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ENERGETICS AND BOND-LENGTHS OF SOME POLYNUCLEAR AROMATIC HYDROCARBONS

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Abstract—Simple HMO calculations are used for the evaluation of ionization potential, electron affinity, and the charge-transfer spectra of 2,4,7-trinitro-9-fluorenone complexes of some recently synthesized polynuclear aromatic hydrocarbons with seven fused rings. Iterative Hückel MO calculations of bond lengths for the same *above* molecules are also reported.

INTRODUCTION

IN THE past few years a number of polynuclear aromatic compounds have been synthesized.[1] Besides their intrinsic interest, these compounds may be of importance because of their biological activity.[2] Since little is known about these compounds aside from their preparation, it is felt that a semi-theoretical investigation would be in order. It is well-known that an *ab initio* description of all the electrons would be prohibitively complex. On the other hand the simple and tractable theories such as the Hückel MO treatment are inadequate for the task. However, in the past few years, a number of modifications have been developed which allow the application of HMO calculations to the description of the electronic properties of these systems. Essentially all such modifications derive the functional dependence of a given observable on two types of parameters, the first being theoretical parameters, which change from molecule to molecule, and the second, empirical parameters, which are characteristic of many molecules.

For example, more explicit recognition of the electron distribution than that provided by HMO can be accomplished by the ω-technique while still retaining the essential simplicity of the HMO method. This technique[3] is based on an iterative procedure in which the HMO matrix elements for a given centre (i.e. the diagonal matrix element) is modified according to the charge density on that centre given by the results of the previous iteration. Under certain conditions[4] the technique converges. Usually the iterative procedure is omitted and only the functional dependence of the convergent form on the various parameters is employed. Thus, for example, the ionization potential is given as:

$$Ip = -\alpha - \chi\beta \text{ with } \chi = m_{h\omega} - \left(\frac{n-1}{n}\right)\omega \tag{1}$$

where ω is determined semi-empirically and n is the number of π-electrons in the

molecule. This latter formula can be rewritten as

$$Ip = -\alpha - m_{hoo}\beta - \frac{1}{n}\omega\beta + \omega\beta$$

$$= a + bm_{hoo} + c\frac{1}{n} \tag{2}$$

giving the dependence of Ip on the "theoretical parameters," m_{hoo} and n, and on the empirical parameters a, b and c (i.e. α, β and ω). The essential point is that a modified Hückel treatment gives the functional dependence on parameters m_{hoo} and n, which can be derived in a relatively simple analytical fashion for each molecule, and on empirically derived parameters a, b, and c, which may be assigned values on the basis of a statistical (e.g. regression) analysis of a limited set of experimental results.

The appropriate values of the empirical parameters for the observable of interest, are reasonably well-established. Using these values and the theoretical parameters obtained from the simple Hückel treatment, satisfactory values for the energetics of many π-electron systems can be found. The results for some polynuclear aromatic hydrocarbons synthesized recently as well as those not synthesized are reported.

An iterative Hückel MO calculation was carried out to obtain the bond lengths of some of the above components. The iterative procedure involves the modification of the off-diagonal matrix elements, this time according to the bond order as found in the previous iteration. Under certain conditions the procedure can be shown to converge[5] and the iterative procedure may be carried out. The bond lengths of the newly synthesized hydrocarbons are reported.

CALCULATIONS

(a) *The Hückel eigenvalues*

The molecular orbitals and eigenvalues given by the Hückel representation of the Schrödinger equation can be obtained by standard computer programmes, e.g. the Eigen subroutine as found in the IBM SSP. The values for m_{hoo} and m_{two} in the eigenvalues for the molecules (Fig. 1) are given in Table 1. With this Table of values of m, the observables of interest may be calculated from the semi-empirical formulae.

(b) *Energetics*

(i) *The ionization potential, Ip*

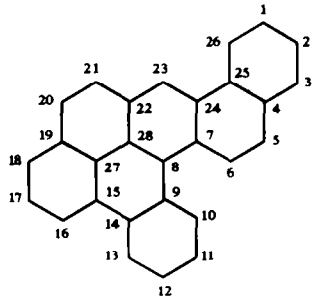
The relation,

$$Ip = 2{\cdot}48\, m_{hoo} + 7{\cdot}07, \tag{3}$$

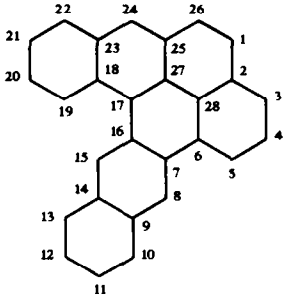
has been used successfully by Streitwieser[12] to give the Ip of a number of organic compounds. On the basis of Eq. (2), a somewhat different expression from (3) has been used to evaluate Ip

$$Ip = 6{\cdot}924 + 2{\cdot}110\, m_{hoo} + (2{\cdot}954/n) \tag{4}$$

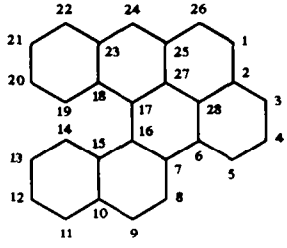
The average values are given in Table 2. The uncertainty quoted refers only to the slightly differing values resulting from using Eq. (3) or (4).



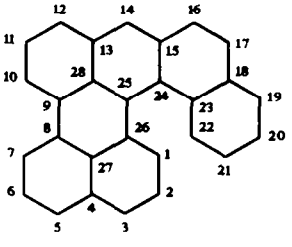
Benzo(e)naphtho(1 2-b)pyrene, **1**



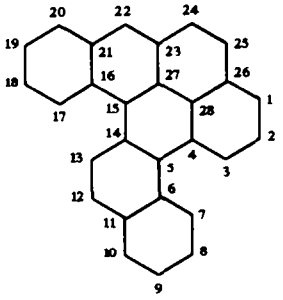
Naphtho(2.3-1)benzo(a) pyrene, **2**



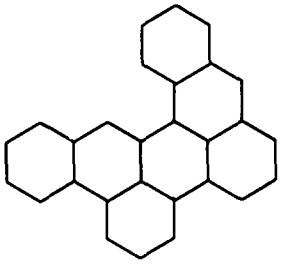
Naphtho(2.1-1)benzo(a)pyrene, **3**



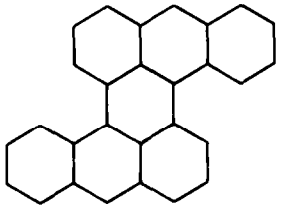
Naphtho(1.2-a)perylene, **4**



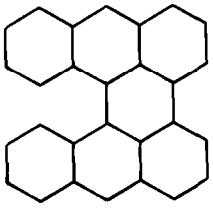
Naphtho(1.2-1)benzo(a)pyrene, **5**



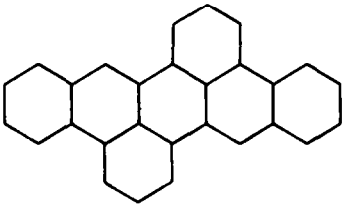
Dibenzo(a.n)perylene, **6**



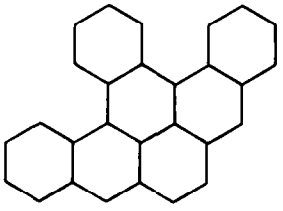
Dibenzo(a.j)perylene, **7**



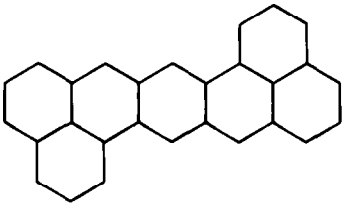
Dibenzo(a.o)perylene, **8**



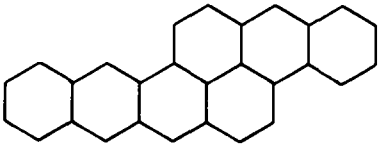
Dibenzo(b.k)perylene, **9**



Tribenzo(1.i.l)pyrene, **10**



Dibenzo(de.op)pentacene, **11**



Anthra(2.1.9-qra)naphthacene, **12**

FIG. 1

TABLE 1. ENERGIES OF THE HIGHEST OCCUPIED AND LOWEST UNOCCUPIED ORBITALS

Compound name	Value of m in $\varepsilon = \alpha + m_i\beta$	
	No.	m_{hoo}
† Benzo(e)naphtho(1.2-b)pyrene	1	0·4044
† Naphtho(2.3.-1)benzo(a)pyrene	2	0·3886
† Naphtho(2.1.-1)benzo(a)pyrene	3	0·3658
† Naphtho(1.2-a)perylene	4	0·2913
† Naphtho(1.2.-1)benzo(a)pyrene	5	0·3784
‡ Dibenzo(z.n)perylene	6	0·2673
‡ Dibenzo(a.j)perylene	7	0·2135
§ Dibenzo(a.0)perylene	8	0·2089
§ Dibenzo(b.k)perylene	9	0·3557
§ Tribenzo(a.i.l)pyrene	10	0·3730
‡ Dibenzo(de.op)pentacene	11	0·1280
‖ Anthra(2.1.9-qra)naphthacene	12	0·2508

† Present work

‡ R. Zahradnik and C. Parkanyi, *Coll. Czech. Chem. Commun.* **30**, 3536 (1965).

§ Our calculations show that the reported m_{hoo} values (‡ above) for molecule 8 seems to be in disagreement with our value [m_{hoo} (reported) = 0·7042].

‖ M Titz and P Hochmann, *Ibid.* **31**, 4168 (1966).

TABLE 2. ENERGETICS OF THE CHOSEN POLYNUCLEAR AROMATIC HYDROCARBONS

Compound No.	Ionization potential (eV)	Electron affinity (eV)	^1L_a Transition		$h\nu_{CT}$ (eV) ±0·08
			Δm	Energy (eV) ±0·07	
1	7·98 ± 0·10	0·68 ± 0·03	0·8088	3·21	2·20
2	7·94 ± 0·09	0·70 ± 0·02	0·7772	3·13	2·16
3	7·89 ± 0·09	0·73 ± 0·02	0·7316	3·02	2·10
4	7·72 ± 0·08	0·83 ± 0·01	0·5826	2·67	1·88
5	7·91 ± 0·08	0·71 ± 0·02	0·7568	3·08	2·13
6	7·66 ± 0·07	0·86 ± 0·01	0·5346	2·57	1·82
7	7·54 ± 0·06	0·93 ± 0·00	0·4270	2·31	1·66
8	7·53 ± 0·06	0·94 ± 0·00	0·4178	2·29	1·65
9	7·68 ± 0·08	0·74 ± 0·02	0·7114	2·98	2·06
10	7·91 ± 0·10	0·72 ± 0·02	0·7460	3·06	2·12
11	7·34 ± 0·05	1·05 ± 0·01	0·2560	1·90	1·42
12	7·63 ± 0·07	0·88 ± 0·00	0·5016	2·49	1·77

(ii) *The Electron affinity, E_a.* The relation,

$$E_a = -\alpha - \left(m_{luo} - \frac{n+1}{n}\omega\right)\beta,$$

has been proposed by Ehrenson[3] for a number of compounds. Becker and Chen[6] used an empirical relationship to arrive at electron affinity.

$$E_a = 1{\cdot}48\, m_{luo} + 1{\cdot}25 \tag{6}$$

where m_{luo} is the β-coefficient of the lowest unoccupied orbital. Values of α, β and ω used by Becker and Chen for evaluating E_a lead to an expression different from (6).

$$E_a = 1{\cdot}37 + 1{\cdot}23\, m_{luo} - (4{\cdot}61/n) \tag{7}$$

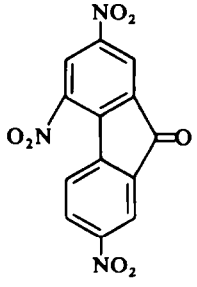
Table 2 gives the average value by the two equations along with the deviation from the average.

(iii) *The energy of the ^1L_a transition* is associated with an electronic transition from the highest occupied MO to the lowest unoccupied MO. A semi-empirical relationship has been obtained[7] between the experimentally determined energy values for ^1L_a transition and Δm (where $\Delta m = m_{hoo} - m_{luo}$) for a series of polynuclear aromatic hydrocarbons. The calculated values of Δm and energy of ^1L_a transition in eV are reported in Table 2.

(iv) *The charge-transfer spectra of* TNF† *adducts.* Vingiello *et al.* isolated TNF adducts with the compounds they synthesized. The observable color change when TNF adducts are made from pure polynuclear aromatic hydrocarbons and some of the thiophen derivatives is a clear indication that the interaction between these molecules and TNF is specific. Lepley[8] has ascribed the characteristic absorption of TNF adducts with a series of polynuclear aromatic hydrocarbons to π–π^* interaction between the aromatic hydrocarbons and 2,4,7-trinitro-9-fluorenone. Anticipation of such an interaction between these newly synthesized hydrocabons has led to the least square regression analysis of Lepley's experimental data and the energy of the highest occupied orbital of the hydrocarbons. Such a relationship between the charge-transfer energy of π-complexes and m_{hoo} is based on Dewar's MO Theory of π-complex interaction.[9] The equation of the regression analysis is given by

$$h\nu_{CT}\,(\text{eV}) = 2{\cdot}83\, m_{hoo} + 1{\cdot}06 \tag{8}$$

where $h\nu_{CT}$ is the charge-transfer energy of TNF adducts and m_{hoo} is the energy of the highest occupied orbital of the neutral polynuclear aromatic hydrocarbons which act as π-donors. The results are indicated in Table 2.

† 

TNF = 2,4,7-trinitro-9-fluorenone

(v) *Stability*. The specific delocalization energy, DE_s, obtained on dividing the delocalization energy by a number of the C—C σ bonds has received some application[11] as a criteria of stability. The value of this quantity for the hydrocarbons studied here lies between 0·34 β and 0·35 β which is approximately the value found for stable molecules.

(c) *Bond length calculations*

For five of the newly synthesized polynuclear hydrocarbons, self-consistent bond-lengths are obtained by the iterative HMO procedure (IHMO). The IHMO procedure involves a functional dependence of bond-length on bond-order and also a functional dependence of the non-zero off-diagonal matrix element in the H matrix (i.e. H) of the matrix representation of the solution of Schrödinger wave equation of conjugated polyenes on bond-length. The two functional forms given by Coulson and Skancke[10] are used for an iterative procedure.

$$R_{lm}^{n} = 1{\cdot}515 - \frac{0{\cdot}18}{1 + (1{\cdot}05\,(1 - p_{lm}^{n})/p_{lm}^{n})} \tag{9}$$

and

$$H_{lm}^{n+1} = H_{lm}^{\circ} \exp\left[-(R_{lm}^{n} - R_s)/0{\cdot}3106\right] \tag{10}\dagger$$

where R_{lm} represents the bond length in Å and p_{lm} refers to the bond order—for the l—m bond, H_{lm} is the matrix element, R_s is the standard carbon–carbon bond distance in benzene. The superscript indicates the number of iterations.

IHMO calculations showed that all the five molecules taken for study show converging results even after the third iteration. Self-consistent bond orders and bond lengths obtained after six iterations are shown in Table 3.

DISCUSSION

Although only compounds **1**, **2**, **3**, **4** and **5** have been synthesized, the calculated properties (in particular the specific delocalization energy) would indicate that it may well be possible to synthesize other members of the group. Further, the low ionization potential and high electron affinity of, for example, naphtho(1.2-a)perylene would indicate that the cation and anion radicals may be stable and their synthesis can be attempted. Comparison‡ of Δm for compounds **11** and **9** or of **11** with **7** and **1** may indicate the contribution of the common structural unit to the characteristics of the molecule. The TNF adducts of the newly synthesized compounds have been isolated[1] and although the charge-transfer energy spectra of these adducts were not obtained, the calculations seem to show that naphtho(1.2-a)perylene—TNF adducts of other members, e.g. dibenzo(de.op)pentacene, with similar low charge-transfer energies could be formed. Further, since some of the compounds, e.g. Benzo(e)naphtho(1.2-b)-pyrene, form TNF adducts which can be isolated in the solid phase, irradiation at the charge-transfer frequency could produce trapped radicals.

No X-ray work has been done on any of these newly synthesized hydrocarbons. The crystallographic work may be hindered because of the fact that none of these

† $H_{lm}^{\circ} = \beta^{\circ}$.

‡ We are indebted to the referee for this suggestion.

TABLE 3. SELF-CONSISTENT BOND ORDERS AND BOND-LENGTHS BENZO(E)NAPHTHO-(1.2.-b)PYRENE

Centre	Centre	Bond order (self-consistent iter)	Bond length Å (self-consistent iter)
1	2	0·6004	1·409
1	26	0·7201	1·387
2	3	0·7246	1·386
3	4	0·5718	1·414
4	5	0·4538	1·435
4	25	0·5801	1·413
5	6	0·8131	1·370
6	7	0·4682	1·433
7	8	0·5529	1·418
7	24	0·5560	1·417
8	9	0·4064	1·444
8	28	0·5895	1·411
9	10	0·5938	1·410
9	14	0·5869	1·412
10	11	0·7078	1·389
11	12	0·6174	1·406
12	13	0·7052	1·390
13	14	0·5999	1·409
14	15	0·3910	1·447
15	16	0·6334	1·403
15	27	0·5543	1·417
16	17	0·6551	1·399
17	18	0·6787	1·395
18	19	0·6062	1·408
19	20	0·4381	1·438
19	27	0·5564	1·417
20	21	0·8294	1·367
21	22	0·4392	1·438
22	23	0·6408	1·402
22	28	0·5170	1·424
23	24	0·6118	1·407
24	25	0·4206	1·441
25	26	0·5831	1·412
27	28	0·4738	1·432

TABLE 3—*continued*

Naphtho(2.3.-1)benzo(a)pyrene

Centre	Centre	Bond order (self-consistent iter)	Bond length Å (self-consistent iter)
1	2	0·4297	1·440
1	26	0·8361	1·366
2	3	0·6056	1·408
2	28	0·5635	1·416
3	4	0·6805	1·394
4	5	0·6525	1·400
5	6	0·6374	1·402
6	7	0·3783	1·449
6	28	0·5589	1·417
7	8	0·6896	1·393
7	16	0·5022	1·427
8	9	0·5688	1·415
9	10	0·5155	1·424
9	14	0·5294	1·422
10	11	0·7688	1·378
11	12	0·5436	1·419
12	13	0·7697	1·378
13	14	0·5133	1·425
14	15	0·5731	1·414
15	16	0·6802	1·394
16	17	0·3980	1·445
17	18	0·5237	1·423
17	27	0·6170	1·406
18	19	0·5332	1·421
18	23	0·5353	1·421
19	20	0·7594	1·380
20	21	0·5508	1·418
21	22	0·7659	1·379
22	23	0·5161	1·424
23	24	0·5680	1·415
24	25	0·6699	1·396
25	26	0·4280	1·440
25	27	0·4980	1·428
27	28	0·4583	1·435

TABLE 3—*continued*

Naphtho(2.1.-1)benzo(a)pyrene

Centre	Centre	Bond order (self-consistent iter)	Bond length Å (self-consistent iter)
1	2	0·4275	1·440
1	26	0·8376	1·365
2	3	0·6220	1·405
2	28	0·5476	1·419
3	4	0·6617	1·398
4	5	0·6720	1·396
5	6	0·6137	1·407
6	7	0·4189	1·442
6	28	0·5536	1·418
7	8	0·5109	1·425
7	16	0·6364	1·402
8	9	0·7831	1·376
9	10	0·4939	1·428
10	11	0·5500	1·418
10	15	0·5668	1·415
11	12	0·7431	1·383
12	13	0·5782	1·413
13	14	0·7406	1·383
14	15	0·5563	1·417
15	16	0·4724	1·432
16	17	0·4483	1·436
17	18	0·5036	1·427
17	27	0·6029	1·409
18	19	0·5435	1·419
18	23	0·5419	1·420
19	20	0·7520	1·381
20	21	0·5590	1·417
21	22	0·7598	1·380
22	23	0·5233	1·423
23	24	0·5548	1·417
24	25	0·6797	1·395
25	26	0·4257	1·440
25	27	0·4881	1·429
27	28	0·4851	1·430

TABLE 3—*continued*

Naphtho(1.2-a)perylene

Centre	Centre	Bond order (self-consistent iter)	Bond length Å self-consistent iter)
1	2	0·5962	1·410
1	26	0·6801	1·395
2	3	0·7355	1·384
3	4	0·5338	1·421
4	5	0·5340	1·421
4	27	0·5535	1·418
5	6	0·7373	1·384
6	7	0·5937	1·410
7	8	0·6855	1·394
8	9	0·3602	1·452
8	27	0·5199	1·424
9	10	0·6978	1·391
9	28	0·5029	1·427
10	11	0·5758	1·414
11	12	0·7508	1·382
12	13	0·5147	1·325
13	14	0·5837	1·412
13	28	0·5217	1·423
14	15	0·6496	1·400
15	16	0·4314	1·439
15	24	0·5223	1·423
16	17	0·8331	1·366
17	18	0·4358	1·439
18	19	0·5824	1·412
18	23	0·5800	1·413
19	20	0·7165	1·388
20	21	0·6065	1·408
21	22	0·7160	1·388
22	23	0·5845	1·412
23	24	0·4248	1·441
24	25	0·6048	1·408
25	26	0·3772	1·449
25	28	0·5595	1·416
26	27	0·5149	1·425

TABLE 3—*continued*

Naphtho(1.2.-1)benzo(a)pyrene

Centre	Centre	Bond order (self-consistent iter)	Bond length Å (self-consistent iter)
1	2	0·6603	1·398
1	26	0·6222	1·405
2	3	0·6742	1·396
3	4	0·6100	1·407
4	5	0·4283	1·440
4	28	0·5520	1·418
5	6	0·4791	1·431
5	14	0·6377	1·402
6	7	0·5539	1·417
6	11	0·5656	1·415
7	8	0·7419	1·383
8	9	0·5775	1·413
9	10	0·7428	1·383
10	11	0·5510	1·418
11	12	0·4921	1·429
12	13	0·7877	1·375
13	14	0·5023	1·427
14	15	0·4376	1·438
15	16	0·5065	1·426
15	27	0·6062	1·408
16	17	0·5421	1·420
16	21	0·5416	1·420
17	18	0·7529	1·381
18	19	0·5583	1·417
19	20	0·7602	1·380
20	21	0·5230	1·423
21	22	0·5552	1·417
22	23	0·6806	1·394
23	24	0·4256	1·441
23	27	0·4870	1·430
24	25	0·8378	1·365
25	26	0·4270	1·440
26	28	0·5481	1·419
27	28	0·4847	1·430

molecules possesses any symmetry, making crystal structure determination more laborious. It is well known that calculated bond lengths of many polynuclear aromatic hydrocarbons are in excellent agreement with the experiment. Even in some of the polynuclear aromatic hydrocarbons for which X-ray work indicated non-planarity, theoretically-predicted bondlengths are in agreement with the experimentally reported values. Consequently the bondlengths reported for these asymmetric species may be of assistance in the X-ray analysis.

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