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SELF-CONSISTENT WAVE FUNCTIONS OF CONJUGATED MOLECULES BY THE ONE-DIMENSIONAL ELECTRON GAS MODEL

APPLICATION TO GEOMETRIES AND ABSORPTION SPECTRA

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Zusammenfassung—Auf der Basis des eindimensionalen Elektronengasmodells wird eine Theorie zur Verbesserung der π-Elektronenwellenfunktionen von konjugierten Molekülen entwickelt, die Unterschiede in den Bindungslängen berücksichtigt. Experimentelle Bindungslängen werden mit durchschnittlich 0·005 Å Abweichung wiedergegeben; Anregungsenergien sind gegenüber dem einfachen Modell wesentlich verbessert. Die Zuverlässigkeit des Modells in Bezug auf Geometrien ist der PPP-SCF Methode vergleichbar.

Abstract—A model based on one-dimensional electron gas theory has been developed which improves the π-electron wave functions of conjugated molecules by taking changes of bond length differences into account. Experimental bond lengths are reproduced with an average deviation of 0·005 Å; excitation energies are markedly improved over the simple model. The reliability of the model with respect to geometries is comparable to the PPP-SCF method.

INTRODUCTION

Recently we have become increasingly interested in a quantum-mechanical scheme, *viz* the one-dimensional free electron gas model[1] which describes the π-electron wave functions of a molecule in terms of standing sine and cosine functions. We have improved these functions by a method which forms the topic of this paper and have used them to calculate the spectral properties of polyene[2] and cyanine type aggregates.[3] We are employing these functions presently to investigate the CD exhibited by dissymmetric systems, such as the corrinoids[4] and pseudo-isocyanine aggregates.[5] We find them easy to handle by digital computers and, equally important in our view, to be easily visualized with respect to their symmetries and nodal characteristics. As one of the results to be discussed below, geometries of conjugated hydrocarbons, from localized polyenes to delocalized aromatics, are calculated with high accuracy. The average deviation between theoretical and experimental bond lengths is found to be about 0·005 Å. Also, the calculation of electronic energies as judged by the absorption spectra of π-electron compounds is significantly improved. With its few assumptions we compare the method to the one most widely used for the calculation of π-systems, namely the PPP-LCAO-SCF-MO method, and find the results remarkably alike.

METHOD

According to the basic assumptions of the one-dimensional electron gas model[6] the π-part of the electronic wave function of a molecule is described as a product of one-electron orbitals ψ_i of energy E_i which extend along the s-coordinate connecting properly hybridized atoms and are obtained as solutions of the one-dimensional Schroedinger equation

$$\frac{d^2\psi_i}{ds^2}+\frac{8\pi^2m}{h^2}(E_i-V(s))\psi_i=0. \qquad (1)$$

In Eq (1) m is the electron mass, h is Planck's constant and $V(s)$ represents the potential function in which the electrons move. For a constant potential the ψ_i are readily obtained as simple sine and cosine functions subject to certain restrictions at branch points and at the ends of a chain.[7] Approximate solutions of Eq (1) with $V(s)$ not a constant have been described elsewhere[8] and we are using the computer program described in that paper for the present purpose.

To obtain improved wave functions from Eq (1) one would want the potential function $V(s)$ to correspond closely to the potential provided by the molecule in its actual geometry. The short 1,2-bond in naphthalene, *e.g.*, should be reflected by a low value of V along this bond. On the other hand one would like the shortness of this bond to come out as a result of the calculations, being a consequence of the high π-density in this part of the molecule. The dilemma that a property has to be known beforehand in order to be calculated is found frequently in approximate schemes of quantum chemistry, and as usual it is solved in an iterative manner. One starts with a trial set of functions calculated from Eq (1) with a constant potential. From the wave functions the π-density is calculated from which in a manner to be discussed below a new potential function is derived. In this potential the wave functions are recalculated, and this cycle is repeated until the wave functions have become self-consistent, *i.e.* until they generate a π-density distribution which suits the assumed potential curve. Finally, from the self-consistent potential thus obtained bond lengths are calculated. For the iteration procedure we need a relation between the π-electron density d in the center of a bond and its potential, which we shall call the bond potential v, and for the final step a relation between bond length l and bond potential has to be established. We consider these steps in turn.

(*a*) *Relation between self-consistent bond potential and π-density.* In the case of linear open-chain polyenes, a sine shape potential with the wave troughs at the double bonds and the wave crests at the single bonds has been used earlier[9] to provide the periodic potential alternations along the conjugated carbon chain due to the alternating bond distances. With an amplitude $V_o = 2{\cdot}4$ eV this model led to good agreement between calculated and observed electronic transition energies. In such a potential, the difference of the π-electron density d between the centers of a double bond and of a single bond is found to be $0{\cdot}66$ Å^{-1}, independent of the number of conjugated double bonds. Since the π-electron density in benzene in the free electron approximation is $6/(6 \times 1{\cdot}39\ \text{Å}) = 0{\cdot}71\ \text{Å}^{-1}$, the following relation for the amplitude V_o of the potential correction sine function due to π-density differences may be used

$$V_o = -\left(\frac{d}{\text{Å}^{-1}} - 0{\cdot}71\right)\frac{1}{0{\cdot}33}2{\cdot}4\,\text{eV}. \qquad (2)$$

According to Eq. (2), $V_o = -2{\cdot}4$, 0, and $+2{\cdot}4$ for $d = 1{\cdot}04$, $0{\cdot}71$ and $0{\cdot}38$ Å^{-1}, respectively.* In the following calculations the sine shape potential function is approximated in each bond by a square well potential in its center of height $v = V_o$ and width $3/5 \times 1{\cdot}39\ \text{Å} = 0{\cdot}84$ Å.

(*b*) *Relation between bond potential and bond length.* For finding the relation between v and l, we use the experimental bond lengths in benzene and in butadiene[10] which cover the range of experimentally observed bond lengths in conjugated systems. For the benzene bond ($l = 1{\cdot}39$ Å) v is by assumption equal to zero, for the butadiene double bond ($l = 1{\cdot}337$ Å) we calculate (step *a*) a bond potential v of $-2{\cdot}76$ eV, while for the single bond in the same compound ($l = 1{\cdot}483$ Å) there results a value for v of $+2{\cdot}51$ eV. The three points may be connected by a smooth curve of the form

$$v = \left(\frac{-2{\cdot}092}{l/\text{Å} - 1{\cdot}158} + 8{\cdot}959\right)\text{eV}. \qquad (3)$$

With Eq 3, bond lengths l may be calculated from the heights v of self consistent bond potentials and *vice versa*, *i.e.* experimental geometries may be used to obtain corrections to the square well free electron gas potential. Eq (3) is shown graphically in Fig 1. The function seems to behave correctly: a change of the bond distance affects the bond potential less and less as the distance between the nuclei increases. This is in accordance with the $1/r$ dependence of the atomic coulomb potential. One might also argue that the bond distance is approaching slowly the length of a pure σ-bond without any π-electron population as the height of the bond potential increases. In the other direction it takes increasingly more potential energy stabilization of the π-electrons to compress the bond against its σ-component.

The basic concepts in our theory of self-consistent wave functions – the bond potential v and bond density d – have their counterparts in LCAO theory[11] and correspond loosely to the resonance integral β and the bond order P, respectively. Our linear dependence of v on d (Eq 2) and the relation between v and l (Eq 3) may be compared to the exponential dependence of β on l and the linear dependence of P on l, which are most commonly employed in LCAO theory. A weak link in LCAO theory seems to be the latter, since in all proposed relations the length of a pure sp^2–sp^2 σ-bond without pπ population is a crucial factor, and values for this bond range from $1{\cdot}46$ to $1{\cdot}52$ Å.[12] However, the linearity between l and P in the region between $1{\cdot}33$ and $1{\cdot}42$ Å seems to be well established.

Our relation $v(d)$ is obtained from an analysis of compounds – the linear polyenes – which show the highest degree of bond alternation. Essentially, our calculation of self-consistent bond densities in other conjugated hydrocarbons is then an interpolation between the two extremes, the single and double bond π-densities in an extended polyene. For the conversion of self-consistent bond potentials into bond lengths we interpolate again, though not linearly, between the short and the long bond of a polyene, *viz* butadiene. Though it appears odd at first sight to use the properties of essentially localized double bonds to describe aromatic molecules, it should be noted that there is no reason to assume any difference between the σ-

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*For high bond potentials the bond densities d vary no longer linearly with v; in bonds with positive potentials greater the $+2$ eV, the electron density decreases less than predicted by Eq (2). However, for the range of bond lengths discussed in this work the deviation from linearity is negligeable.

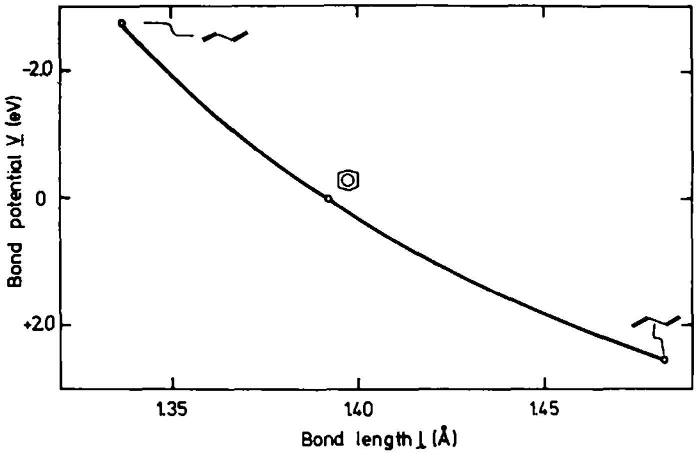

Fig 1. Plot of the function $v(l)$ with calibration points.

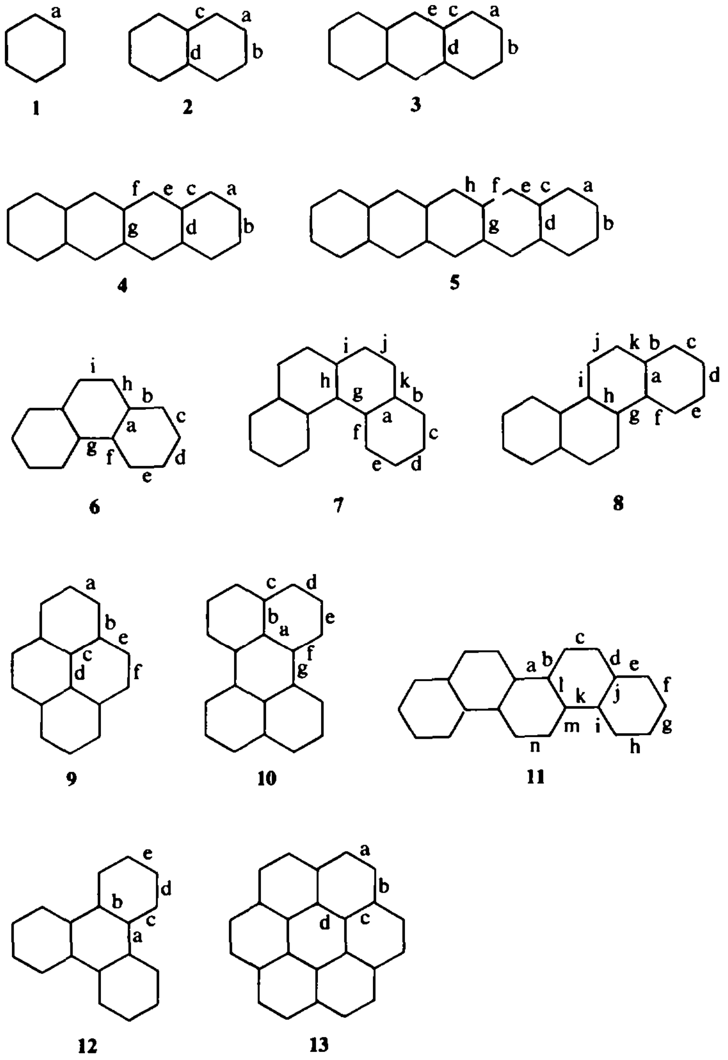

Fig 2. Key to compounds of Table 1.

bonds of a polyene and of an aromatic hydrocarbon in the absence of π-electrons and thus their response to π-electron density. The different π-electron distribution in these compounds, and thus their classification into aromatic and non-aromatic molecules, is primarily a consequence of the topology of the σ-frame work, which is of no influence on the localized σ-electrons, but of crucial importance to the delocalized π-electrons.

RESULTS AND DISCUSSION

(*a*) *Aromatic hydrocarbons*

In Table 1, the bond lengths of several aromatic hydrocarbons calculated by the described method are compared with experimental values where available, and with results obtained with an LCAO–PPP method, for which we take as a representative example the comprehensive work of Lo and Whitehead.[13] The correlation between calculated and observed bond lengths is more visually depicted in Fig. 3. In this figure the vertical lines represent the uncertainty in the experimental values and include the averaging over the molecular system in order to obtain a symmetric structure from the often distorted crystal structure. As one can see from Table 1, most bond lengths are calculated to within 1/100 Å of the experimental values, a very satisfactory result of our model. Most of the bonds which deviate more significantly from the calculated value show a very high experimental uncertainty and deserve more discussion. Partly the experimental results do not seem very convincing, and errors are possible. Consider the *b*-bond in the linearly annelated polyacenes, 1 through 5. One observes experimentally a steady increase of the length of this bond from 1·397 Å in benzene to 1·441 Å in pentacene, except for tetracene where a value of 1·479 Å is reported.* This value seems abnormally high and the calculated value of 1·427 Å appears to be more reasonable. Another case in point is the *f*-bond in pyrene, 9, for which experimental bond lengths ranging from 1·320 to 1·367 Å may be found in the literature. The calculated value of 1·355 Å is well within the range of these results and may be closer to reality than some experimental values.

In many cases, like the previous ones, there is a significantly better correspondence between the theoretical results obtained with different models than between calculated and observed values. The excellent agreement between our model and the PPP–SCF method[13] may be seen from Fig 4. Almost all calculated values agree to less than 0·005 Å with each other! From this we conclude that the modified wave functions of the free electron gas model form as reliable a basis for predicting the geometries of aromatic hydrocarbons as the more sophisticated and time-consuming self-consistent field methods of the LCAO theory.

(*b*) *Non-aromatic conjugated hydrocarbons*

The molecules to be discussed in the following

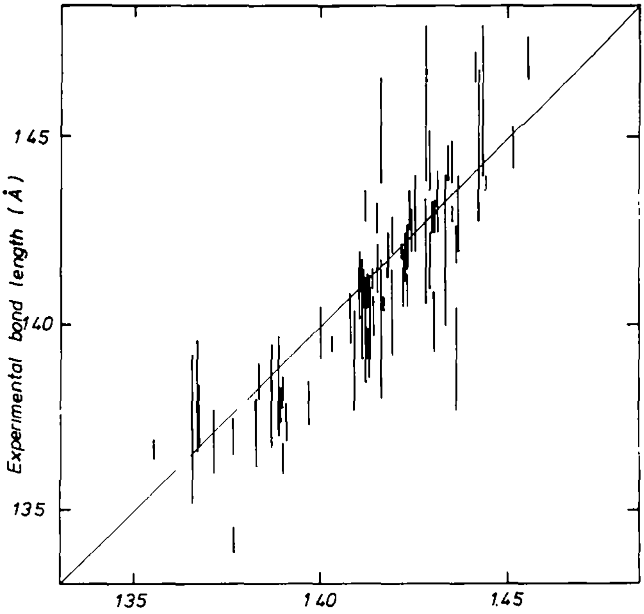

Fig 3. Plot of experimental *vs* calculated bond lengths of Table 1. Vertical lines represent uncertainty in the experimental values.

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*See Table 1 for references to these values.

Table 1. Comparison of theoretical and experimental bond lengths in several aromatic hydrocarbons

		Bond length (Å)		
Compound	Bond[a]	Exptl	This work	Lo/Whitehead[b]
1, Benzene	a	1·397[c]		
2, Naphthalene	a	1·364[d]	1·371	1·382
	b	1·415	1·421	1·419
	c	1·421	1·422	1·426
	d	1·418	1·417	1·420
3, Anthracene	a	1·375[e]	1·367	1·374
	b	1·418	1·428	1·428
	c	1·444	1·428	1·436
	d	1·433	1·430	1·427
	e	1·405	1·412	1·408
4, Tetracene	a	1·381[f]	1·367	1·369
	b	1·459	1·427	1·434
	c	1·420	1·427	1·442
	d	1·420	1·432	1·432
	e	1·390	1·408	1·400
	f	1·404	1·418	1·419
	g	1·460	1·442	1·432
5, Pentacene	a	1·36[g]	1·366	1·368
	b	1·44	1·427	1·435
	c	1·43	1·427	1·443
	d	1·45	1·433	1·434
	e	1·38	1·405	1·397
	f	1·41	1·421	1·424
	g	1·46	1·440	1·436
	h	1·40	1·415	1·411
6, Phenanthrene	a	1·404[h]	1·415	1·412
	b	1·457	1·415	1·419
	c	1·381	1·386	1·387
	d	1·398	1·411	1·414
	e	1·383	1·388	1·388
	f	1·405	1·410	1·413
	g	1·448	1·441	1·448
	h	1·390	1·435	1·443
	i	1·372	1·365	1·365
7, 3,4-Benzphenanthrene	a	1·431[i]	1·422	1·414
	b	1·391	1·412	1·422
	c	1·374	1·390	1·385
	d	1·409	1·410	1·416
	e	1·378	1·389	1·385
	f	1·433	1·411	1·421
	g	1·446	1·435	1·441
	h	1·412	1·413	1·402
	i	1·430	1·429	1·437
	j	1·342	1·376	1·370
	k	1·443	1·433	1·438
8, Chrysene	a	1·409[j]	1·422	1·414
	b	1·428	1·414	1·422
	c	1·363	1·389	1·385
	d	1·394	1·412	1·416
	e	1·381	1·389	1·385
	f	1·409	1·412	1·421
	g	1·468	1·440	1·442
	h	1·401	1·413	1·402
	i	1·428	1·428	1·435
	j	1·369	1·376	1·371
	k	1·421	1·435	1·438
9, Pyrene	a	1·395[p] 1·380[k]	1·402	1·399
	b	1·406 1·420	1·415	1·409
	c	1·425 1·417	1·421	1·421
	d	1·430 1·417	1·434	1·434
	e	1·438 1·442	1·442	1·446
	f	1·367 1·320	1·355	1·363

Table 1 – *Continued*

Compound	Bond[a]	Exptl	Bond length (Å) This work	Lo/ Whitehead[b]
10, Perylene	a	1·425[l]	1·423	1·429
	b	1·424	1·418	1·397
	c	1·400	1·429	1·427
	d	1·370	1·382	1·383
	e	1·418	1·421	1·417
	f	1·397	1·399	1·391
	g	1·471	1·454	1·461
11, Picene	a		1·429	1·435
	b		1·433	1·437
	c		1·370	1·369
	d		1·438	1·440
	e		1·412	1·421
	f		1·391	1·386
	g		1·410	1·415
	h		1·391	1·386
	i		1·410	1·420
	j		1·420	1·413
	k		1·441	1·444
	l		1·418	1·406
	m		1·424	1·429
	n		1·393	1·378
12, Triphenylene	a	1·447[m]	1·450	1·456
	b	1·415	1·414	1·410
	c	1·416	1·410	1·412
	d	1·377	1·396	1·393
	e	1·402	1·408	1·408
13, Coronene	a	1·362[n] 1·385[o]	1·382	1·377
	b	1·444 1·415	1·432	1·430
	c	1·381 1·430	1·424	1·416
	d	1·438 1·430	1·435	1·431

[a] Bond designations according to Fig 2.
[b] D. H. Lo and M. A. Whitehead, *Can. J. Chem.* **46**, 2027 (1968).
[c] B. P. Stoicheff, *Can. J. Phys.* **32**, 339 (1954).
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[g] R. B. Campbell, J. M. Robertson, and J. Trotter, *Ibid.* **14**, 705 (1961).
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[o] J. M. Robertson and J. G. White, *J. Chem. Soc.* 607 (1945); *Ibid.* 358 (1947) (X-ray).
[p] A. C. Hazell, F. K. Larsen and M. S. Lehmann, *Acta Cryst.* **B28**, 2977 (1972).

may at least partially be represented by localized double and single bonds. The marked bond alternation in butadiene which we used for calibrating the degree of bond alternation in other molecules persists through the higher polyenes. Except for a somewhat stronger alternation of the outermost bonds the bond lengths oscillate between 1·346 and 1·448 Å (Table 2, **14**) in close agreement with PPP results.[13] This confirms the predictions of Kuhn[14] who used a treatment similar to the present one and found that linear polyenes show alternating bond lengths even if the number of conjugated double bonds is very large. A documentation to the history of this problem is given elsewhere.[15] In the α,ω-diphenylpolyenes **15** and **16** the structure of the polyene chain is basically unchanged from the unsubstituted polyenes (Table 2) and the phenyl rings show typical aromatic bond lengths. This suggests that π-electron delocalization from the chain into the ring structures is relatively unimportant. Examples of non-linear polyenes which may be described in terms of localized double and single

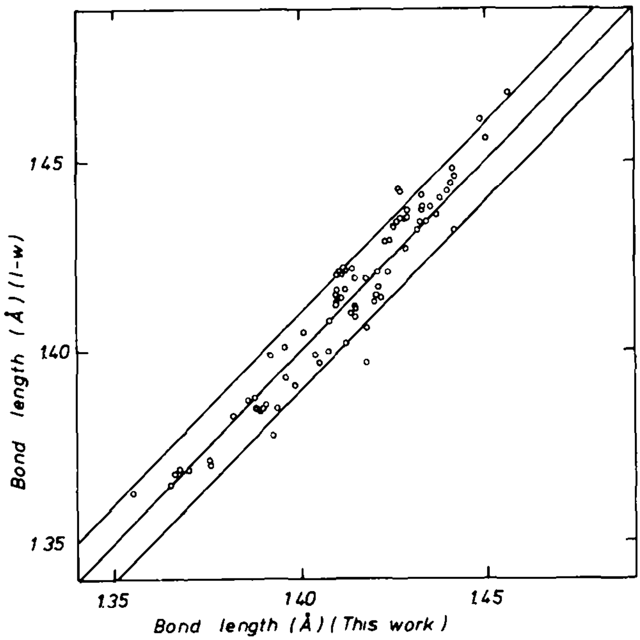

Fig 4. Plot of bond lengths calculated by PPP-SCF theory (Table 1, last entry) *vs* bond lengths obtained using self-consistent wave functions. The two outer lines represent a deviation of 0·01 Å.

Table 2. Calculated bond lengths (Å) of compounds 14 through 20

Compound	a[a] (g)	b (h)	c (i)	d	e	f
14	1·341 (1·346)	1·458 (1·448)	1·346 (1·346)	1·454	1·346	1·448
15	1·399	1·392	1·405	1·458	1·340	
16	1·399	1·391	1·405	1·456	1·342	1·461
17	1·337	1·472	1·363			
18	1·366	1·467				
19	1·366	1·467				
20	1·366	1·470				

[a]Bond designations according to Fig 5.

bonds only are also included in Table 2 (compounds 17 to 20). The proposed structures are in agreement with other calculations.[13, 16]

For some final structures we have compiled in Table 3 our results of several non-alternating hydrocarbons, together with experimental and other theoretical values. In view of the scarcity of experimental material the agreement is satisfactory.

(*c*) *π-Electron energy levels*. As mentioned in the Introduction we are employing the self-consistent wave functions mainly for the calculation of spectral properties of conjugated hydrocarbons. The fact that the structures of these compounds are reproduced with our method with unexpected accuracy is not necessarily an indication of the ability of the method to describe excited state properties. In Table 4 the energy difference between the highest occupied and the lowest empty orbital, as calculated by the free electron gas model and by the self consistent model, is compared to the energy of the experimentally observed electronic excitation which can be identified with a transition between these orbitals. We restrict our discussion to this transition because it is (a) usually easily identified in the absorption spectrum and because (b) configuration interaction which is quite important for the transitions between other electronic states plays a minor role in this instance. Configuration interaction may be included in our model[17] but for our purposes so far has not been a necessity.

While the general trend of the transition energies is already satisfactorily reproduced with the free electron gas model, comparable to the success of Hückel theory in correlating these transitions,[12] the calculated energies are with the one exception of benzene too small. Introduction of bond length

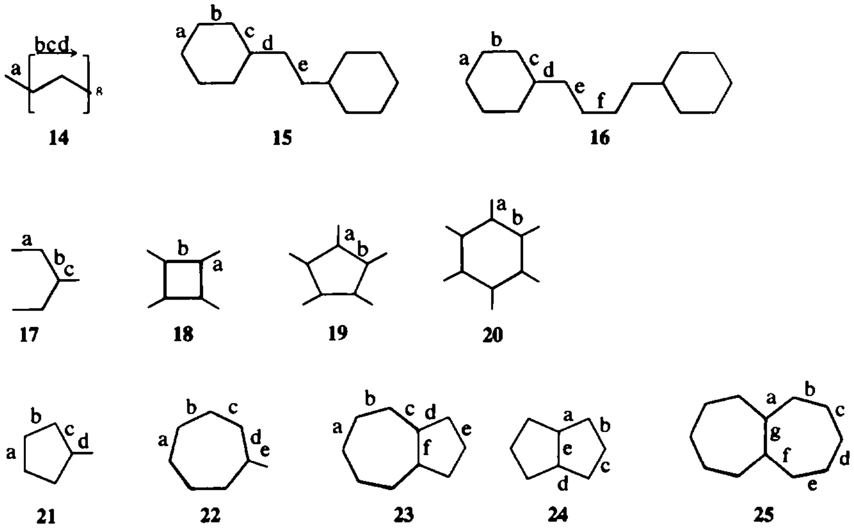

Fig 5. Key to compounds of Tables 2 and 3.

Table 3. Comparison of theoretical and experimental bond lengths (Å) in non-alternating hydrocarbons

Compound	Bond[a]	Exptl.	This work	PPP[b]
21, Fulvene	a	1·435[c]	1·441	1·454
	b	1·346	1·339	1·353
	c	1·439	1·437	1·466
	d	1·343	1·396	1·351
22, Heptafulvene	a		1·347	1·354
	b		1·456	1·458
	c		1·347	1·352
	d		1·464	1·467
	e		1·346	1·351
23, Azulene	a	1·394[d]	1·420	1·400
	b	1·398	1·388	1·398
	c	1·391	1·441	1·406
	d	1·400	1·382	1·405
	e	1·392	1·379	1·397
	f	1·498	1·422	1·467
24, Pentalene	a		1·371	1·361
	b		1·446	1·457
	c		1·333	1·353
	d		1·488	1·457
	e		1·481	1·456
25, Heptalene	a		1·355	1·361
	b		1·467	1·455
	c		1·342	1·355
	d		1·470	1·460
	e		1·338	1·352
	f		1·470	1·465
	g		1·467	1·463

[a] Key to molecules and bonds see Fig 5.

[b] C. R. de Llano and M. J. S. Dewar, cited in Ref. 16, p. 178.

[c] N. Norman and B. Post, *Acta Cryst.* 14, 503 (1961).

[d] A. W. Hanson, *Ibid.* 19, 19 (1965).

Table 4. Transition energies (in $10^{-2}\,cm^{-1}$) of some conjugated hydrocarbons

Compound[a]	Free electron gas	Modified electron gas	Experimental[b]
1	523	523	484
2	260	330	347
3	188	238	264
4	130	170	212
5	98	130	174
6	259	282	340
10	182	210	228
12	278	289	349
14	826	213	227
15	184	275	313
16	150	255	284

[a] For key to compounds see Figs 2 and 5.

[b] Values taken from compilation by Streitwieser, Ref. 12, p. 213, 218.

differences markedly improves the energies, mainly by stabilizing the highest occupied molecular orbital which usually resembles quite closely the total π-electron distribution. The transition energies of other types of compounds, such as cyanine dyes, have been reproduced equally well.[3]

Our aim is not to calculate absorption spectra of conjugated molecules on an absolute scale; clearly our method with its neglect of electron repulsion and correlation would be much too crude for that. We are in our work[2-5] mainly interested in the energy changes which take place when different chromophores are brought into close contact. The scheme which we have developed above significantly improves the calculation of spectral shifts if the known structures of the chromophores are included *via* Eq (3) in the model. With chromophores of unknown geometries the theory permits a prediction of the extent of charge localization at specific sites of the molecule which influences greatly the energy interaction terms between different chromophores. The reliability of these predictions is indicated by the success of the method to reproduce experimental geometries. We find that the self-consistent wave-functions present an acceptable compromise between sophistication and numerical manageability.

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