

Quantum-Chemical Treatment of Cyclization Reactions: XXIV.* Superposition–Additivity Approach

Yu. B. Vysotskii, Ya. V. Zaikovskaya, and I. N. Solonskii

Donbass State Academy of Building Construction and Architecture,
ul. Derzhavina 2, Makeevka, Donetsk oblast, 339023 Ukraine

Received August 26, 1998

Abstract—The superposition–additivity approach which is characterized by a very simple calculation scheme provides a sufficiently reliable description of electronic structure, physicochemical parameters, and chemical behavior (specifically, in electrocyclic ring closure reactions) of large organic molecules with conjugated double bonds on the basis of the calculation or experimental data for less extended analogs.

We previously reported [2] on the application of the constrained perturbation theory to description of the effect of aromatic fusion on the reactivity indices of hexatrienes in electrocyclic ring-closing reactions. This approach was shown to reliably reflect the relations found in [3] for the effect of fusion on the electrocyclization of 1,3,5-hexatriene. It should be emphasized that the zero-order perturbation theory gives the energy of a fused system in the following form:

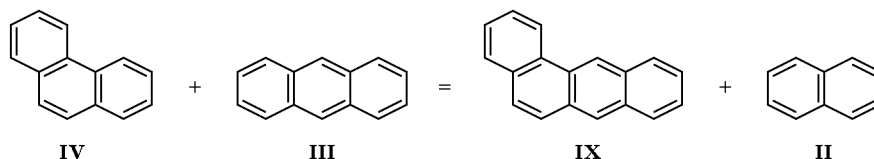
$$E^{AB} = E^A + E^B - E^E, \quad (1)$$

where E^A and E^B are the energies of the fused fragments, and E^E is the energy of the ethylene molecule which corresponds to the common part of molecular graphs **A** and **B** formed by their superposition [2]. An analogous expression can be written for orders of bonds, residual charges, and other parameters, since the latter can be obtained by differentiation of the energy with respect to the resonance and Coulomb integrals and small parameters of external perturbations. We can presume that expressions like (1) should also be valid not only for aromatic fusion but also

for combination (superposition) of any molecular graphs, i.e., when the region of overlap is more complex. The main postulate of the superposition–additivity approach is that superposition of molecular graphs (structures) is characterized by additivity of atom contributions to chemical bonds. When the same result can be obtained by different methods, i.e., by superposition of different molecular graphs (e.g., phenanthrene and anthracene or benzanthracene and naphthalene), the molecular structure and properties of one molecule can be derived from the structures (properties) of the three others. For the above structures, we can write the following superposition–additivity scheme: benzanthracene = phenanthrene + anthracene – naphthalene (Scheme 1). This approach was applied by us previously [4] to oxazolium ion, and we showed that its electronic structure parameters can be represented as the sums of the corresponding values for furan and pyrrole minus those for cyclopentadienyl anion. In this case, the numbers of π -electron centers in all graphs being superimposed were similar.

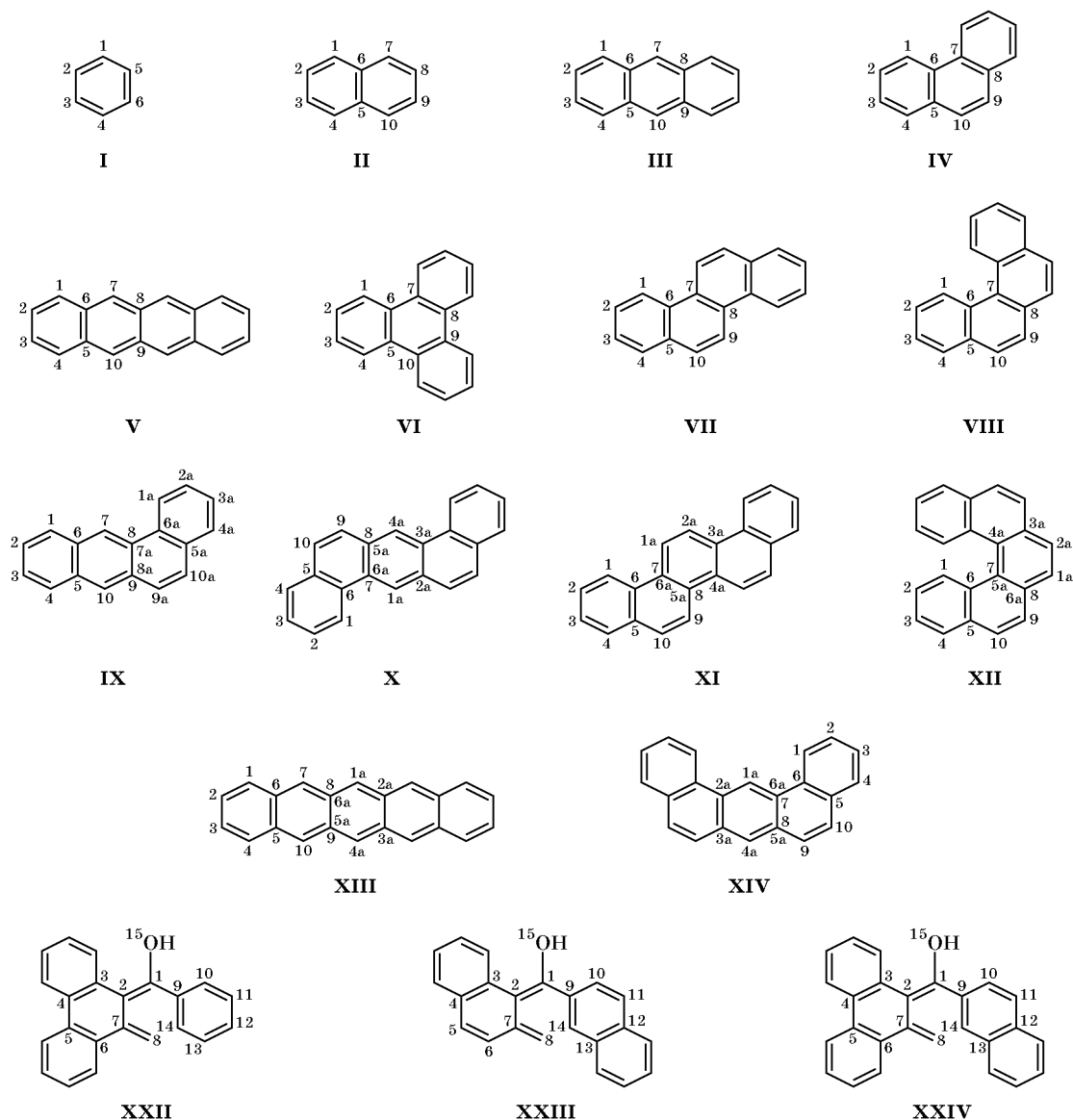
Calculation of the energies of polynuclear aromatic hydrocarbons using Eq. (1) with variation of graphs

Scheme 1.



* For communication XXIII, see [1].

Scheme 2.



A and **B** (Scheme 2) well reproduces the results of direct calculations. Taking into account that these quantities are closely related to the enthalpies of formation ΔH_f^0 and enthalpies of atomization ΔH_{at}^0 whose experimental values are available [5–8], Table 1 contains ΔH_{at}^0 values calculated by the superposition–additivity (SA) scheme [Eq. (1)]. In terms of the SA approach, both calculation (SA-I) and experimental data (SA-II) can be taken as initial parameters. The following ΔH_{at}^0 values for ethylene and butadiene were used, kcal/mol: 528.1 (537.7) and 976.3 (969.7), respectively (the experimental data [6] are given in parentheses); the direct calculations were performed by the formulas given in [5].

The data in Table 1 show that the superposition–additivity scheme well reproduces both the direct calculation and experimental data; however, it does not reflect differences between linear and angular isomers: the resulting value is approximately equal to the halfsum of the corresponding parameters for the same molecular graphs (cf. **III** and **IV**, **VI** and **VII**, and **X** and **XIV**). When isomeric structures are described by different superposition schemes (cf. **VIII** and **IX**, **X** and **XIII**), the SA calculations provide reliable description of the existing differences.

It should be noted that better coincidence between the results of SA and direct calculation (or experimental data) is observed for structures with larger

region of overlap of two superimposed molecules. As an example, below are given the results of calculations of the enthalpy of atomization of pentacene molecule (XIII), performed for superposition of different molecular graphs, kcal/mol: $V + I - E = 4413.4$; $V + II - I = 4395.2$; $V + III - II = 4390.7$; $2V - III = 4389.6$; 4389.5 kcal/mol is the value obtained by direct calculation. Numerous other examples can be given; using Table 1, everybody can make sure that the above statement is valid. Therefore, Table 1 contains calculation results for the scheme corresponding to maximal region of overlap of graphs A and B.

It should be emphasized that the SA scheme provides reliable description of not only *ortho*- but also *peri*-fused systems (molecules XVI, XVII, and XIX), as well as bridged systems (e.g., XV), non-alternant hydrocarbons (XX, XXI), and molecules containing antiaromatic $4n$ -rings [e.g., biphenylene (XVIII)] (Table 1). Probably, the SA approach can be extended to heterocyclic molecules, radicals, ions,

and carbene-like species and to calculation of other physicochemical parameters.

As an illustration of the potential of the SA scheme, Table 1 also contains the results of calculation of the dipole polarizabilities and molar diamagnetic susceptibilities. The SA calculations were performed on the basis of direct calculation data, according to which $\alpha = 41.1$ and $80.53 \times 10^{-24} \text{ cm}^3$ [8] and $\chi_m = -18.05$ and $-32.49 \times 10^{-6} \text{ cm}^3/\text{mol}$, respectively, for ethylene and butadiene (the values were calculated by the procedure reported in [9]). The calculated data show a good agreement with the experimental values (see [9, 10] and references therein). As above stated, better reproducibility of the experimental data was observed for schemes involving larger region of overlap. The greatest discrepancy between the SA and precise calculations of χ_m was found for the coronene molecule. Presumably, the reason is that an additional aromatic ring appears as a result of superposition, which is not taken into

Table 1. Enthalpies of atomization, dipole polarizabilities $\bar{\alpha}$, and diamagnetic susceptibilities χ_m of aromatic hydrocarbons

Comp. no.	Compound name	Scheme	ΔH_{at} , kcal/mol				
			calculation			experiment	
			SA-I	SA-II	direct	[5]	[7, 8]
I	Benzene	–	–	–	1318.26	1399.34	1318.16
II	Naphthalene	2I–E ^a	2108.4	2089.6	2089.28	2089.7	2089.6
III	Anthracene	2II–I	2860.3	2860.1	2856.8	2858.4	2858.0
IV	Phenanthrene	2II–I	2860.3	2860.1	2865.3	2864.14	2858.4
V	Tetracene	2III–II	3624.3	3627.2	3623.2	3633.5	3633.3
VI	Triphenylene	2IV–II	3641.7	3638.6	3645.0	3638.1	3631.7
VII	Chrysene	2IV–II	3641.7	3638.6	3640.2	3637.4	3637.3
VIII	Benzo[<i>c</i>]phenanthrene	2IV–II	3641.7	3638.6	3640.0 ^b	–	3631.5
IX	Benz[<i>a</i>]anthracene	IV+III–II	3633.0	3632.9	3634.4 ^b	–	3631.7
X	Dibenz[<i>a,h</i>]anthracene	2IX–III	4412.0	4405.4	4411.5 ^b	–	–
XI	Picene	2VII–IV	4414.9	4410.7	4415.4 ^b	–	–
XII	Dibenzo[<i>c,d</i>]phenanthrene	2VIII–IV	4414.5	4404.6	4415.1 ^b	–	–
XIII	Pentacene	2V–III	4389.6	4408.6	4389.5 ^b	–	–
XIV	Dibenz[<i>a,j</i>]anthracene	2IX–III	4412.0	4405.4	4411.5 ^b	–	–
XV	Biphenyl	2I–2E–Bu ^c	2556.6	2540.9	2531.2	2528.4	2531.1
XVI	Pyrene	2IV–XV	3199.8	3199.9	3198.6	–	3202.7
XVII	Perylene	2II–4E–2Bu	4018.8	3993.2	3973.4	–	3967.4
XVIII	Biphenylene	2I–4E+2Bu	2476.7	2452.5	2399.4 ^b	–	2352.1
XIX	Coronene	2IX–2I	4641.4	–	4653.9 ^b	–	–
XX	Acenaphthylene	II–3E+2Bu	2457.6	2434.2	2399.9	2405.9	2405.6
XXI	Fluoranthene	1+II–4E+2Bu	3247.7	3222.8	3188.4	3185.0	3184.8

Table 1. (Contd.)

Comp. no.	$\bar{\alpha} \times 10^{-24}, \text{ cm}^3$			$\chi_m \times 10^{-6}, \text{ cm}^3/\text{mol}$		
	calculation		experiment	calculation		experiment
	SA	direct		SA	direct	
I	–	95.2	98.7; 99	–	53.7	54.8
II	152.4	169.0	165.7; 173.6	89.4	91.2	91.9
III	242.8	252.3	253.3; 253.7	128.7	130.0	130.0
IV	242.8	239.7	253.3; 246.7	128.7	128.1	127.9
V	335.6	345.2	328.3	168.8	169.4	168.0
VI	310.4	310.0	306.3	165.0	161.4	156.6
VII	310.4	322.0	318.2; 328	165.0	164.7	167.0
VIII	310.4	315.3	–	165.0	165.1	–
IX	323.0	328.2	328.6	166.9	164.7	172.5
X	404.1	403.3 ^d	413; 406.1	199.4	203.2	192.7
XI	404.3	403.0	–	201.3	202.3	–
XII	320.9	–	–	202.1	202.1	–
XIII	438.1	440.5	–	208.8	207.0	–
XIV	404.1	399.5	–	199.4	200.8	–
XV	188.7	–	–	103.6	108.2	103.3
XVI	290.7	291.9 ^d	282; 293.3	153.0	153.0	155.0
XVII	334.7	378.9 ^d	–	175.2	175.7	171
XVIII	187.1	–	–	100.2	90.3	88±3
XIX	433.5	437.7	424.9; 447.7	222.8	250.6	–
XX	206.8	–	–	102.1	99.6	105
XXI	260.9	284.3 ^d	282; 293.3	153.0	153.0	155

^a Ethylene.

^b Calculated according to [5].

^c Butadiene.

^d Data of [8]; the other $\bar{\alpha}$ and χ_m values were calculated according to [9].

account by the SA scheme (2**VIII** – 2**I** gives $4 \times 2 - 2 = 6$ aromatic rings against the seven rings present).

Apart from treatment of the quantities χ_m and $\bar{\alpha}$, the proposed approach is also applicable to π -electron contributions to these quantities. Let us briefly consider the relative π -electron diamagnetic susceptibilities $\chi' = \chi^\pi / \chi_{\text{CH}}^\pi$ which can be regarded as aromaticity indices (see, e.g., [11]; the relation between the aromaticity and electrocyclization indices will be discussed elsewhere). In terms of the SA approach, the relative diamagnetic susceptibility χ' of benzoid hydrocarbons is the result of repeated benzene ring fusion; taking into account that π -electron contribution to diamagnetic susceptibility of ethylene is equal to zero, the χ' value of a polynuclear benzoid hydrocarbon will be equal to the number of benzene rings. This is the real case [12]. It corresponds to a simple additivity schemes, and the error

of such description increases with increase in the number of benzene rings. The accuracy of the SA scheme increases as the region of overlap of superimposed graphs rises (see above). For example, the use of different superposition schemes for the penta-cene molecule gives the following χ' values: 5**I** – 4**E** = 5.000; 2**III** – **I** = 5.846; **V** + **III** – **II** = 5.962; 2**V** – **III** = 5.999; the direct calculation gives 6.018.

Insofar as the π -electron ring current matrix can be expressed through elements of the density matrix and appropriate correction for magnetic field induction [13], the SA approach can also be applied to description of π -electron ring currents. As stated above, the best results are obtained for superimposition of structures with maximal overlap region. Below are given the ring currents calculated by the SA scheme under the condition of maximal overlap of the superimposed structures (in parentheses are given

the results of direct calculation): tetracene: $i_A = 1.071$ (1.051), $i_B = 1.266$ (1.330); chrysene: $i_A = 1.131$ (1.143), $i_B = 1.012$ (1.065); pentacene: $i_A = 1.051$ (1.038), $i_B = 1.310$ (1.297), $i_C = 1.379$ (1.348); hexacene: $i_A = 1.038$ (1.032), $i_B = 1.284$ (1.288), $i_C = 1.315$ (1.348).

Unlike such integral parameters as ΔH_{at}^0 , $\bar{\alpha}$, χ_m , and even π -electron ring currents, the superposition-additivity treatment of tensor components of diamagnetic susceptibility, dipole polarizability, dipole moments, and other vector and local molecular parameters gives, in keeping with experimental data, different values for different isomers. First of all, this is the result of the vector (tensor) character of the above quantities and the necessity of taking into account mutual arrangement of the molecular graphs being superimposed. As an example, below are given the calculated proton chemical shifts of dibenz[*a,h*]-anthracene, δ , ppm: 1-H: 8.67, 8.77 (8.70, 8.80); 2-H: 7.52, 7.59 (7.56, 7.62); 3-H: 7.51, 7.52 (7.59, 7.55); 4-H: 7.77, 7.75 (7.87, 7.82); 5-H: 7.79, 7.63 (7.84, 7.67); 6-H: 7.89, 7.82 (7.92, 7.88); 7-H: 9.15, 8.97 (9.18, 9.07). Here, the first value was obtained by the direct SA calculation, and the second, by SA calculation on the basis of experimental data [14]; the first value in parentheses correspond to the direct calculation, and the second is experimental value [14]. It is seen that the SA calculation results are well consistent with the experimental data.

Another example illustrates SA treatment of ^{13}C chemical shifts of chrysene (the values are given in the same order as above; the experimental ^{13}C chemical shifts were taken from [15, 16]), δ_C , ppm: C^1 : 127.0, 122.4 (126.8, 128.5); C^2 : 126.3, 126.3 (126.4, 126.3); C^3 : 126.3, 126.3 (126.4, 126.6); C^4 : 126.7, 128.3 (127.0, 123.1); C^{4a} : 131.8, 124.8 (132.3, 130.5); C^{4b} : 132.8, 128.5 (132.9, 128.2); C^5 : 127.6, 127.2 (127.8, 127.2); C^6 : 127.6, 127.3 (127.4, 127.3); C^{6a} : 132.1, 132.6 (131.8, 132.1). The δ_C values of pentacene dication, calculated by the SA method from experimental data [17] (in parentheses) according to the scheme **2IV** – **III**, are as follows, ppm: C^1 : 150.1 (144.1); C^2 : 138.5 (142.9); C^5 : 157.2 (163.4); C^6 : 158.8 (171.6); C^{4a} : 131.4 (134.5); C^{5a} : 141.7 (139.8). We can conclude that the superposition-additivity approach provides adequate description of magnetic shielding of carbon nuclei. Greater deviations from the experimental values for dications may be due to effect of the counterion.

As a final illustration of applications of the SA scheme for description of physicochemical parameters of molecules, we give hyperfine coupling constants

(μT) with protons in the ESR spectra of radical anions derived quinoxaline, and 1,5- and 1,8-naphthyridines, which were obtained on the basis of the calculated data for quinoline and naphthalene radical anions [18]. Quinoxaline: $a_{\text{H}} = 290$ (293, 333, 327), $a_{5\text{-H}} = 216$ (214, 238, 222), $a_{6\text{-H}} = 146$ (150, 145, 140); 1,5-naphthyridine: $a_{2\text{-H}} = 313$ (317, 295, 289), $a_{3\text{-H}} = 122$ (125, 169, 172), $a_{4\text{-H}} = 518$ (517, 577, 570); 1,8-naphthyridine: $a_{2\text{-H}} = 402$ (405, 438, 398), $a_{3\text{-H}} = 34$ (37, 50, 73), $a_{4\text{-H}} = 600$ (597, 669, 639). The first number in parentheses was calculated by the direct method [18], and the others are experimental values given in the same publication.

When studying thermal isomerizations, the most interesting parameters are long-range orders of bonds $P_{ik}(0)$ which characterize electrocyclic ring-closing reactions. Naturally, these parameters can be determined using the superposition-additivity approach. Table 2 contains the results of direct calculation and calculation by the SA scheme of some bond orders between chemically nonbonded atoms in alternant hydrocarbons, which were chosen in such a way that the region of overlap of the superimposed molecular graphs be the largest possible. For convenience, the atoms were numbered as shown in Scheme 2. It is seen that the results of SA calculations agree well with the direct calculation data, and the agreement becomes better as the region of overlap of the superimposed structures increases. When the region of overlap of structures **A** and **B** ($\mathbf{A} \cap \mathbf{B}$) corresponds to benzene molecule and the number of bonds n is 17, the standard deviation for the direct and SA calculation $S_0 = 0.031$; when $\mathbf{A} \cap \mathbf{B} =$ naphthalene and $n = 60$, $S_0 = 0.011$; and when $\mathbf{A} \cap \mathbf{B} =$ anthracene or phenanthrene and $n = 70$, $S_0 = 0.003$.

Table 3 contains analogous results for the quantity $P_{ik}(0)$ (for details of construction of Table 3, see [2, 3]). Here, for $\mathbf{A} \cap \mathbf{B} =$ benzene and $n = 17$, $S_0 = 0.046$; for $\mathbf{A} \cap \mathbf{B} =$ naphthalene and $n = 60$, $S_0 = 0.017$. Hence we expect for $\mathbf{A} \cap \mathbf{B} =$ anthracene or phenanthrene (compounds **X–XIV**, Table 3) $S_0 < 0.005$. These data are sufficiently reliable; taking into account that the $P_{ik}(0)$ indices for 70 22-atom hexatrienes were calculated without a computer on the basis of data given in [3], advantages of the proposed procedure become obvious. Analysis of the data presented in this work shows that the conclusions drawn for tetracyclic fused systems can be extended to pentacyclic systems.

In particular, the SA approach can be applied to the Elbs reaction [19, 20]. Using the electronic structure parameters of six tricyclic intermediates of the Elbs reaction (see Table 1 in [20]), the SA calculation

Table 2. Orders of bonds $P_{ik}(0)$ in benzoid hydrocarbons, calculated by the superposition–additivity scheme

Comp. no.	Calculation scheme	Order of broken bond											
		1–2	2–3	3–4	4–5	5–6	6–1	6–7	7–8	8–9	9–10	10–5	
I	Direct	0.667											
II	Direct	0.733	0.596	0.733	0.532	0.546							
III	Direct	0.749	0.576	0.749	0.520	0.496	0.521	0.607					
	2II–I	0.733	0.596	0.733	0.532	0.475 ^a	0.532	0.598					
IV	Direct	0.708	0.620	0.712	0.573	0.558	0.585	0.445	0.558	0.487	0.792		
	2II–I	0.733	0.596	0.733	0.532	0.612	0.532	0.397	0.612	0.461	0.799		
V	Direct	0.754	0.570	0.754	0.514	0.485	0.514	0.623	0.579	0.469			
	2III–II	0.749	0.576	0.749	0.521	0.475	0.521	0.623	0.596	0.445			
VI	Direct	0.692	0.638	0.692	0.604	0.576	0.604	0.407					
	2IV–II	0.687	0.644	0.687	0.585	0.570	0.626	0.400					
VII	Direct	0.714	0.673	0.719	0.564	0.551	0.576	0.465	0.593	0.523	0.770	0.506	
	2IV–II	0.708	0.620	0.712	0.573	0.537	0.585	0.486	0.570	0.540	0.767	0.511	
VIII	Direct	0.716	0.612	0.718	0.565	0.548	0.572	0.476	0.594	0.510	0.775	0.505	
	2IV–II	0.708	0.620	0.712	0.573	0.533	0.585	0.498	0.570	0.528	0.771	0.511	
IX	Direct	0.742	0.584	0.743	0.531	0.509	0.532	0.581	0.650	0.511	0.637	0.586	
		0.700 ^b	0.627	0.705	0.581	0.652	0.594	0.428	0.511	0.470	0.804	0.472	
	III+IV–II	0.749	0.576	0.749	0.521	0.520	0.521	0.582	0.660	0.508	0.643	0.586	
		0.708 ^b	0.620	0.712	0.573	0.574	0.585	0.434	0.508	0.476	0.808	0.467	
X	Direct	0.703	0.624	0.708	0.578	0.560	0.591	0.434	0.527	0.478	0.799	0.478	
		0.610 ^b	0.527	0.629									
	2IX–III	0.700	0.627	0.705	0.581	0.556	0.594	0.438	0.524	0.481	0.797	0.480	
		0.611 ^b	0.524	0.629									
XI	Direct	0.712	0.615	0.716	0.567	0.553	0.580	0.458	0.582	0.514	0.776	0.500	
		0.746 ^b	0.544	0.582	0.488								
	2VII–IV	0.714	0.613	0.719	0.564	0.558	0.576	0.456	0.586	0.514	0.776	0.499	
		0.748 ^b	0.542	0.586									
XII	Direct	0.712	0.615	0.716	0.568	0.551	0.577	0.466	0.580	0.504	0.780	0.504	
		0.757 ^b	0.530	0.580	0.515								
	2VIII–IV	0.716	0.612	0.718	0.565	0.556	0.572	0.463	0.584	0.502	0.781	0.497	
		0.758 ^b	0.528	0.584	0.507								
XIII	Direct	0.756	0.567	0.756	0.512	0.481	0.512	0.629	0.571	0.460	0.571	0.629	
		0.595 ^b											
	2V–III	0.754	0.570	0.754	0.514	0.479	0.514	0.628	0.572	0.458	0.572	0.628	
	0.595 ^b												
XIV	Direct	0.704	0.634	0.708	0.578	0.560	0.590	0.436	0.528	0.476	0.799	0.478	
		0.624 ^b	0.528	0.615									
	2IX–III	0.700	0.627	0.706	0.581	0.555	0.594	0.439	0.524	0.480	0.798	0.480	
		0.624 ^b	0.524	0.616									

^a For atom numbering, see Scheme 2.^b The values given in the second line refer to the bonds with 1a, 2a, etc. indices (e.g., for benz[*a*]anthracene, $P_{1a,2a} = 0.700$).

Table 3. Electrocyclic ring-closing indices $P_{ik}(0)$ of 1,3,5-hexatrienes into cyclodienes, calculated by the superposition-additivity scheme

Comp. no.	Calculation scheme	Order of broken bond											
		1-2	2-3	3-4	4-5	5-6	6-1	6-7	7-8	8-9	9-10	10-5	
I	Direct	0.296											
II	Direct	0.335	0.109	0.335	0.163	0.229							
III	Direct	0.415	0.132	0.415	0.127	0.174	0.127	0.211					
	2II-I	0.385	0.169	0.385	0.163	0.102	0.163	0.252					
IV	Direct	0.335	0.203	0.338	0.157	0.250	0.199	0.090	0.250	0.092	0.496		
	2II-I	0.385	0.169	0.385	0.163	0.318	0.163	0.030	0.318	0.036	0.474		
V	Direct	0.425	0.120	0.425	0.115	0.164	0.115	0.228	0.161	0.144			
	2III-II	0.415	0.132	0.415	0.127	0.137	0.127	0.241	0.175	0.119			
VI	Direct	0.307	0.232	0.307	0.229	0.260	0.229	0.050					
	2IV-II	0.288	0.237	0.288	0.233	0.271	0.233	0.019					
VII	Direct	0.349	0.191	0.352	0.185	0.242	0.187	0.108	0.288	0.112	0.433	0.110	
	2IV-II	0.335	0.203	0.338	0.197	0.203	0.199	0.124	0.271	0.128	0.446	0.126	
VIII	Direct	0.349	0.190	0.351	0.184	0.239	0.185	0.109	0.291	0.111	0.443	0.110	
	2IV-II	0.335	0.203	0.338	0.197	0.200	0.199	0.126	0.271	0.125	0.449	0.126	
IX	Direct	0.398	0.145	0.399	0.136	0.192	0.140	0.182	0.262	0.171	0.257	0.184	
		0.317 ^a	0.213	0.321	0.206	0.252	0.210	0.070	0.171	0.072	0.528	0.072	
	III+IV-II	0.415	0.132	0.415	0.132	0.208	0.127	0.161	0.247	0.195	0.245	0.164	
		0.335 ^a	0.203	0.338	0.197	0.280	0.199	0.054	0.195	0.056	0.536	0.055	
X	2IX-III	0.338	0.203	0.335	0.197	0.230	0.199	0.079	0.189	0.085	0.511	0.085	
		0.228 ^a	0.189	0.235									
XI	2VII-IV	0.349	0.191	0.352	0.185	0.256	0.187	0.096	0.280	0.100	0.447	0.098	
		0.370 ^a	0.130	0.280	0.126								
XII	2VIII-IV	0.349	0.190	0.351	0.184	0.253	0.185	0.095	0.280	0.098	0.456	0.097	
		0.390 ^a	0.129	0.280	0.128								
XIII	2V-III	0.425	0.120	0.425	0.115	0.142	0.115	0.238	0.149	0.124	0.149	0.238	
		0.178 ^a											
XIV	2IX-III	0.177	0.213	0.321	0.206	0.235	0.210	0.083	0.189	0.051	0.512	0.085	
		0.233 ^a	0.189	0.230									

^a See note ^b to Table 2.

gives residual π -electron charges and orders of bonds (including long-range ones) for 18 tetra- and pentacyclic intermediates, e.g., structures **XXII-XXIV** (see Scheme 2; the atom numbering is the same as in [20]). Comparison with the intermediates described in [20] shows that molecular graphs **XXII-XXIV** can be represented by the following SA schemes: **XXII** = **IIIa** + **VIa** - **Ia**; **XXIII** = **IIIa** + **VIIa** - **Ia**; **XXIV** = **XXII** + **XXIII** - **IIIa** (structures **Ia**, **IIIa**, **VIa**, and **VIIa**, as well as the corresponding parameters, were given in [20]). Taking into account that the maximal

charge is localized on the oxygen atom and on the hexatriene fragment, the applicability of the SA method to charge distribution is illustrated below by the calculated residual π -electron charges on these atoms, orders of bonds in the hexatriene fragment, and orders of closing bonds. As above, the values obtained by direct calculation are given in parentheses. For compounds **XXII-XXIV** we obtained, respectively: $P_{1,1} = 0.106$ (0.108), 0.108 (0.108), 0.107 (0.107); $P_{2,2} = -0.099$ (-0.101), -0.102 (-0.102), -0.099 (-0.098); $P_{7,7} = 0.002$ (0.002), 0.002 (0.002), 0.002

(0.002); $P_{8,8} = -0.086$ (-0.085), -0.089 (-0.088), -0.088 (-0.086); $P_{9,9} = -0.030$ (-0.033), -0.029 (-0.030), -0.033 (-0.035); $P_{14,14} = 0.025$ (0.025), 0.026 (0.026), 0.030 (0.031); $P_{15,15} = 0.116$ (0.116), 0.117 (0.117), 0.116 (0.116). The maximal deviation from the direct calculation values is about 0.002. A similar pattern is observed for the orders of bonds: $P_{1,2} = 0.677$ (0.676), 0.685 (0.684), 0.673 (0.673); $P_{2,7} = 0.416$ (0.416), 0.414 (0.414), 0.419 (0.420); $P_{7,8} = 0.786$ (0.786), 0.788 (0.787), 0.782 (0.783); $P_{1,9} = 0.427$ (0.431), 0.410 (0.409), 0.434 (0.437); $P_{9,14} = 0.655$ (0.651), 0.663 (0.660), 0.702 (0.711). The long-range bond orders $P_{8,14}(0)$ are equal, respectively, to 0.212 (0.218), 0.215 (0.222), 0.249 (0.254).

Analogous calculations can be performed for the other naphtho-naphtho, benzo-phenanthreno, naphtho-phenanthreno, and phenanthreno-phenanthreno 3-hydroxyhexatrienes fused through the 1-2 and 4-5 bonds. Comparison of the calculated data for these structures with those given in Table 3 shows that, as with compound **1a** [19], introduction of a hydroxy group into position 3 somewhat reduces the order of the closing bond (approximately by 0.012).

As might be expected [2, 3], the greatest decrease in $P_{8,14}(0)$ is observed on simultaneous closure of 3-hydroxyhexatriene by an essentially single bond at the 1-2 bond (in the above-considered cases, by the C^2-C^3 bond of naphthalene; see Table 2) and by an essentially double bond at the 4-5 bond (in the given case, by the C^9-C^{10} bond of phenanthrene). We thus obtain a structure with $P_{8,14}(0) = 0.097$. Naturally, the greatest increase in the order of the same long-range bond is observed in the opposite case: closure at the hexatriene 1-2 bond by an essentially double bond of phenanthrene (e.g., C^9-C^{10}) or at the 4-5 bond by an essentially single bond, e.g., C^2-C^3 of naphthalene. In the resulting structure, $P_{8,14}(0) = 0.307$ (cf. [2, 3]).

Thus, despite very simple calculation procedure, the proposed superposition-additivity approach allows us to describe with sufficient reliability electronic structure, physical parameters, and chemical behavior of large organic molecules on the basis of calculated or experimental data for their less extended analogs.

REFERENCES

- Vysotskii, Yu.B. and Zaikovskaya, Ya.V., *Russ. J. Org. Chem.*, 1999, vol. 35, no. 10, pp. 1432-1435.
- Vysotskii, Yu.B., Zaikovskaya, Ya.V., and Solon-skii, I.N., *Russ. J. Org. Chem.*, 1995, vol. 31, no. 5, pp. 677-681.
- Vysotskii, Yu.B., Zaikovskaya, Ya.V., Solon-skii, I.N., and Ivanitsyn, I.P., *Russ. J. Org. Chem.*, 1995, vol. 31, no. 5, pp. 682-686.
- Vysotskii, Yu.B., Kovach, N.A., and Shvaika, O.P., *Khim. Geterotsykl. Soedin.*, 1977, no. 9, pp. 1186-1191.
- Mestechkin, M.M. and Vysotskii, Yu.B., *Zh. Strukt. Khim.*, 1983, vol. 24, no. 3, pp. 164-167.
- Stull, R.D., Westrum, E.F., Jr., and Sinke, G.C., *The Chemical Thermodynamics of Organic Compounds*, New York: Wiley, 1969.
- Dewar, M.J.C. and de Liano, C., *J. Am. Chem. Soc.*, 1969, vol. 91, no. 4, pp. 789-793.
- Zivcovic, N.H., *Teor. Chem. Acta* (Berlin), 1982, vol. 61, no. 2, pp. 363-368.
- Malykhanov, Yu.B., *Teor. Eksp. Khim.*, 1977, vol. 13, no. 4, pp. 464-471.
- Vysotskii, Yu.B., *Zh. Strukt. Khim.*, 1981, vol. 22, no. 1, pp. 151-155.
- Vysotskii, Yu.B., Balabanov, E.Yu., and Solon-skii, I.N., *Struktura organicheskikh soedinenii i mekhanizmy reaktsii* (Structure of Organic Compounds and Reaction Mechanisms), Kiev: Naukova Dumka, 1990, pp. 47-75.
- Cock, M. and Katritzky, A.R., *Adv. Heterocycl. Chem.*, 1974, vol. 17, pp. 255-276.
- Vysotskii, Yu.B., *Zh. Strukt. Khim.*, 1978, vol. 19, no. 4, pp. 605-612.
- Haigh, C.W. and Mallion, R.B., *Mol. Phys.*, 1970, vol. 15, no. 4, pp. 737-750.
- Nelson, G.L. and Williams, E.A., *Prog. Org. Chem.*, Taft, R.W., Ed., New York: Wiley, 1976, vol. 12, pp. 229-344.
- Bax, A., Farretti, J.A., Nashed, N., and Jerina, D.M., *J. Org. Chem.*, 1985, vol. 50, no. 17, pp. 3029-3034.
- Forsyth, D.A. and Olah, G.A., *J. Am. Chem. Soc.*, 1976, vol. 98, no. 14, pp. 4086-4090.
- Vysotskii, Yu.B., Balabanov, E.Yu., Kachurin, O.I., and Gutyrya, L.S., *Teor. Eksp. Khim.*, 1989, vol. 25, no. 2, pp. 155-161.
- Vysotskii, Yu.B., Zaikovskaya, Ya.V., Kachurin, O.I., and Bratchun, V.I., *Zh. Org. Khim.*, 1993, vol. 29, no. 5, pp. 957-963.
- Vysotskii, Yu.B., Zaikovskaya, Ya.V., Kachurin, O.I., and Bratchun, V.I., *Zh. Org. Khim.*, 1993, vol. 29, no. 5, pp. 964-971.