Estimating and Approximating the Total π-Electron Energy of Benzenoid Hydrocarbons

I. Gutman, J. H. Koolen[a], V. Moulton[b], M. Parac[c], T. Soldatović, and D. Vidović
Faculty of Science, University of Kragujevac, P. O. Box 60, YU-34000 Kragujevac, Yugoslavia
[a] FSPM-Strukturbildungsprozesse, University of Bielefeld, D-33501 Bielefeld, Germany
[b] Physics and Mathematics Department (FMI), Mid Sweden University,
Sundsvall, S-85170, Sweden
[c] Faculty of Physical Chemistry, University of Belgrade, YU-11001 Beograd, Yugoslavia
Reprint requests to Prof. I. G.; Fax: +381 34 335040; E-mail: gutman@knez.uis.kg.ac.yu

Z. Naturforsch. **55 a,** 507–512 (2000); received January 27, 2000

Lower and upper bounds as well as approximate formulas for the total π-electron energy (E) of benzenoid hydrocarbons are deduced, depending only on the number of carbon atoms (n) and number of carbon-carbon bonds (m). These are better than the several previously known (n, m)-type estimates and approximations for E.

Key words: Total π-Electron Energy; Benzenoid Hydrocarbons.

Introduction

In this paper we are concerned with the total π-electron energy (E) of conjugated hydrocarbons, as calculated within the tight-binding Hückel molecular-orbital (HMO) model. As usual we express E in the units of the HMO resonance integral β. At the very beginning we wish to remind the readers that E is related not only to π-electrons, but also pertains to the (experimentally measurable) enthalpies of the underlying compounds. In particular, the heats of atomization are reproduced via [1].

$$\Delta H_a = -\left[n_{\mathrm{CH}}\, E_{\mathrm{CH}} + m\, E^0_{\mathrm{CC}} + \beta'\, E\right], \qquad (1)$$

where n_{CH} and m are the numbers of carbon-hydrogen and carbon-carbon bonds, respectively, whereas the optimal values of the constants E_{CH}, E^0_{CC}, and β' are –411.09 kJ/mol, –325.18 kJ/mol and –137.00 kJ/mol, respectively. The quantity β' is not just the HMO carbon-carbon resonance integral, but contains contributions coming from the compression/extension of the carbon-carbon bonds. Formula (1) is applicable to conjugated hydrocarbons the molecules of which do not deviate much from planarity and in which steric effects are relatively small. Benzenoid hydrocarbons are typical compounds satisfying these conditions. For them (1) yields enthalpies that are in surprisingly good agreement with experimental values; for details see the original article of Schaad and Hess [1], pp. 135 - 136 and 151 - 153 of the book [2] or the review [3]. Recall that n_{CH} in (1) is equal to $3n - 2m$.

A remarkable property of E is that its gross part (well over 99%) is determined by only two structural parameters: the number of carbon atoms (n) and the number of carbon-carbon bonds (m). This fact has been known for a long time (see e. g. [4, 5]), but was put on a quantitative footing by McClelland in 1971 [6]. McClelland showed that

$$E \le \sqrt{2mn} \qquad (2)$$

and that for a suitably chosen constant A, the expression

$$E \approx A\sqrt{2mn} \qquad (3)$$

is a very good approximation for E. This especially holds for benzenoid hydrocarbons. Comparative studies [3, 7, 8] of several dozens of (n, m)-type formulas for E (which were put forward in the chemical literature between the 1950s and 1990s) revealed that, at least in the case of benzenoid hydrocarbons, none is better than the McClelland approximation (3).

For a long time the McClelland upper bound (2) was the only (n, m)-type estimate for E, valid for all

0932–0784 / 00 / 0500–0507 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

conjugated hydrocarbons. Recently some other generally valid upper and lower bounds for E, depending solely on n and/or m were communicated [9, 10]. On the other hand, quite a few (n, m)-type lower and upper bounds applicable only to benzenoid molecules were obtained. These are:

$$E \le 2\sqrt{m + \frac{1}{2}\sqrt{n(n-2)(m^2-9m+6n)}}, \qquad (4)$$

$$E \le 2\sqrt{\frac{2m}{n} + \frac{1}{n}\sqrt{(9mn-6n^2-2m^2)(n-2)}} \qquad (5)$$

$$+\,(n-2)\sqrt{\frac{2m}{n} - \frac{1}{n}\sqrt{\frac{36\,mn-24\,n^2-8\,m^2}{n-2}}},$$

$$E \ge \sqrt{4m^3/(9m-6n)}, \qquad (6)$$

and

$$E \ge \sqrt{3/5}\sqrt{2mn}. \qquad (7)$$

The upper bounds (4) and (5) originate from [11] and [12, 13], the lower bounds (6) and (7) from [14] and [15], respectively. For lower bounds similar to, but weaker than (7), see [16, 17].

Quite recently two more (n, m)-type estimates for E were deduced by us [10]:

$$E \le \frac{2m}{n} + \sqrt{(n-1)\left[2m - \left(\frac{2m}{n}\right)^2\right]} \qquad (8)$$

and

$$E \le 2\left(\frac{2m}{n}\right) + \sqrt{(n-2)\left[2m - 2\left(\frac{2m}{n}\right)^2\right]}. \qquad (9)$$

Inequality (8) is satisfied by all (molecular) graphs whereas (9) is valid for all bipartite (molecular) graphs. Thus, both (8) and (9) hold for benzenoid hydrocarbons.

It is easy to see that the right-hand sides of (8) and (9) are special cases, for $\gamma = 1$ and $\gamma = 2$, respectively, of an auxiliary function $E^\star(\gamma)$, defined as

$$E^\star(\gamma) = \gamma\left(\frac{2m}{n}\right) + \sqrt{(n-\gamma)\left[2m - \gamma\left(\frac{2m}{n}\right)^2\right]}. \qquad (10)$$

It is also easy to verify that for $\gamma = 0$ the function $E^\star(\gamma)$ reduces to the right-hand side of the McClelland inequality (2). These observations motivated us to focus our attention on $E^\star(\gamma)$.

In what follows we determine the main analytical properties of $E^\star(\gamma)$ and by means of it arrive at novel (n, m)-type lower and upper bounds for the total π-electron energy of benzenoid hydrocarbons, superior to all previously known (above listed) results of this kind. We also obtain novel (n, m)-type approximate expressions for E, some of which being (slightly) better than the McClelland formula (3).

The Function $E^\star(\gamma)$

In this section it will be assumed that $2m > n$, a condition which in the case of benzenoid molecules is certainly obeyed. If so, then the γ-dependence of the function $E^\star$ has the form shown in Figure 1.

The function $E^\star(\gamma)$ is real-valued for $\gamma < \gamma_1$ and $\gamma > \gamma_2$, where $\gamma_1 = n^2/(2m)$ and $\gamma_2 = n$. In the interval $(-\infty, \gamma_1)$ the function monotonically decreases, whereas in the interval $(\gamma_2, +\infty)$ it monotonically increases. Besides,

$$\lim_{\gamma \to -\infty} E^\star(\gamma) = \frac{1}{2}(n + 2m), \qquad (11)$$

$$E^\star(\gamma_1) = n, \qquad E^\star(\gamma_2) = 2m,$$

and

$$\lim_{\gamma \to +\infty} \frac{E^\star(\gamma)}{\gamma} = 2\left(\frac{2m}{n}\right).$$

Note that

$$\lim_{\gamma \to -\infty} E^\star(\gamma) = \frac{1}{2}\left[E^\star(\gamma_1) + E^\star(\gamma_2)\right].$$

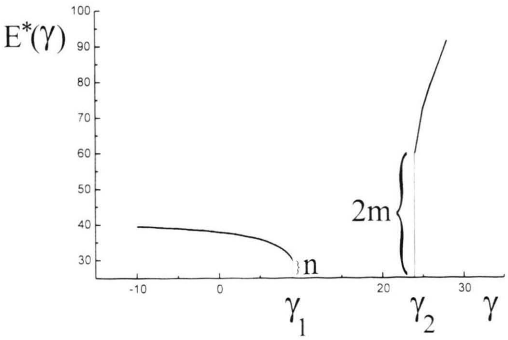

Fig. 1. The γ-dependence of the function $E^\star$, Eq. (10), for typical values of the parameters n and m; $n = 24$, $m = 30$ (coronene); $\gamma_1 = n^2/(2m) = 9.6$; $\gamma_2 = n = 24$.

From the monotonicity of $E^\star$ it follows that

$$E^\star(2) < E^\star(1) < E^\star(0),$$

which implies that for all choices of the parameters n and m (such that $2m > n$), the upper bound (9) is better than (8), which, in turn, is better than (2). In fact, any value of $E^\star(\gamma)$ for $\gamma < 2$ is necessarily an upper bound for E.

On the Equation $E^\star(\gamma) = E$

The inequality $E < E^\star(\gamma)$ may be obeyed also for some $\gamma > 2$. However, for $\gamma = \gamma_1$ the inequality $E > E^\star(\gamma)$ must hold because the total π-electron energy of any conjugated molecule is necessarily greater than n [18]. Therefore, in the interval $(2, \gamma_1)$ there exists a value of γ (which, in view of the monotonicity of $E^\star$, is unique), such that $E^\star(\gamma) = E$; we denote it by $\gamma^\star$.

Direct calculation gives

$$\gamma^\star = \frac{n(2\,m\,n - E^2)}{2m(n + 2m - 2E)}.$$

Hence, the actual value of $\gamma^\star$ depends not only on n and m, but (through E) also on the finer details of the molecular structure.

Now, if in any class of conjugated molecules $\gamma^\star_{\text{min}}$ and $\gamma^\star_{\text{max}}$ are the smallest and greatest values of $\gamma^\star$, then, because of the monotonicity of $E^\star$,

$$E^\star(\gamma^\star_{\text{max}}) \le E \le E^\star(\gamma^\star_{\text{min}}). \tag{12}$$

Recall that $E^\star(\gamma^\star_{max})$ and $E^\star(\gamma^\star_{min})$ are certain functions of the variables n and m.

In order to learn more on the $\gamma^\star$-values of benzenoid hydrocarbons and their structure-dependence, we calculated them for numerous representatives of this class of conjugated compounds. A detailed examination of the results obtained revealed an intriguing property thereof: there exists a good linear correlation between $\gamma^\star$ and n; moreover, the regression line $\gamma^\star \approx a\,n + b$ has a small, near-zero, b-value. (Of course, the values of a and b are sample-dependent.)

An illustrative example is shown in Figure 2.

The results of our numerical studies indicate that the quantity $g = \gamma^\star/n$ will vary within rather narrow limits. Indeed, we identified the benzenoid systems with maximal and minimal g-value. These are naphthalene ($g_{\text{max}} = 0.32146\ldots$) and the (infinite) graphite lattice ($g_{\text{min}} = 0.23212\ldots$). The latter g-value was calculated from the data reported in [20].

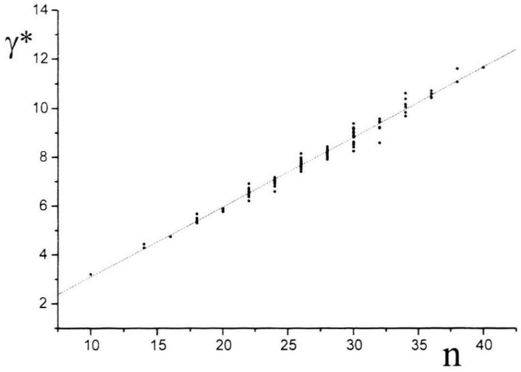

Fig. 2. Correlation between $\gamma^\star$ and n for benzenoid hydrocarbons from the book of Zahradnik and Pancir [19] (105 Kekuléan benzenoids) and the respective regression line: $\gamma^\star = (0.286 \pm 0.004)\,n + (0.2 \pm 0.1)$; the correlation coefficient is 0.989.

Thus, as a special case of the relations (12) we get the estimates

$$E^\star(n g_{\text{max}}) \le E \le E^\star(n g_{\text{min}}), \tag{13}$$

which hold for all benzenoid hydrocarbons and which, in a certain sense, are the best possible. Somewhat weaker, but algebraically more appealing bounds for the total π-electron energy of benzenoid systems are obtained when in (13) the values $1/3$ and $1/5$ are substituted instead of g_{max} and g_{min}, respectively. This results in

$$\frac{2}{3}\left(m + \sqrt{3\,m\,n - 2\,m^2}\right) \tag{14}$$

$$< E < \frac{2}{5}\left(m + \sqrt{10\,m\,n - 4\,m^2}\right).$$

In the left part of Table 1 we compare the lower bounds (6), (7) and (14) for a few chemically relevant values of n and for all possible [21, 22] values of m that can occur in benzenoid hydrocarbons. It is seen that the new estimate (14) is far superior to any of the previously reported ones.

In the right part of Table 1 we compare the upper bounds (2), (4), (5), (8), (9) and (14) for the same choice of the parameters n and m. For $n > 22$ the new estimate (14) is better than any of the previously reported ones. For $n \le 22$ (that is for just a few benzenoid systems) the Cioslowski inequality (5) [12, 13] is better than ours.

Table 1. Bounds for the total π-electron energy of benzenoid hydrocarbons C_nH_{3n-2m}; for details see text.

		— Lower bonds —			— Upper bonds —					
n	m	Eq. (6)	Eq. (7)	Eq. (14)	Eq. (2)	Eq. (4)	Eq. (5)	Eq. (8)	Eq. (9)	Eq. (14)
10	11	11.6839	11.4891	13.5872	14.8324	14.3523	14.0100	14.6274	14.3277	14.3277
14	16	16.5247	16.3951	19.0994	21.1660	20.6621	20.0887	20.9427	20.6529	20.3485
16	19	19.1262	19.0997	21.8560	24.6577	24.1292	23.4266	24.4066	24.0907	23.5800
18	21	21.3854	21.2979	24.5830	27.4955	26.9812	26.1937	27.2621	26.9776	26.3600
20	24	24.0000	24.0000	27.3137	30.9839	30.4530	29.5446	30.7295	30.4250	29.5840
21	25	25.1259	25.0998	28.6852	32.4037	31.8785	30.9298	32.1571	31.8651	30.9762
22	26	26.2537	26.1992	30.0525	33.8231	33.3033	32.3153	33.5835	33.3022	32.3672
22	27	26.6326	26.6983	30.0000	34.4674	33.9252	32.9018	34.1954	33.8747	32.7964
23	28	27.7533	27.7993	31.3859	35.8887	35.3516	34.2884	35.6248	35.3165	34.1922
24	29	28.8758	28.8998	32.7663	37.3095	36.7772	35.6751	37.0530	36.7555	35.5867
24	30	29.2770	29.3939	32.6491	37.9473	37.3972	36.2636	37.6603	37.3265	36.0000
26	31	31.1258	31.0998	35.5140	40.1497	39.6264	38.4492	39.9058	39.6268	38.3723
26	32	31.5114	31.5975	35.4440	40.7922	40.2508	39.0394	40.5210	40.2099	38.7969
30	36	36.0000	36.0000	40.9706	46.4758	45.9501	44.5929	46.2288	45.9514	44.3760
30	37	36.3904	36.4966	40.8874	47.1169	46.5760	45.1858	46.8463	46.5419	44.7973
30	38	36.8085	36.9865	40.7101	47.7493	47.1959	45.7776	47.4542	47.1214	45.1973
34	41	40.8756	40.8999	46.4238	52.8015	52.2741	50.7447	52.5521	52.2760	50.3788
34	42	41.2695	41.3957	46.3303	53.4416	52.9011	51.3397	53.1714	52.8719	50.7976
34	43	41.6876	41.8856	46.1532	54.0740	53.5225	51.9333	53.7824	53.4585	51.1976
40	49	48.3867	48.4974	54.5553	62.6099	62.0751	60.2838	62.3491	62.0648	59.5920
40	50	48.7950	48.9898	54.4152	63.2456	62.7007	60.8805	62.9669	62.6628	60.0000
40	51	49.2224	49.4773	54.1990	63.8749	63.3214	61.4755	63.5779	63.2533	60.3920
40	52	49.6670	49.9600	53.8963	64.4981	63.9371	62.0687	64.1821	63.8365	60.7680
50	61	60.3844	60.4979	68.2186	78.1025	77.5714	75.4123	77.8474	77.5743	74.3856
50	62	60.7866	60.9918	68.0998	78.7401	78.2006	76.0126	78.4710	78.1827	74.7984
50	63	61.2048	61.4817	67.9230	79.3725	78.8256	76.6114	79.0891	78.7852	75.1984
50	64	61.6376	61.9677	67.6822	80.0000	79.4465	77.2084	79.7019	79.3821	75.5856
50	65	62.0837	62.4500	67.3703	80.6226	80.0632	77.8036	80.3095	79.9733	75.9600
50	66	62.5421	62.9285	66.9783	81.2404	80.6760	78.3969	80.9119	80.5589	76.3215
60	74	72.7808	72.9932	81.7747	94.2338	93.6979	91.1675	93.9709	93.6926	89.5947
60	75	73.1925	73.4847	81.6228	94.8683	94.3260	91.7692	94.5937	94.3029	90.0000
60	76	73.6170	73.9730	81.4202	95.4987	94.9505	92.3693	95.2121	94.9084	90.3947
60	77	74.0532	74.4580	81.1625	96.1249	95.5714	92.9678	95.8261	95.5093	90.7787
60	78	74.5004	74.9400	80.8444	96.7471	96.1888	93.5645	96.4358	96.1057	91.1520
60	79	74.9578	75.4188	80.4596	97.3653	96.8027	94.1594	97.0413	96.6975	91.5146
60	80	75.4247	75.8947	80.0000	97.9796	97.4132	94.7526	97.6427	97.2850	91.8665

New (n, m)-Type Approximate Formulas for E

The main result communicated in this section is the novel (n, m)-type approximation (17) for the total π-electron energy of benzenoid hydrocarbons.

We have already seen that for each conjugated molecule there is a value of γ for which $E^\star(\gamma) = E$. This suggests that for a given class of conjugated molecules one may find a γ which (on average) optimizes the approximation

$$E^\star(\gamma) \approx E \tag{15}$$

for all members of the class.

For a representative (frequently employed [3]) set of 105 polycyclic Kekuléan benzenoid hydrocarbons from the book of Zahradnik and Pancir [19], we found that the choice $\gamma = 0.294$ minimizes the average relative error of (15). The minimum of this error is surprisingly sharp: whereas for $\gamma = 0.294$ it is 0.49%, for $\gamma = 0.284$ and $\gamma = 0.304$ it increases to 0.81% and 0.62%, respectively.

In view of the success of the McClelland approximation (3), which is equal to $AE^\star(0)$, it is purposeful to examine the formula $A\,E^\star(\gamma)$ as an extended, and possibly better approximation for total π-electron energy. This formula can be optimized with respect to both A and γ.

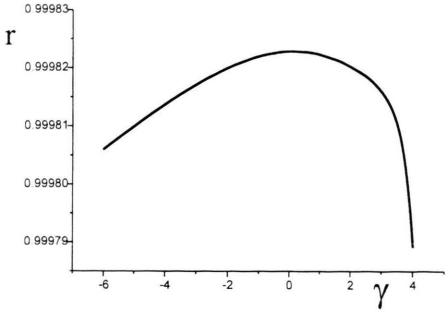

Fig. 3. The correlation coefficient r of the approximation (16), calculated for the Zahradnik-Pancir data set [19]; the maximum ($r = 0.999823$) is attained at $\gamma = +0.1$, which practically coincides with the McClelland approximation (3).

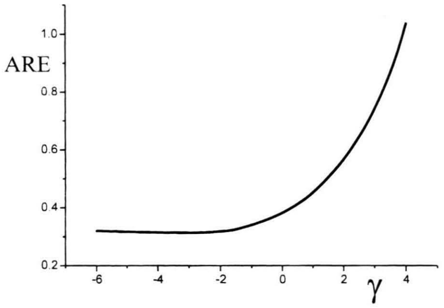

Fig. 4. The average relative error ARE (in %) of the approximation (5), calculated for the Zahradnik-Pancir data set [19]; the (very shallow) minimum (ARE = 0.31%) is attained at $\gamma = -2.9$, significantly far from, and significantly better than the McClelland approximation (3).

The quality of the approximation (16)

$$E \approx AE^\star(\gamma) \tag{16}$$

was tested using the above described standard data base [19]. The main results obtained are shown in Figs. 3 and 4.

An intriguing finding is that the McClelland formula (3) has the highest correlation coefficient among all approximate expressions of the type (16). This corroborates the earlier conclusion [3, 7, 8, 16, 23] that the (n, m)-dependence of the total π-electron energy of benzenoid hydrocarbons is well represented by the function $\sqrt{2mn}$. This, however, does not require that the McClelland approximation be the most accurate one in the class of formulas (16) considered.

Indeed, from a practical point of view the best approximate formula is the one having the smallest average relative error, ARE. Without losing accuracy we may set $\gamma = -3$ instead of the optimal value $\gamma = -2.9$, cf. Figure 4. Whereas the ARE of the formula (16) for $\gamma = -3$ is 0.313%, the McClelland formula ($\gamma = 0$) has $ARE = 0.382\%$. Thus the new approximation

$$E \approx AE^\star(-3) = A\left[\sqrt{(n+3)\left(2m+\frac{12m^2}{n^2}\right)} - \frac{6m}{n}\right] \tag{17}$$

with $A = 0.896 \pm 0.003$ is (on average) by some 22% more accurate than the McClelland formula. Within the Zahradnik-Pancir sample [19] the maximal observed error of formula (17) is 1.0%. The respective correlation coefficient is $r = 0.999817$, insignificantly differing from the maximal value $r = 0.999823$ at $\gamma = 0$.

From Fig. 4 is seen that the accuracy of the approximation (16) (as measured by the average relative error) rapidly improves as γ decreases, but for $\gamma < -2$ becomes almost constant. This is a direct consequence of the property (11) of the function $E^\star(\gamma)$, cf. Figure 1.

In summary, the (n, m)-type formula (17) is somewhat (by some 20%) more accurate than the classical McClelland formula. It is capable of reproducing (on average) some 99.7% of the total π-electron energy.

[1] L. J. Schaad and B. A. Hess, J. Amer. Chem. Soc. **94**, 3068 (1972).
[2] I. Gutman and O. E. Polansky, Mathematical Concepts in Organic Chemistry, Springer-Verlag, Berlin 1986.
[3] I. Gutman, Topics Curr. Chem. **162**, 29 (1992).
[4] G. G. Hall, Proc. Roy. Soc. London **A 229**, 251 (1955).
[5] G. G. Hall, Trans. Faraday Soc. **53**, 573 (1957).
[6] B. J. McClelland, J. Chem. Phys. **54**, 640 (1971).
[7] I. Gutman, L. Nedeljković, and A. V. Teodorović, J. Serb. Chem. Soc. **48**, 495 (1983).
[8] I. Gutman, S. Marković, A. V. Teodorović, and Ž. Bugarčić, J. Serb. Chem. Soc. **51**, 145 (1986).
[9] G. Caporossi, D. Cvetković, I. Gutman, and P. Hansen, J. Chem. Inf. Comput. Sci. **39**, 984 (1999).
[10] J. H. Koolen, V. Moulton, and I. Gutman, Chem. Phys. Letters, in press.

[11] L. Türker, Commun. Math. Chem. (MATCH) **16**, 83 (1984).
[12] J. Cioslowski, Z. Naturforsch. **40a**, 1167 (1985).
[13] J. Cioslowski and I. Gutman, Z. Naturforsch. **41a**, 861 (1986).
[14] J. Cioslowski, Int. J. Quantum Chem. **34**, 217 (1988).
[15] D. Babić and I. Gutman, Commun. Math. Chem. (MATCH) **32**, 7 (1995).
[16] I. Gutman, J. Chem. Soc. Faraday Trans. **86**, 3373 (1990).
[17] L. Türker, Commun. Math. Chem. (MATCH) **30**, 243 (1994).
[18] W. England and K. Ruedenberg, J. Amer. Chem. Soc. **95**, 8769 (1973).
[19] R. Zahradnik and J. Pancir, HMO Energy Characteristics, Plenum Press, New York 1970.
[20] I. Gutman, S. J. Cyvin, and V. Ivanov-Petrović, Z. Naturforsch. **53a**, 699 (1998).
[21] J. R. Dias, Z. Naturforsch. **44a**, 765 (1989).
[22] J. Brunvoll and S. J. Cyvin, Z. Naturforsch. **45a**, 69 (1990).
[23] J. Cioslowski and O. E. Polansky, Theor. Chim. Acta **74**, 55 (1988).