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The Effect of Alkyl Groups on the Electronic Spectra of Benzenoid Hydrocarbons

By

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Alkyl substitution of benzenoid hydrocarbons shifts their ^1L_a band to longer wavelengths. A statistical analysis of the available data for naphthalene, phenanthrene and 1,2-benzanthracene indicates that simple Hückel theory does not yield as good a prediction for these shifts as has previously been assumed. It is shown that a significant improvement results if many electron wavefunctions are used and if mixing between the configurations Ψ_1^{-1} and Ψ_2^{-2} is introduced.

Unter dem Einfluß von Alkylsubstituenten verschiebt sich die ^1L_a Bande aromatischer Kohlenwasserstoffe nach längeren Wellenlängen. Eine statistische Analyse der Daten für Naphthalin, Phenanthren und 1,2-Benzanthracen deutet darauf hin, daß das einfache Hückelsche Verfahren weniger gute Voraussagen dieser Verschiebungen liefert, als allgemein angenommen wird. Es kann gezeigt werden, daß die Verwendung von Mehrelektronen-Wellenfunktionen und die Einbeziehung der Wechselwirkung zwischen den Konfigurationen Ψ_1^{-1} und Ψ_2^{-2} zu einer signifikanten Verbesserung der Voraussagen führt.

L'introduction d'un groupe alkyle sur un hydrocarbure benzènoïde provoque un déplacement de la bande ^1L_a vers les grandes longueurs d'onde. Une analyse statistique des données existant pour le naphthalène, le phénanthrène et le 1,2-benzanthracène montre que la simple théorie de Hückel ne permet pas de prévoir ce déplacement aussi exactement qu'on l'admet en général. L'utilisation de fonctions d'onde polyélectroniques et l'introduction de l'interaction entre les configurations Ψ_1^{-1} et Ψ_2^{-2} conduit, au contraire, à une amélioration significative des résultats.

Alkyl groups produce a bathochromic shift of the electronic absorption bands of benzenoid hydrocarbons, except in a few cases (e.g. ortho-substituted diphenyls) where the geometry of the hydrocarbon is changed by a steric effect of the substituent. It is well known that such spectral changes are due predominantly to the weak mesomeric (hyperconjugative) effect of the methyl group, since the first-order inductive effect is zero for these compounds because their ground and excited states have the same uniform electron density: in non-alternants such as azulene this is not so [*7*] and the shifts are predominantly due to the first-order inductive effect.

It has been stated that Hückel molecular orbital theory can give a quantitative interpretation of the shifts of the ^1L_a band (Clar's *p*-band) on alkyl substitution [*17*]. This band is associated with the excitation of an electron from the highest bonding to the lowest antibonding molecular orbital. In this paper we shall show by a statistical analysis of the experimental results that this theory is not as good as has previously been supposed.

The highest bonding (ψ_1) and lowest antibonding (ψ_{-1}) Hückel orbitals of an alternant hydrocarbon will be written as follows:

$$\psi_1 = \sum_\mu c_{1\mu}\,\varphi_\mu \qquad E_1 = \alpha + m_1\beta$$

$$\psi_{-1} = \sum_\mu c_{-1\mu}\,\varphi_\mu \qquad E_{-1} = \alpha - m_1\beta$$

where the symbols have their usual meaning. It follows, by second-order perturbation theory, that a π-type orbital of an alkyl group (ψ_s, s = substituent) at the position ϱ, of energy $\alpha + m_s\beta$ will change the excitation energy of $\psi_1 \rightarrow \psi_{-1}$ by an amount

$$\Delta E_\varrho = \frac{H^2_{-1s}}{E_{-1} - E_s} - \frac{H^2_{1s}}{E_1 - E_s}$$

$$= \left(\frac{c^2_{-1\varrho}}{-m_1 - m_s} - \frac{c^2_{1\varrho}}{m_1 - m_s}\right)\frac{\beta_s^2}{\beta} \tag{1}$$

where $\beta_s = \int \varphi_\varrho \boldsymbol{H}\,\psi_s\,d\tau$ is the resonance integral across the substituent-hydrocarbon bond. Since for an alternant hydrocarbon $c^2_{-1\varrho} = c^2_{1\varrho}$, this reduces to

$$\Delta E_\varrho = c^2_{1\varrho}\left(\frac{2m_1}{m_s^2 - m_1^2}\right)\frac{\beta_s^2}{\beta} \tag{2}$$

a relationship first obtained by Longuet-Higgins and Sowden [*11*]. If there is more than one substituent, expression (2) must be summed over all positions of substitution.

Since β is a negative quantity, a bathochromic shift is predicted if $m_s > m_1$ (i.e. the substituent orbital ψ_s has a lower energy than ψ_1). This is the case for an alkyl group.

Expression (2) can be tested at three levels.

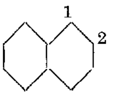
A. For polysubstitution in a given hydrocarbon the shifts should be additive for each substituent: this is the result which follows if the inductive effect of the methyl groups can be neglected, and if the second-order perturbation theory which is used to derive (2) is valid.

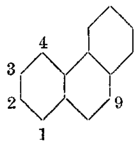
B. For polysubstitution in a given hydrocarbon $\Delta E \propto \sum_\varrho c^2_{1\varrho}$ where $c_{1\varrho}$ are the Hückel coefficients of the highest bonding orbital.

C. For different hydrocarbons it is predicted that as the frequency of the ^1L_a band ($-2m_1\beta$) decreases, then at the same time $m_s^2 - m_1^2$ will increase, and the effect of an alkyl group should decrease.

Finally, one may ask whether constants β_s and m_s can be found which give a quantitative fit to the known experimental facts.

There are only two hydrocarbons for which sufficient data to test the first prediction are available; these are naphthalene and phenanthrene. The relevant experimental data are given in the appendix.





For each position of substitution the values for the frequency shifts which give the best additivity relationship have been calculated by standard statistical methods. For example, the expression

$$\tilde{\nu}_{\text{pred}}\,(\text{cm}^{-1}) = 36255 - 702\,x_1 - 132\,x_2 \quad (3)$$

where x_1 is the number of methyl groups in the 1, 4, 5 and 8 positions, and x_2 the number in the 2, 3, 6 and 7 positions, gives the best linear correlation between observed and calculated frequencies. The best linear correlation for phenanthrene (for *any* alkyl group, but neglecting the sterically hindered 4,5 dialkylphenanthrenes) is

$$\tilde{\nu}_{\text{pred}}\,(\text{cm}^{-1}) = 34108 - 697\,x_1 - 140\,x_2 - 255\,x_3 - 492\,x_4 - 342\,x_9. \quad (4)$$

Graphs of $\tilde{\nu}_{\text{obs}}$ against $\tilde{\nu}_{\text{pred}}$ for these two series are shown in Fig. 1 and 2.

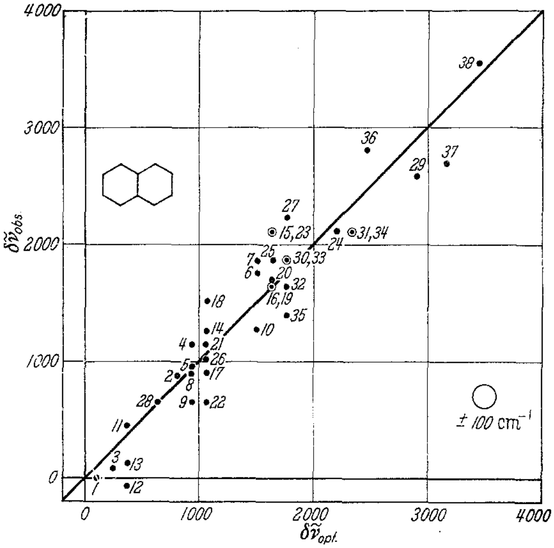


Fig. 1. Optimal regression for naphthalenes (Formula (3)). $\delta\,\tilde{\nu}_{\text{obs}} = \tilde{\nu}_{\text{obs}}$ (naphthalene) — $\tilde{\nu}_{\text{obs}}$. $\delta\,\tilde{\nu}_{\text{opt}} = \tilde{\nu}_{\text{obs}}$ (naphthalene) — $\tilde{\nu}_{\text{pred}}$ (from (3)). The circle ± 100 cm^{-1} indicates the size of the experimental error

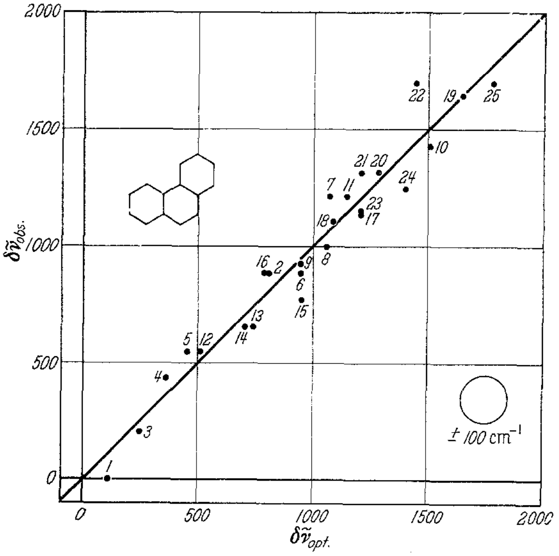


Fig. 2. Optimal regression for phenanthrenes. (Formula (4)). $\delta\,\tilde{\nu}_{\text{obs}} = \tilde{\nu}_{\text{obs}}$ (phenanthrene) — $\tilde{\nu}_{\text{obs}}$. $\delta\,\tilde{\nu}_{\text{opt}} = \tilde{\nu}_{\text{obs}}$ (phenanthrene) — $\tilde{\nu}_{\text{pred}}$ (from (4)). The circle ± 100 cm^{-1} indicates the size of the experimental error

The standard deviations of $\tilde{\nu}_{\text{pred}}$ relative to $\tilde{\nu}_{\text{obs}}$, assuming additivity, is 273 cm^{-1} for naphthalene and 115 cm^{-1} for phenanthrene. The corresponding standard deviation from additivity for the alkyl azulenes is 90 cm^{-1} [7]. The additivity is as good for phenanthrene as for azulene but considerably worse for naphthalene. The position of the absorption maximum of naphthalene and phenanthrene can be read to about ± 100 cm^{-1} (azulene has a sharper spectrum and can be read more accurately), so that the deviation from additivity for naphthalene shows a limitation of the theory rather than of the experiment, and is probably due to the neglect of the second order inductive effect which is known to be important in benzene. This relative importance of the inductive and mesomeric shifts may decrease as the size of the hydrocarbon increases. The possibility of steric effects in 1,2-, 2,3- and 1,8-dialkyl naphthalenes has been examined, but the scatter about the regression line cannot be significantly reduced by ignoring these compounds or by including additional repulsion terms for 1,2-, 2,3- and 1,8-related groups.

The optimal line for naphthalene would be obtained if the ratio of the Hückel coefficients were $c_2^2/c_1^2 = 132/702 = 0.19$. In fact the ratio is 0.38. However, if one plots $\tilde{\nu}_{\text{obs}}$ against $\sum\limits_{\varrho} c_{1\varrho}^2$ using the Hückel coefficients, then the regression line is

$$\tilde{\nu}_{\text{pred}}\,(\text{cm}^{-1}) = 36383 - 373 \sum_{\varrho} c_{1\varrho}^2$$

and the standard deviation about this line is 299 cm^{-1}, hardly worse than for the optimal fit. This means that the deviation from additivity in the case of naphthalene is too great to permit a test of prediction B.

For phenanthrene, the optimal relationship between the coefficients would be as follows, (taking $c_1^2 = 1.00$)

$$c_1^2 = 1.00,\ c_2^2 = 0.20,\ c_3^2 = 0.37,\ c_4^2 = 0.71,\ c_9^2 = 0.49.$$

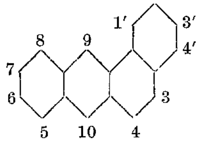
In this case there is considerable deviation from the Hückel values

$$c_1^2 = 1.00,\ c_2^2 = 0.02,\ c_3^2 = 0.85,\ c_4^2 = 0.47,\ c_9^2 = 1.50.$$

In fact for phenanthrene all one can say is that the Hückel model predicts a bathochromic shift with increasing number of alkyl groups. But this is certainly a statement of limited interest.

We have examined the possibility that for phenanthrene the Hückel coefficients are in poor agreement with the best regression coefficients because of bond localization. For example, the 9,10-bond may be shorter than average and the 4′-5′-bond may be longer. But variation of β for each bond of phenanthrene (within the limits 0.8—1.2) gives in no case a set of coefficients which are close to the best regression coefficients: c_9^2/c_1^2 is always greater than unity, and c_2^2/c_1^2 is always less than 0.05.

There is one other hydrocarbon, 1,2-benzanthracene, for which there are sufficient data to test prediction B. For the correlation between $\tilde{\nu}_{\text{obs}}$ and $\sum\limits_{\varrho} c_{1\varrho}^2$, the standard deviation is 191 cm^{-1}, or a little more than the best regression line for phenanthrene, and much better than either the best or the Hückel regression line for naphthalene.



We have shown that the simple one-electron theory developed by Longuet-Higgins and Sowden does not lead to good agreement particularly in the case of phenanthrene. We turn to an analysis of the problem using many electron wave functions.

The ${}^1L_a$ band can be represented to a first approximation by the transition $\Psi_0 \to \Psi_1^{-1}$, where Ψ_1^{-1} is a singlet state differing from the ground state Ψ_0 by the excitation of an electron from orbital ψ_1 to orbital ψ_{-1}. The effect of hyperconjugation is introduced into this scheme through states Ψ_s^{-1} in which an electron is donated from the substituent orbital ψ_s into one of the vacant hydrocarbon orbitals, for example ψ_{-1} [*14*]. Although this state interacts with both Ψ_0 and Ψ_1^{-1} it has been shown that interaction of Ψ_s^{-1} with Ψ_0 should be neglected when only singly-excited states are taken into account [*14*].

The matrix element of the Hamiltonian between Ψ_1^{-1} and Ψ_s^{-1} is

$$\langle \Psi_1^{-1} | \mathscr{H} | \Psi_s^{-1} \rangle = H_{1s} = c_{1\varrho}\beta_s. \tag{6}$$

The energy of Ψ_s^{-1} is equal to the ionization potential of the substituent ($\boldsymbol{I}_s$) less the electron affinity of the aromatic hydrocarbon ($\boldsymbol{A}_H$), and less the coulombic interaction of the donated electron with the hole it has left behind ($\boldsymbol{C}_\varrho$). This last term will not be the same for each position of substitution. If Ψ_s^{-1} has a greater energy than Ψ_1^{-1}, then second order perturbation theory predicts a bathochromic shift of the ${}^1L_a$ band:

$$-\Delta E_\varrho = \frac{c_{1\varrho}^2\,\beta_s^2}{\boldsymbol{I}_s - \boldsymbol{A}_H - \boldsymbol{C}_\varrho - E\,(\Psi_1^{-1})}. \tag{7}$$

For several substituents each of the different Ψ_s^{-1} states will contribute individually to the bathochromic shift according to expression (7). The total effect for more than one substituent is then

$$-\Delta E = \sum_\varrho \frac{c_{1\varrho}^2\,\beta_s^2}{\boldsymbol{I}_s - \boldsymbol{A}_H - \boldsymbol{C}_\varrho - E\,(\Psi_1^{-1})}. \tag{8}$$

We see that this expression has some similarity with (2); the shifts should be additive for each substituent as was found to be the case for phenanthrene and to a smaller extent for naphthalene. But one should observe a linear correlation between the observed shift and $\sum_\varrho c_1^2$ only if the coulomb term $\boldsymbol{C}_\varrho$ is almost independent of the position of substitution. On the basis of a point charge approximation, and assuming a bond length of 1.46 Å for the substituent-hydrocarbon bond, one finds that $\boldsymbol{C}_\varrho$ is 5.0 eV and 4.2 eV for 1- and 2-substituted naphthalenes respectively. Inserting the values $\boldsymbol{I}_s = 13.0$ eV (the ionization potential of methane), $\boldsymbol{A}_H = -0.4$ eV [*6*], $E\,(\Psi_1^{-1}) = 4.5$ eV (the ${}^1L_a$ band energy), the denominator in expression (7) reduces to 3.9 eV and 4.7 eV for the 1 and 2 positions respectively. The ratio of the shifts is then

$$\frac{E_2}{E_1} = \frac{0.069}{0.181} \cdot \frac{3.9}{4.7} = 0.31. \tag{9}$$

The improvement is not very significant and it is obvious that this method does not yield satisfactory ratios.

At this point one may well ask whether the wave function based on a single electron configuration is in fact a satisfactory representation of the ${}^1L_a$ excited state. It can be shown by a calculation which includes configuration interaction that a better wave function for the ${}^1L_a$ state of naphthalene is

$$\xi\,\Psi_1^{-1} + \lambda\,\Psi_2^{-2}. \tag{10}$$

With such a wave function the ${}^1L_a$ state interacts with the charge transfer states Ψ_s^{-1} and Ψ_s^{-2} and the depression of the ${}^1L_a$ band is

$$-\Delta E = \sum_{\varrho} \left[\frac{\xi^2 c_{1\varrho}^2}{I_s - A_{H1} - C_{\varrho 1} - E\,(\Psi_1^{-1})} + \frac{\lambda^2 c_{2\varrho}^2}{I_s - A_{H2} - C_{\varrho 2} - E\,(\Psi_2^{-2})} \right] \beta_s^2 \quad (11)$$

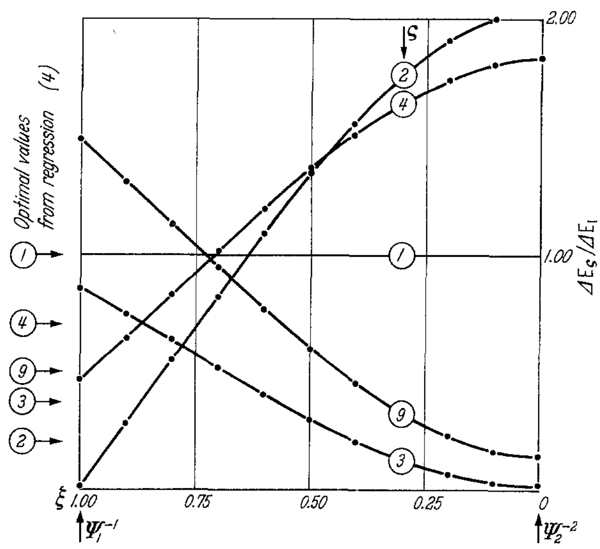


Fig. 3. Phenanthrene; Dependence of $\Delta E_\varrho/\Delta E_1$ (formula (12)) on the mixing parameter. ξ Values on the left of the diagram are those yielding the optimal regression (4)

A_{H1} is the first and A_{H2} the second electron affinity of the hydrocarbon. If we neglect the difference in the two denominators and any variation in the denominators with the position of substitution, then we predict

$$\Delta E_\varrho \propto (\xi^2 c_{1\varrho}^2 + \lambda^2 c_{2\varrho}^2). \quad (12)$$

Fig. 3 shows in the case of phenanthrene the ratios of $\Delta E_\varrho/\Delta E_1$ for various values of ξ; $(\lambda^2 + \xi^2 = 1)$. It is seen that a small amount of mixing between Ψ_1^{-1} and Ψ_2^{-2} makes a large difference in the predicted shifts. For each position the agreement with experiment is improved as ξ is decreased.

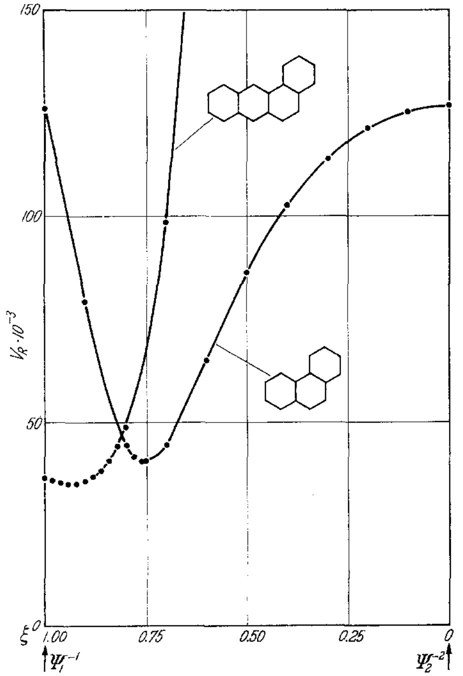


Fig. 4. Dependence of the remainder variance V_R for the regressions of $\tilde{\nu}_{\text{obs}}$ on $\tilde{\nu}_{\text{pred}}$ from $\sum_\varrho \frac{\Delta E_\varrho}{\Delta E_1}$ (formula (12)) on the mixing parameter ξ

The remainder variance V_R — a measure for the scatter about the regression — of $\tilde{\nu}_{\text{pred}}$ on $\tilde{\nu}_{\text{obs}}$ for phenanthrene as a function of ξ is shown in Fig. 4. The improvement is very striking and with $\xi = 0.76$ the standard error is as small as that for 1,2-benzanthracene and smaller than the value obtained for naphthalene. The regression is shown in Fig. 5.

We have examined the possibility that the mixing of Ψ_1^{-1} and Ψ_2^{-2} would improve the calculations for naphthalene and 1,2-benzanthracene. However the standard deviation for naphthalene due to non-additivity is so large, that we would be unable to detect any significant improvement or worsening of our results even for substantial amounts of Ψ_2^{-2} in the ^1L_a wave function. Also for 1,2-benzanthracene it can be seen from Fig. 4, that the remainder variance is insensitive to ξ in the region of $\xi = 1.0$ to 0.8. Only for phenanthrene is a mixture of Ψ_1^{-1} and Ψ_2^{-2} necessary to obtain reasonable agreement between theory and experiment.

We have calculated the wave functions of the ^1L_a states for the three molecules we have been discussing, using a simplified version of the PARISER-PARR-POPLE method [21]. The following ratios of the coefficients ξ and λ have been obtained: naphthalene $\lambda/\xi = 0.39$, phenanthrene $\lambda/\xi = 0.41$, 1,2-benzanthracene $\lambda/\xi = 0.14$. It is interesting that this supports the deductions from Fig. 4 that mixing is important for phenanthrene, but not for 1,2-benzanthracene.

The slopes b of the regression lines are as follows: Naphthalene $b = -3700$ cm^{-1} (on HÜCKEL coefficients); Phenanthrene $b = -5200$ cm^{-1} (Formula (12) with $\xi = 0.76$); 1,2-benzanthracene $b = -6400$ cm^{-1} (Formula (12) with $\xi = 0.94$). These differences are not large enough to test prediction C or its equivalent in the many electron treatment. As the value of the mean c_ϱ^2 is roughly proportional to the inverse of the number of carbon atoms (n) we obtain the following values for b/n: Naphthalene 370 cm^{-1}, Phenanthrene 370 cm^{-1}, 1,2-Benzanthracene 360 cm^{-1}.

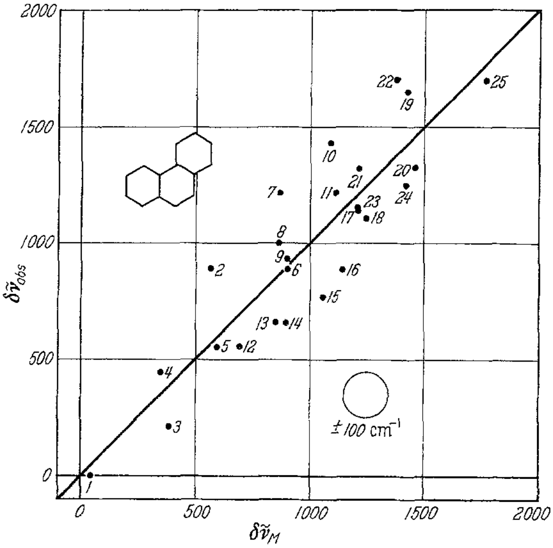


Fig. 5. Regression of $\tilde{\nu}_{\text{obs}}$ on $\tilde{\nu}_M$ $\left(\text{from} \sum_\varrho \frac{\Delta E}{\Delta E_1}\right)$ (formula (12)) for minimal remainder variance. $\delta\tilde{\nu}_{\text{obs}} = \tilde{\nu}_{\text{obs}}$ (phenanthrene) — $\tilde{\nu}_{\text{obs}}$. $\delta\tilde{\nu}_M = \tilde{\nu}_{\text{obs}}$ (phenanthrene) — $\tilde{\nu}_M$ (from regression on the $\sum_\varrho \frac{\Delta E_\varrho}{\Delta E_1}$ for $\xi = 0{,}76$)

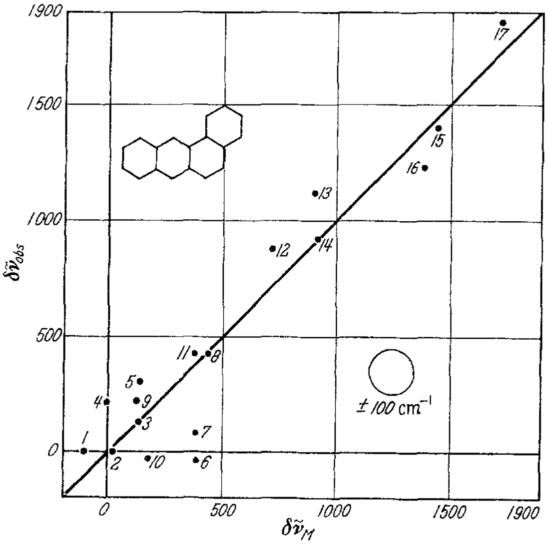


Fig. 6. Regression of $\tilde{\nu}_{\text{obs}}$ on $\tilde{\nu}_M$ from $\sum_\varrho \frac{\Delta E_\varrho}{\Delta E_1}$ (formula (12)) for minimal remainder variance. $\delta\tilde{\nu}_{\text{obs}} = \tilde{\nu}_{\text{obs}}$ (1,2-benzanthracene) — $\tilde{\nu}_{\text{obs}}$. $\delta\tilde{\nu}_M = \tilde{\nu}_{\text{obs}}$ (1,2-benzanthracene) — $\tilde{\nu}_M$ (from regression on the $\sum_\varrho \frac{\Delta E_\varrho}{\Delta E_1}$ for $\xi = 0.94$)

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Appendix 1

Table 1. *The mean frequency of the* ^1L_a *band of methylsubstituted naphthalenes*

Nr.	ϱ	Ref.	$\tilde{\nu}_{\text{obs}}$ a)	$\Delta\,\tilde{\nu}_{\text{opt}}$ b)	$\sum c_\varrho^2$ c)	$\Delta\,\tilde{\nu}_H$ d)
1	—	3	36360	105	0.0000	— 23
2	1	3, 19	35480	— 72	0.1809	—229
3	2	3	36280	157	0.0691	154
4	1, 2	3, 4, 19	35210	—210	0.2500	—241
5	1, 3	3, 4	35400	— 20	0.2500	— 51
6	1, 4	3, 4	34600	—250	0.3618	—435
7	1, 5	3, 4	34500	—350	0.3618	—535
8	1, 6	3, 4	35460	40	0.2500	9
9	1, 7	3, 4	35710	290	0.2500	259
10	1, 8	3, 4	35090	240	0.3618	55
11	2, 3	3, 4	35910	— 80	0.1382	42
12	2, 6	3, 4, 19	36430	439	0.1382	562
13	2, 7	3, 4	36230	240	0.1382	362
14	1, 2, 3	9	35090	—198	0.3191	—104
15	1, 2, 4	9	34250	—468	0.4309	—527
16	1, 2, 5	9	34720	2	0.4309	— 57
17	1, 2, 6	9, 19	35460	172	0.3191	266
18	1, 2, 7	9	34840	—448	0.3191	—354
19	1, 2, 8	9	34720	2	0.4309	— 57
20	1, 3, 5	9	34660	— 58	0.4309	—117
21	1, 3, 6	9, 18	35210	— 78	0.3191	16
22	1, 3, 7	9	35710	422	0.3191	516
23	1, 3, 8	9	34250	—468	0.4309	—527
24	1, 4, 5	9	34250	102	0.5427	—110
25	1, 4, 6	9, 18	34480	—238	0.4309	—297
26	1, 6, 7	4	35340	52	0.3191	146
27	1, 2, 3, 4	12	34130	—456	0.5000	—389
28	2, 3, 6, 7	12	35710	— 16	0.2764	357
29	1, 4, 5, 8	12	33780	334	0.7236	94
30	1, 4, 6, 7	12	34480	—106	0.5000	—394
31	1, 4, 5, 7	12	34250	234	0.6118	147
32	1, 2, 4, 6	20	34720	134	0.5000	201
33	1, 2, 6, 8	18	34480	—106	0.5000	—394
34	1, 2, 5, 8	18	34250	234	0.6118	147
35	1, 2, 5, 6	19	34970	384	0.5000	451
36	1, 2, 3, 4, 5	12	33560	—324	0.6809	—285
37	1, 2, 3, 4, 5, 8	12	33670	489	0.8618	499
38	1, 2, 3, 4, 5, 6, 7, 8	12	32790	—127	1.0000	135

Table 2. *The mean frequencies of the* ^1L_a *band of alkylsubstituted phenanthrenes*

Nr.	ϱ	Ref.	$\tilde{\nu}_{\text{obs}}$ a)	$\Delta\,\tilde{\nu}_{\text{opt}}$ b)	$\sum \frac{c_\varrho^2}{c_1^2}$ e)	$\Delta\,\tilde{\nu}_H$ d)	$\sum \frac{\Delta E_\varrho}{\Delta E_1}$ f)	$\Delta\tilde{\nu}_M$ g)
1	—	1, 8, 16	34220	112	0.0000	466	0.0000	49
2	1	1	33330	— 81	1.0000	—101	1.0000	—324
3	2	8	34010	42	0.0153	261	0.6590	180
4	3	16	33780	— 73	0.8560	303	0.5847	— 88
5	9	5	33670	— 96	1.4884	397	1.0556	45
6	1, 2	1, 8, 13	33330	59	1.0153	— 96	1.6590	17
7	1, 3	1	33000	—156	1.8560	—154	1.5847	—351
8	1, 6	8, 16	33220	64	1.8560	66	1.5847	—131
9	1, 7	1, 8, 13	33290	19	1.0153	—136	1.6590	— 23

Table 2 (continued).

Nr.	ϱ	Ref.	$\tilde{\nu}_{\text{obs}}$ a)	$\Delta\tilde{\nu}_{\text{opt}}$ b)	$\sum \frac{c_\varrho^2}{c_1^2}$ e)	$\Delta\tilde{\nu}_H$ d)	$\sum \frac{\Delta E_\varrho}{\Delta E_1}$ f)	$\Delta\tilde{\nu}_M$ g)
10	1, 8	1, 16	32790	76	2.0000	—318	2.0000	—347
11	1, 9	1	33000	— 69	2.4884	50	2.0556	—108
12	2, 3	1	33670	— 43	0.8713	197	1.2437	142
13	2, 5	1, 16	33560	84	0.3625	— 38	1.5606	196
14	3, 10	16	33560	49	2.3444	563	1.6403	237
15	4, 9	1	33450	176	1.8356	328	1.9572	291
16	9, 10	5	33330	— 93	2.9768	538	2.1112	250
17	1, 2, 6	8, 16	33080	64	1.8713	— 70	2.2437	69
18	1, 2, 7	1	33110	— 21	1.0306	—311	2.3180	138
19	1, 2, 8	1, 8	32570	— 4	2.0153	—533	2.6590	—226
20	1, 2, 9	8	32900	— 29	2.5037	— 45	2.7146	133
21	1, 3, 7	1	32900	—116	1.8713	—250	2.2437	—111
22	1, 4, 7	1	32520	—259	1.3625	—755	2.5606	—327
23	1, 6, 7	1, 16	33070	54	1.8713	— 80	2.2437	59
24	1, 6, 9	16	32970	156	3.3444	296	2.6403	164
25	1, 2, 7, 8	8	32520	86	2.0306	—578	3.3180	65
(26)	(4, 5) h)	15	(31950)					

Table 3. *The mean frequencies of the ^1L_a band of methyl-substituted 1,2-benzanthracene*

Nr.	ϱ	Ref.	$\tilde{\nu}_{\text{obs}}$ a)	$\sum_\varrho \frac{c_\varrho^2}{c_1^2}$ e)	$\Delta\tilde{\nu}_H$ d)	$\sum_\varrho \frac{\Delta E_\varrho}{\Delta E_1}$ f)	$\Delta\tilde{\nu}_M$ g)
1	—	10	29330	0.0000	— 54	0.0000	—106
2	1′	10	29330	0.0001	— 54	0.1543	21
3	2′	2	29200	0.2659	20	0.2914	3
4	3′	2	29110	0.0581	—230	0.1227	—255
5	4′	2	29030	0.1653	—227	0.2981	—162
6	3	2	29370	0.5381	400	0.5933	420
7	4	10	29240	0.5727	296	0.5932	290
8	5	10	28900	0.6772	37	0.6622	6
9	6	2	29110	0.2430	— 87	0.2806	— 96
10	7	2	29370	0.3600	263	0.3496	220
11	8	10	28900	0.5841	— 35	0.5939	— 50
12	9	10	28450	1.0000	—165	1.0000	—167
13	10	10	28210	1.2809	—189	1.2341	—216
14	5, 8	10	28410	1.2613	— 4	1.2561	2
15	5, 10	10	27930	1.9581	52	1.8963	46
16	8, 10	10	28090	1.8650	140	1.8280	157
17	9, 10	10	27470	2.2809	—160	2.2341	—137

a) Observed position of the ^1L_a band, in cm^{-1}.

b) Difference in cm^{-1} between $\tilde{\nu}_{\text{obs}}$ and $\tilde{\nu}_{\text{pred}}$ calculated according to the optimal regression (3) (naphthalene) or regression (4) (phenanthrene): $\Delta\tilde{\nu}_{\text{opt}} = \tilde{\nu}_{\text{obs}} - \tilde{\nu}_{\text{pred}}$.

c) Squared HÜCKEL coefficients summed over all substituted positions.

d) Difference in cm^{-1} between $\tilde{\nu}_{\text{obs}}$ and $\tilde{\nu}_H$ calculated from the regression on the HÜCKEL values: $\Delta\tilde{\nu}_H = \tilde{\nu}_{\text{obs}} - \tilde{\nu}_H$.

e) Relative, squared HÜCKEL coefficients summed over all substituted positions.

f) Relative values from equation (12), (summed over all positions): phenanthrene $\xi = 0.76$, 1,2-benzanthracene $\xi = 0.94$.

g) Difference in cm^{-1} between $\tilde{\nu}_{\text{obs}}$ and $\tilde{\nu}_M$ calculated from the regression with minimal remainder variance on the $\sum_\varrho \Delta E_\varrho/\Delta E_1$-values: $\Delta\tilde{\nu}_M = \tilde{\nu}_{\text{obs}} - \tilde{\nu}_M$.

h) Sterically strained compound, not included in the regressions.

Appendix 2

Summary of the analysis of variance

All values have been rounded. Sum of squares and variance in cm^{-2}, standard deviation in cm^{-1}. D.F. = degrees of freedom.

Compound	Approximation	Sum of squares . 10^{-3}			D.F.	Variance V_R . 10^{-3}	Standard Deviation
		Total	Due to the regression	Remainder			
Naphthalene	Optimal regression (Formula (3))	25 467	22 855	2 613	35	74.7	273
	Hückel (Formula (2))		22 239	3 228	36	89.7	299
Phenanthrene	Optimal regression (Formula (4))	4669	4 419	250	19	13.2	115
	Hückel ((12) with $\xi = 1.0$)		1 762	2 906	23	126.4	356
	Formula (12) with $\xi = 0.76$		3 737	932	23	40.5	201
1,2-Benzanthracene	Hückel ((12) with $\xi = 1.0$)	5482	4 933	548	15	36.5	191
	Formula (12) with $\xi = 0.94$		4 945	536	15	35.8	189

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