Ph		0.3425	3.7279	0.9998	3 (2-4)	11
MeO-  -(CH=CH-) _n CH=  -OMe		0.9356	1.1311	0.9937	4 (1-4)	12
Me ₂ N-  -(CH=CH-) _n CH=  -NMe ₂		0.7804	0.9440	0.9971	3 (1-3)	12
[Ph-CH(CH=CH-) _n Ph] ⁺	CH ₂ Cl ₂	1.0194	1.5007	0.9938	6 (1-6)	12
[Ph-CH(CH=CH-) _n Ph] ⁻ Na ⁺	Et ₂ O	1.3796	0.7129	0.9823	4 (1-4)	13
[Me ₂ C=CH(CH=CH-) _n CMe ₂] ⁺	80% H ₂ SO ₄	0.8506	2.4231	0.9943	4 (2-5)	9

[†] in all TABLES: a and b are in cm⁻¹; references are the sources of the experimental data.

* N is the sample size (# of experimental points used). In the parentheses are given the minimum n and the maximum n pairs.

[‡] abbreviation for isooctane.

TABLE 2. Homologous lines of the first peaks in the electronic absorption spectra for polyacetylene homologous series⁺

Homologs	Solvent	10 ⁻⁴ ×a	10 ⁻⁴ ×b	r	N*	ref.
Me-(C≡C-) _n Me	EtOH	0.9539	6.0773	0.9999	4 (2-5)	14, 15
Me ₃ C-(C≡C-) _n CMe ₃	EtOH	1.1333	5.5493	0.9986	6 (2-7)	16
Et ₃ Si-(C≡C-) _n H	MeOH	1.7986	7.5117	0.9993	4 (3-8)	17
Et ₃ Si-(C≡C-) _n SiEt ₃	MeOH	1.1889	4.7751	1.0000	3 (2-4)	17
	MeOH	1.0792	5.5641	0.9998	3 (2-4)	18
	MeOH	1.7447	2.7528	0.9853	4 (1-4)	18
Ph-(C≡C-) _n Ph	MeOH	1.8190	2.3091	0.9774	5 (1-5)	19

⁺ see notes in TABLE 1.

* see notes in TABLE 1.










TABLE 3. Homologous lines for different peaks in electronic absorption spectra⁺

Homologs	Peak	10 ⁻⁴ ×a	10 ⁻⁴ ×b	r	N*
H-(CH=CH-) _n H (Solvent: i-Oct; ref.: 4, 5)	λ ₁	1.2912	6.5378	0.9992	6 (3-10)
	λ ₂	1.4918	6.2973	0.9996	6 (3-10)
	λ ₃	1.6310	6.3311	0.9994	6 (3-10)
	λ ₄	1.7809	6.3049	0.9992	6 (3-10)
Ph-(CH=CH-) _n Ph (Solvent: CHCl ₃ ; ref.: 20.)	λ ₁	1.7470	2.2990	0.9917	6 (2-7)
	λ ₂	2.0259	1.8199	0.9735	7 (1-7)
	λ ₃	2.1509	1.8458	0.9789	7 (1-7)

⁺ see notes in TABLE 1.

* see notes in TABLE 1.

TABLE 4. Effects of terminals on homologous lines: first peaks in electronic absorption spectra[†] (Solvent: EtOH)

Homologs	$10^{-4}\epsilon_a$	$10^{-4}\epsilon_b$	r	N^*	ref.
Me-(CH=CH-) _n CHO	1.5501	4.2462	0.9999	4 (2-5)	21
Ph-(CH=CH-) _n CHO	1.9004	2.3021	0.9961	5 (1-5)	2
 (CH=CH-) _n CHO	1.9708	1.6724	0.9932	4 (1-5)	2
 (CH=CH-) _n CHO	2,0826	1.5570	0.9999	3 (1-3)	2
 (CH=CH-) _n CHO	1.7486	1.5789	1.0000	2 (1-2)	2
 (CH=CH-) _n C(=O)Ph	1.9370	1.4241	0.9928	4 (1-6)	2
 (CH=CH-) _n C(=O)Ph	2.0872	1.2124	0.9991	3 (1-3)	2
 (CH=CH-) _n C(=O)Ph	1.8672	0.9973	0.9977	3 (1-3)	2
Ph-(CH=CH-) _n C(=O) 	1.9061	1.7798	0.9929	5 (1-6)	2
Ph-(CH=CH-) _n C(=O) 	2.0665	1.4828	0.9960	3 (1-3)	2
Ph-(CH=CH-) _n C(=O) 	2.1385	1.2613	0.9924	4 (1-4)	2

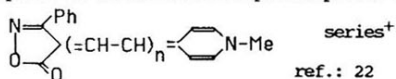
[†] see notes in TABLE 1.

* see notes in TABLE 1.

The small differences in effects of different terminals of the same kind on the homologous lines can be distinguished if the solvent effects

charges in the homologs since the dipole moment of water is larger than that of pyridine, and the polar solvent helps in the charge separation in a solute molecule²². More example of this kind of effects of solvents can be seen in TABLE 6. Since charge separation is difficult in homologs $\text{Ph-CH=CH-})_n\text{CHO}$, the effects of solvent on this series is different.

TABLE 5. Effects of solvent on homologous lines: first peaks in electronic absorption spectra for



Solvent	$10^{-4}x_a$	$10^{-4}x_b$	r	N*
90% $\text{C}_5\text{H}_5\text{N-H}_2\text{O}$	1.0407	1.3700	1.0000	3 (1-3)
50% $\text{C}_5\text{H}_5\text{N-H}_2\text{O}$	1.4111	1.0013	0.9914	3 (1-3)
H_2O	1.7505	0.7715	0.9984	3 (1-3)







⁺ see notes in Table 1.

* see notes in Table 1.

3.2 Photoelectron emission spectra and other properties

Photoelectron spectroscopy is a technique to measure the ionization energy which is a property related to the energy level. Eq (14) is applicable to the first peaks of the photoelectron spectra. The fitting results are given in TABLE 7. It can be seen that the same terminal effects as discussed previously showed up here. It is interesting to point

Table 6. Effects of solvents on homologous lines: first peaks in electronic absorption spectra[†] ref: 2

Homologs	10 ⁻⁴ ×a		10 ⁻⁴ ×b		r		N*
	EtOH	Cy [§]	EtOH	Cy [§]	EtOH	Cy [§]	
Ph-(CH=CH) _n CHO	1.9004	2.0004	2.3021	2.2734	0.9961	0.9903	5 (1-5)
 (CH=CH) _n CHO	1.9708	2.0690	1.6724	1.6596	0.9932	0.9704	4 (1-5)
 (CH=CH) _n C(=O)Ph	1.9370	1.9861	1.4241	1.6003	0.9927	0.9857	4 (1-6)
Ph-(CH=CH) _n C(=O) 	1.9061	1.9861	1.7798	1.8287	0.9920	0.9806	5 (1-6)
Ph-(CH=CH) _n C(=O) 	2.1385	2.2189	1.2613	1.3327	0.9924	0.9796	4 (1-4)
Solvent:	EtOH	Hx ^{&}	EtOH	Hx ^{&}	EtOH	Hx ^{&}	
 (CH=CH) _n C(=O)Ph	2.0872	2.0784	1.2124	1.4271	0.9991	0.9716	3 (1-3)
Ph-(CH=CH) _n C(=O) 	2.0665	2.1080	1.4828	1.6336	0.9960	0.9768	4 (1-4)

[†] see notes in Table 1.

* see notes in Table 1. N's for homologous lines in solvent EtOH are the same

as in Table 4.

[§] abbreviation for cyclohexane.

[&] abbreviation for hexane.

out that the values of a in TABLE 7 are much larger than those in previous Tables. This can be understood from our theory. (see eqs (12) and (14) and note that in the energy difference of HOMO and LUMO the constant parameter α disappears.)

Table 7. Homologous lines of the first peaks in the photoelectron spectra[†]

Homologs	$10^{-4} \times a$	$10^{-4} \times b$	r	N*	ref.
H-(CH=CH-) _n H	4.5722	5.4993	0.9996	4 (1-4)	23, 24
Me-(CH=CH-) _n CHO	5.5628	3.4553	0.9753	3 (1-3)	25, 26, 27
Ph-(CH=CH-) _n Ph	5.3314	1.5187	0.9966	6 (1-6)	25, 26
H-(C≡C-) _n H	5.8727	4.6884	0.9999	4 (1-4)	28, 29
Me ₃ C-(C≡C-) _n CMe ₃	6.0106	1.8323	0.9984	5 (1-5)	30

[†] see notes in Table 1.

* see notes in Table 1.

Eq (14) is also applicable to other properties, such as the half-wave potential of redox polarography, and the affinity potential.

3.3 Validity of eq (14) as the rule of homologous linearity

As shown in TABLES 1-7 all the correlation coefficients (r) are larger than 0.97. Extension of eq (14) to other homologs such as polyphenylene series, linear polyacene series, and straight chain alkane series or to other properties which are not closely related to the HOMO & LUMO energy also gives very good correlation coefficients. As a matter of fact about 600 homologous lines have been fitted, more than 94.5% of which have a correlation coefficient larger than 0.95. This means that eq (14) represents the rule of homologous linearity very well.

IV Conclusion remarks

The rule of homologous linearity is a very general rule. As a

theoretical approach homologous equation (14) is derived starting from a particular homologous series-polyene series with arbitrary terminals for the HOMO & LUMO related properties. It is satisfactorily extended to the other series and to the other properties.

Acknowledgement. Z. Zhou thanks Professor Sun Chiachung for helpful discussion and Professor Robert G. Parr for constant encouragement.

Appendix

In this appendix we prove that eq (12) is the zeroth order approximation to eq (11). We rewrite eq (11) as

$$\begin{aligned} \epsilon_f = \alpha \pm 2\sqrt{\eta\beta} \left(\cos \frac{(t-1)\pi}{2(n+1)(2n+1+t)} \sin \frac{\pi}{2(n+1)} \right. \\ \left. + \sin \frac{(t-1)\pi}{2(n+1)(2n+1+t)} \cos \frac{\pi}{2(n+1)} \right) \end{aligned} \quad (A1).$$

Let

$$x = \frac{(t-1)\pi}{2(n+1)(2n+1+t)}.$$

We have

$$\begin{aligned} \epsilon_f = \alpha \pm 2\sqrt{\eta\beta} \left\{ \left[\sum_{k=0}^{\infty} \frac{(-1)^k x^{2k}}{(2k)!} \right] \sin \frac{\pi}{2(n+1)} \right. \\ \left. + \sum_{k=0}^{\infty} \frac{(-1)^k x^{2k}}{(2k+1)!} \cos \frac{\pi}{2(n+1)} \right\} \end{aligned} \quad (A2).$$

To the zeroth order we get

$$\epsilon_f = \alpha \pm 2\sqrt{\eta\beta} \sin \frac{\pi}{2(n+1)} \quad (12).$$

Hence the larger the n value the better our approximation here. As a matter of fact this zeroth order approximation is good enough for fitting the experimental data available to us (about 600 series). As we can see from the given tables that the contributions from the high order terms are very small. Our calculation also shows that the zeroth order approximation here is much better than another approximation (HMO with equal bond length) which has

$$f(n) = \sin \frac{\pi}{2(2n+1)} \quad (A3).$$

The reason is that the terminal effects are completely ignored if eq.(A3) is used. In eq.(12) α does really contain the second term in eq.(A1) and $2\sqrt{\eta\beta}$ does really contain a factor $\cos x$ (note x is a small number). Our results still show that x is indeed small enough to make a and b in eq (1) constant and large enough to reflect the terminal effects in the homologs.

References

- (1) See, for example, (a) Jiang, M. *Sci. Sin.* **1977**, 20, 539; (b) Xu, G. *Sci. Sin.* **1980**, 23, 136.
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