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SELF-CONSISTENT ITERATIVE TECHNIQUE FOR BOND-LENGTH CALCULATIONS—IV

NON-ALTERNANT HYDROCARBONS

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Abstract—The applicability of the self-consistent iterative procedure for bond-length calculations is examined for some non-alternant hydrocarbons. The results obtained by our calculations are reported. The bond alternation and the pseudo-Jahn-Teller distortion are investigated.

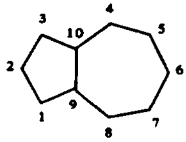
INTRODUCTION

IN EARLIER papers,[1] a simple method has been suggested to evaluate the bond-lengths of alternant hydrocarbons. In view of its apparent success in yielding the bond-lengths in agreement with experimental data and in view of recent interest in non-alternant hydrocarbons[2–6] the method is extended to non-alternant hydrocarbons. The success of this method lies in the proper choice of delta, δ, the perturbation parameter. Thus, the main objective of this paper is to suggest a delta value appropriate to non-alternant hydrocarbons and to examine the results of sample calculations.

As has been indicated in the first paper of this series,[1] the choice of delta for alternant hydrocarbons is made by comparing the theoretical results and selecting a delta value which yields results in agreement with the experimental ones. An extension of this procedure to non-alternant hydrocarbons is hampered by the fact that experimental data are scarce. However, using the available experimental results and qualitative arguments, a partial justification of the choice of delta could be made. To this end, the bond-length calculations were carried out for azulene for which experimental results are available. The results of the calculations indicate that except for the transannular bond all the other bonds are insensitive to changes in delta. The bond-length of the transannular bond ("central" bond) increases as the value of delta is increased. It is found that a high value of delta is necessary to reproduce experimental results. The results given in Table 1 for azulene suggested that a high value of delta (say, 0·75) would be appropriate for calculations of other non-alternant hydrocarbons. However, this could not be directly ratified as the experimental bond-length data are not available for such molecules.

An indirect justification of this choice of δ can be developed if it is noted that on account of strain, most of the non-alternant hydrocarbons deviate from planarity. Now, if it can also be shown that a high value of delta is necessary for any strained

TABLE 1.[a] SELF-CONSISTENT BOND-LENGTH RESULTS[b] IN ANGSTROM UNITS

Name of the molecule	Bond	This[c] work	Expt[d]	Theoretical[e]
Azulene	1–2	1·400	1·391 ± 0·021	1·399
	1–9	1·404	1·413 ± 0·015	1·407
	6–7	1·402	1·385 ± 0·021	1·403
	7–8	1·398	1·401 ± 0·018	1·398
	8–9	1·407	1·383 ± 0·004	1·403
	9–10	1·468	1·483 ± 0·004	1·473

[a] The numbering of the molecules may not agree with the conventional numbering system. The above numbering was done for computational purposes.

[b] Since numerous references that give the bond-length results (both theoretical and experimental) are available in literature, only a selective few are indicated in Table 1.

[c] Though a higher value of delta, 0·90, yields bond-lengths for azulene in agreement with previously reported experimental values, use of the same value for benzazulenes and dibenzazulenes show a divergence in bond-length results.

[d] Ref. 13.

[e] Ref. 2. Theoretical-SCF–PPP.

π-electron systems for which experimental results are available, then the choice of a high delta for non-alternant hydrocarbons gains credence. To this end, we carried out the calculations for fulvene, 3,4-dimethylene cyclobutene and cyclooctatetraene. Indeed, as is clear from Table 2, to obtain results in agreement with the experimental results,[7–11] a high value of delta (0·75) was required.

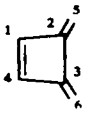
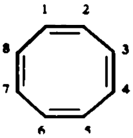
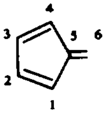
It might also be pointed out that in the long chain polyenes, where a high delta value was required,[1] there is probably considerable twisting (a form of strain) resulting in the same bond alternation noticed in several non-alternant hydrocarbons. Again, a high value of δ for strained π-electron systems, i.e. non-alternant hydrocarbons is supported.

APPLICATIONS

Case a

Fusion of alternant fragments to azulene. As has been pointed out earlier, the delta that was used for the calculations has a high value, 0·75. With this value of delta, the bond-length results obtained for benz[*a*]azulene, benz[*e*]azulene, benz[*f*]azulene, dibenz[*a.b*]azulene, dibenz[*a.e*]azulene and dibenz[*a.g*]azulene are given in Table 3. From the results, it could be noticed that with annelation, there is no change in the "central" bond-length in these molecules. Thus, for example, the 6–14 bond in benz[*a*]azulene, the 9–13 bond in benz[*e*]azulene and the 8–12 bond in benz[*g*]azulene are of the same length and they are a little different from the central bond in azulene. The same annelation effect is noted in the central bond, namely the 9–17 bond, the 6–16 bond and the 7–15 bond in dibenz[*a.b*]azulene, dibenz[*a.g*]azulene and dibenz[*a.e*]azulene respectively. Though the annelation has no effect on the "central" bond, this is not true of other bonds in the azulene fragment of these molecules. For example, Table 3 indicates that except for dibenz[*a.b*]azulene, annelation consistently introduces *bond-alternation.*

TABLE 2. SELF-CONSISTENT BOND-LENGTH RESULTS IN ANGSTROM UNITS

Name of the molecule	Bond	This work	Expt. result	Theoretical
3,4-dimethylenecyclobutene	1–2	1·485	1·488 ± 0·009[a]	1·468[b]
	1–4	1·343	1·357 ± 0·005	1·354
	2–3	1·488	1·516 ± 0·020	1·476
	2–5	1·342	1·335 ± 0·003	1·350
Cyclooctatetraene	1–2	1·343	1·340[c]	1·354[d]
	2–3	1·483	1·476	1·461
Fulvene	1–2	1·345	1·340 ± 0·006[e] (1.346 ± 0·010[f])	1·357[b]
	1–5	1·480	1·476 ± 0·008 (1·439 ± 0·008)	1·464
	2–3	1·477	1·462 ± 0·009 (1·435 ± 0·016)	1·450
	5–6	1·345	1·347 ± 0·010 (1·343 ± 0·011)	1·354

[a] Ref. 9.

[b] Ref. 8. Theoretical—SCF–PPP.

[c] Ref. 11.

[d] Ref. 10. The calculations in their work and in our work were done assuming a planar model. Theoretical—SCF–PPP.

[e] Ref. 20.

[f] The results given in parenthesis are taken from reference 7. The results obtained after "anisotropic" least square refinement correspond to the crystal structure of dimethylfulvene. For comparison with our results, the Fourier results after "isotropic" least squares refinement quoted in the above reference are given as follows: 1–2: 1·343°A; 1–5: 1·457°A; 2–3: 1·477°A; 5–6: 1·343°A.

Case b

Fusion of 5-membered and 7-membered ring systems to an alternant hydrocarbon unit. In order to examine whether the fusion of five- and seven-membered ring systems to an alternant hydrocarbon unit would bring about changes that are different from the ones studied in *Case a*, the representative molecules acenaphthylene, fluoranthene and acepleiadylene were studied.

Even though the crystal structure data are not available for acenaphthylene, the experimental data on the related compounds acenaphthene,[12] acenaphthenequinone[13] and *cis*-1,2-acenaphthenediol[14] (Fig 1) seem to show that a considerable amount of

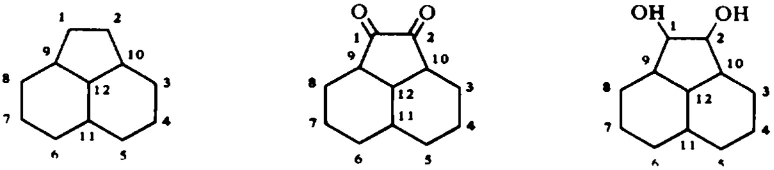


FIG 1

TABLE 3.[a] SELF-CONSISTENT BOND-LENGTH RESULTS IN ANGSTROM UNITS

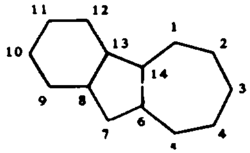
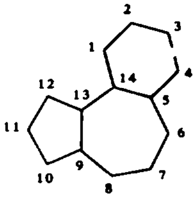
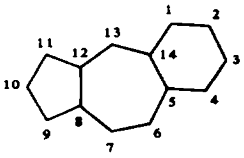
Name of the molecule	Bond	This work	PPP[b]	SPO[b]
Benz[*a*]azulene	1– 2	1·465	1·437	1·450
	1–14	1·355	1·375	1·366
	2 –3	1·351	1·369	1·360
	3– 4	1·467	1·437	1·450
	4– 5	1·350	1·366	1·357
	5– 6	1·469	1·449	1·461
	6– 7	1·355	1·370	1·362
	6–14	1·476	1·465	1·469
	7– 8	1·465	1·441	1·450
	8– 9	1·417	1·417	1·414
	8–13	1·392	1·405	1·397
	9–10	1·380	1·382	1·379
	10–11	1·417	1·412	1·416
	11–22	1·380	1·384	1·380
	12–13	1·417	1·415	1·418
	13–14	1·470	1·447	1·455
Benz[*f*]azulene	1– 2	1·381	1·394	1·381
	1–14	1·416	1·414	1·417
	2– 3	1·416	1·411	1·414
	3– 4	1·381	1·384	1·382
	4– 5	1·417	1·413	1·415
	5– 6	1·467	1·446	1·457
	5–14	1·392	1·405	1·397
	6– 7	1·351	1·366	1·358
	7– 8	1·464	1·437	1·449
	8– 9	1·356	1·377	1·367
	9–10	1·467	1·438	1·449
	9–13	1·476	1·464	1·468
	10–11	1·351	1·370	1·363
	11–12	1·464	1·431	1·441
	12–13	1·355	1·373	1·366
	13–14	1·469	1·451	1·468
Benz[*f*]azulene	1– 2	1·380	1·383	1·380
	1–14	1·418	1·415	1·417
	2– 3	1·417	1·413	1·417
	3– 4	1·381	1·382	1·379
	4– 5	1·417	1·416	1·419
	5– 6	1·469	1·446	1·457
	5–14	1·392	1·405	1·396
	6– 7	1·350	1·362	1·355
	7– 8	1·470	1·448	1·461
	8– 9	1·355	1·374	1·365
	8–12	1·476	1·448	1·461
	9–10	1·465	1·430	1·441
	10–11	1·350	1·370	1·362
	11–12	1·469	1·439	1·450
	12–13	1·355	1·374	1·365
	13–14	1·465	1·445	1·455

TABLE 3. *cont.*

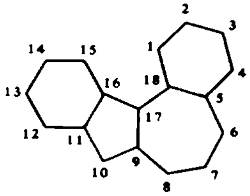
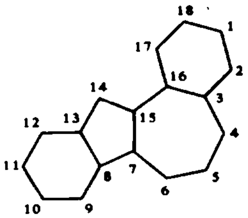
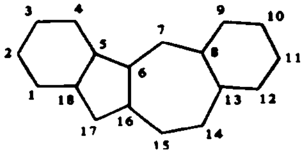
Name of the molecule	Bond	This work	PPP[b]	SPO[b]
Dibenz[*a.b*]azulene  	1– 2	1·362		
	1–18	1·443		
	2– 3	1·445		
	3– 4	1·362		
	4– 5	1·444		
	5– 6	1·410		
	5–18	1·416		
	6– 7	1·398		
	7– 8	1·400		
	8– 9	1·409		
	9–10	1·404		
	9–17	1·463		
	10–11	1·405		
	11–12	1·447		
	11–16	1·419		
	12–13	1·360		
	13–14	1·448		
	14–15	1·361		
	15–16	1·446		
	16–17	1·408		
	17–18	1·413		
Dibenz[*a.e*]azulene  	1– 2	1·388		
	1–18	1·408		
	2– 3	1·409		
	3– 4	1·472		
	3–16	1·396		
	4– 5	1·348		
	5– 6	1·470		
	6– 7	1·352		
	7– 8	1·474		
	7–15	1·477		
	8– 9	1·409		
	8–13	1·396		
	9–10	1·387		
	10–11	1·409		
	11–12	1·387		
	12–13	1·410		
	13–14	1·470		
	14–15	1·352		
	15–16	1·474		
	16–17	1·408		
	17–18	1·388		
Dibenz[*a.g*]azulene  	1– 2	1·387		
	1–18	1·410		
	2– 3	1·409		
	3– 4	1·387		
	4– 5	1·409		
	5– 6	1·474		
	5–18	1·396		

TABLE 3. *cont.*

Name of the molecule	Bond	This work	ϱPP[b]	SPO[b]
	6– 7	1·352		
	6–16	1·477		
	7– 8	1·470		
	8– 9	1·410		
	8–13	1·396		
	9–10	1·387		
	10–11	1·409		
	11–12	1·387		
	12–13	1·409		
	13–14	1·473		
	14–15	1·347		
	15–16	1·474		
	16–17	1·352		
	17–18	1·471		

[a] The numbering of the molecules may not agree with the conventional numbering system. The above numbering was done for computational purposes.

[b] Ref 21.

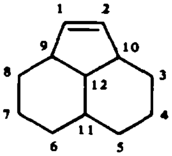
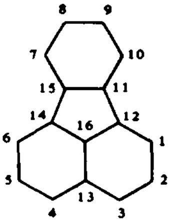
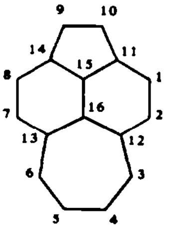
strain is involved in fusing the five-membered ring to the naphthalene unit. It is expected that such a strain in the case of acenaphthylene would result in the $\overline{9-1-2-10}$ unit to be out of the plane of the molecule, thus leading to less delocalization in the $\overline{9-1-2-10}$ part of the molecule. The consequence of this would be *bond-alternation* in the $\overline{9-1-2-10}$ unit which can be seen from calculations reported in Table 4. Similar calculations on fluoranthene and acepleiadylene show that in fluoranthene the 11–12 and 14–15 bonds are long and in acepleiadylene, the units $\overline{14-9-10-11}$ and $\overline{12-3-4-5-6-13}$ exhibit bond-alternation. The results of these calculations are given in Table 4.

Case c

The pseudo-Jahn–Teller distortion. Although the above work suggests that the delta-type perturbation of the Hückel MO approach is feasible for non-alternant hydrocarbons, the applicability of the method in its present form for π-electron systems that may show the pseudo-Jahn–Teller distortion[16] (for example, pentalene and heptalene) needs to be investigated. Since simple molecular orbital calculations, for example, Hückel molecular orbital calculations, for pentalene and heptalene conserve D_{2h} symmetry, the bond-length results obtained by the delta technique for any delta value (including 0·75) correspond to the D_{2h} symmetry of the system. Because of pseudo-Jahn–Teller distortion, a structure belonging to the point group C_{2h} in which the peripheral bond-lengths alternate may be more favourable energetically[3,4,6,16,17] than the one belonging to the point group, D_{2h}.

In order to examine the applicability of the δ-technique when the symmetry of the point group of these molecules has been lowered, the calculations were repeated by deliberately introducing a slight alternation in the input H-matrix elements for the

TABLE 4. SELF-CONSISTENT BOND-LENGTH RESULTS IN ANGSTROM UNITS

Name of the molecule	Bond	This work	Expt I	Expt II
Acenaphthylene	1– 2	1·346	—[a]	—[b]
	2–10	1·476	1·478	1·477
	10–12	1·437	1·414	1·407
	3–10	1·372	1·363	1·407
	3– 4	1·432	1·463	1·482
	4– 5	1·368	1·368	1·314
	5–11	1·435	1·396	1·425
	11–12	1·395	1·406	(1·470)
Fluoranthene	1– 2	1·432		
	1–12	1·372		
	2– 3	1·368		
	3–13	1·436		
	8– 9	1·400		
	9–10	1·394		
	10–11	1·401		
	11–12	1·476		
	11–15	1·402		
	12–16	1·437		
	13–16	1·395		
Acepleiadylene	1– 2	1·418	1·399[c]	
	1–11	1·382	1·383	
	2–12	1·382	1·406	
	3–12	1·469	1·444	
	3– 4	1·349	1·356	
	4– 5	1·470	1·427	
	9–10	1·350	1·364	
	10–11	1·469	1·457	
	11–15	1·430	1·424	
	12–16	1·430	1·456	
	15–16	1·405	1·395	

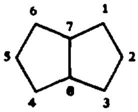
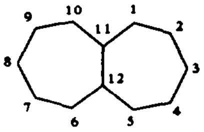
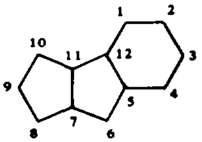
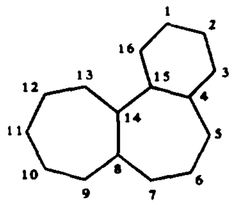
[a] Ref 13. The data given in Table 4 correspond to the molecule, acenaphthoquinone. Only mean values are quoted.

[b] Ref 14. The data correspond to the crystal structure of *cis*-1,2-acenaphthenediol. Only mean values are quoted.

[c] Ref 15. The experimental results indicated in Table 4 correspond to acepleiadylene in its complex state with 1,3,5-trinitrobenzene.

peripheral bonds. This was done by selecting several values for the ratio H_{1-m}(long)/H_{1-m}(short). When extreme values of the initial perturbation (i.e. H_{1-m}(long)/H_{1-m}(short) = 0·995 or 0·600) are assumed, very slow convergence is noted for low values of delta and slow divergence sets in for high values of delta. However, for an initial perturbation corresponding to the ratio H_{1-m}(long)/H_{1-m}(short) = 0·90, rapid convergence is attained for delta values in the range 0·45–0·75. In this range of delta values, as is indicated in Table 5, it is the delta value, 0·55 that yields results in agreement with those of Francois and Julg.[4] (Clearly the selection of 0·55 for δ is partly governed by the initial perturbation).

TABLE 5. SELF-CONSISTENT BOND-LENGTH RESULTS IN ANGSTROM UNITS

Name of the molecule	Bond	This work	Theoretical
Pentalene	1– 2	1·347[a]	1·349[b]
	2– 3	1·475	1·460
	1– 7	1·478	1·481
	3– 8	1·352	1·357
	7– 8	1·471	1·464
Heptalene	1– 2	1·349[a]	1·350[b]
	1–11	1·472	1·469
	2– 3	1·470	1·464
	3– 4	1·350	1·352
	4– 5	1·468	1·462
	5–12	1·355	1·358
	11–12	1·472	1·469
Benzo[*a*]pentalene	1– 2	1·403[c]	
	1–12	1·393	
	2– 3	1·393	
	3– 4	1·402	
	4– 5	1·394	
	5– 6	1·478	
	5–12	1·408	
	6– 7	1·349	
	7– 8	1·481	
	7–11	1·478	
	8– 9	1·345	
	9–10	1·479	
	10–11	1·349	
	11–12	1·482	
Benzo[*a*]heptalene	1– 2	1·398[c]	
	1–16	1·397	
	2– 3	1·397	
	3– 4	1·399	
	4– 5	1·476	
	4–15	1·404	
	5– 6	1·347	
	6– 7	1·474	
	7– 8	1·350	
	8– 9	1·478	
	8–14	1·477	
	9–10	1·346	
	10–11	1·477	
	11–12	1·347	
	12–13	1·474	
	13–14	1·351	
	14–15	1·478	
	15–16	1·398	

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[a] The delta value that is used for the calculation is 0·55.

[b] Ref 4. Theoretical–Hückel iterative.

[c] The delta value, 0·75, is used for the calculations.

It should be emphasized that for those systems (such as benz[*a*]pentalene and benz[*a*]heptalene) which contain the pentalene and heptalene fragments but which do not exhibit the pseudo-Jahn–Teller effect (i.e. the symmetry has been lowered by annelation) then there is no need for an initial perturbation and the usual value of $\delta = 0{\cdot}75$ can be used. The calculated results for benz[*a*]pentalene and benz[*a*]heptalene are reported in Table 5.

METHOD OF CALCULATION

The Coulson–Golebiewski bond order-bond length relation[18]

$$R^{n}_{1-m} = 1{\cdot}517 - 0{\cdot}18\, p^{n}_{1-m} \tag{1}$$

and

$$\mathrm{H}^{n}_{1-m} = \mathrm{H}^{\circ}_{1-m} + \delta(p^{n-1}_{1-m} - p^{s}) \tag{2}$$

are used for the calculations. (The procedure has been indicated in part I of this series.) H_{1-m} is the bond-integral; p_{1-m} is the bond-order; R_{1-m} is the bond-length; p^{s} is the bond-order of a standard bond; δ is the perturbation; the superscript indicates the number of iterations carried out. The self-consistent results obtained after eight iterations were used for analysis. The calculations were carried out on an IBM 360/50K computer.

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