

Application of group separation reaction formalism for analysis of non-valence effects of organic compounds: three-carbon rings

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An authors' methodology based on the graph theory was used to construct the complete set of group separation reactions (homodesmotic reactions, HDRs) for 12 cyclic and bicyclic derivatives of cyclopropane and cyclopropene. The standard absolute enthalpies of all participants of the HDRs were calculated using the composite methods G3 and G4. It was shown that the heat of an HDR is determined by the difference between the strain energy E_s of the cyclic compound and the energy of sp^3 – sp^3 *gauche* interactions in the HDR products. The additivity rule was shown to hold for the *gauche* effect, which made it possible to determine the E_s values for the compounds and to trace their dependence on the structural features of C_3 cyclic hydrocarbons.

Key words: homodesmotic reaction, ring strain energy, cyclopropane, cyclopropene, *gauche* effect.

Determination of the individual thermodynamic characteristics of organic compounds and study of structure–property relationships based on them are important issues for physical organic chemistry. Most of experimental methods for determining thermodynamic characteristics of a substance (enthalpy of formation, bond dissociation energy, *etc.*) require large time and resource expenses; therefore, as an alternative, theoretical calculations of these characteristics are used. Theoretical methods, combining simplicity, rapidity, high accuracy, and possibility of algorithmization and automation, become more and more significant and demanded in research practice.

From the practical standpoint, the method of comparative analysis based on the principle of maximum similarity between the structures of the test compound and the auxiliary reference structures is, in our opinion, one of the most well designed theoretical approaches for studying the molecular energy balance. It is possible to select a group of compounds for which the local environment of each atom of the test molecule is reproduced in one of the reference compounds. This approach determines the essence of homodesmotic (*homo* means equal, the same; *desmos* is the bond) methodology.^{1–4} This methodology consists in the design of homodesmotic reactions (HDRs), that is, formal thermochemical reactions in which several balances should hold, namely, mass, group, isogyric, and bond balances and the balance of non-valence effects. If all balances are maintained, the heat of HDR ($\Delta_r H^\circ$) is equal to zero, which corresponds to the HDR energy bal-

ance. The high accuracy of homodesmotic approach for calculation of the enthalpies of formation of acyclic organic compounds was noted previously.^{5,6} An indisputable benefit of the HDR method is the fact that for some genetically related compounds, it is possible to obtain a set of mutually correlated enthalpies of formation. This concept is utilized for the development of so-called active thermochemical tables.⁷

In the practice of thermochemical calculations, one or, more rarely, two or three homodesmotic equations are selected for a test compound. This approach may result in an erroneous value for a thermochemical characteristic if, for example, the energy of the reference compound was determined inaccurately. It is more appropriate to use a correlated set of HDRs, which makes it possible to verify the reproducibility of calculations and analyze the reasons for deviations, thus increasing the reliability of the theoretical determination of thermodynamic values. In the general case, the number of HDRs that can be used for a test compound is unlimited. With some limitations on the method of formation of HDRs, the unlimited complete set can be reduced to a finite number. In this case, however, the researcher is faced with two problems: first, the routine treatment of large arrays of information and, second, the appearance of mutually correlated HDRs, *i.e.*, formal reactions being mere combinations of two (or more) other HDRs included in the same set. It was proposed^{6,8} to solve these problems by means of an automated algorithm for construction of group separation reactions

(GSRs) based on the theoretical graph representation of analyzed structures.

The physical meaning of an ideal HDR is to balance all bonded and non-valence energy interactions in the reactants and products of a formal reaction, which leads to an overall thermochemical balance. Hence, if some balance is not observed, the heat of HDR would characterize the energy of unbalanced interactions. One of the problems of theoretical methods for determining the thermochemical characteristics of organic compounds is the difficulty to take into account the non-valence interactions of steric origin. Indeed, in the well designed group additivity thermochemical increment method proposed by Benson,⁹ the non-valence effects (1,4-, 1,5-interactions, ring strain energy) are considered by introducing corrections, which are often approximate, and this disturbs the harmony of Benson's calculation protocol. Here we demonstrate that our GSR concept allows one to reliably take into account non-valence steric effects by designing the complete set of HDRs with uncompensated bonded interactions. This problem was solved in relation to the steric effect of cyclic compounds. Indeed, the ring strain energy (E_s) is a fundamental characteristic of a cyclic organic compound, which largely determines its chemical properties. The reliable direct experimental determination of E_s is difficult. As investigation objects, we chose 12 hydrocarbons containing three-membered saturated and unsaturated rings.

Calculation Methods

The following molecules with three-membered rings were chosen: cyclopropene (**1**), cyclopropane (**2**), methylenecyclopropane (**3**), 1-methylcyclopropane (**4**), ethynylcyclopropane (**5**), vinylcyclopropane (**6**), bicyclobutane (**7**), methylcyclopropane (**8**), spiropentane (**9**), *trans*-1,2-dimethylcyclopropane (**10**), 1,1-dimethylcyclopropane (**11**), and 1,1'-bicyclopopyl (**12**). The complete set of homodesmotic reactions was composed for these compounds according to the theoretical graph method. The enthalpies of formation of compounds involved in HDRs were taken from previous publications;^{10,11} the absolute enthalpies are summarized in Table 1.

Previously,⁵ the standard enthalpies of formation were calculated in terms of the GSR method for a test set of acyclic organic compounds in a simple (B3LYP/6-31G(d)), moderately complex (M06-2X/cc-pVTZ), and complex (G3) quantum chemical approximations. It was noted that high calculation accuracy (average absolute error ≤ 2 kJ mol⁻¹) is achieved irrespective of the complexity of the calculation method. However, in the cited publication, the complete set of HDRs was composed with observation of balances in non-valence effects and, in the vast majority of cases, the heat of HDR was $\Delta_r H^\circ \approx 0$. In the present study, the design of HDRs is based on the required off-balance in the ring strain energy E_s , which gives rise to large heats of HDRs. In this situation, the choice of the calculation method is less unambiguous. We performed comparative analysis of the M06-2X/cc-pVTZ, G3, and G4 quantum chemical methods in relation to the simplest C₃ rings, cyclopropene (**1**) and cyclopropane (**2**), and calculated the $\Delta_r H^\circ$ values. It was found that the heats of HDRs determined by composite methods (G3, G4)

coincide within the error of determination (± 1.4 kJ mol⁻¹), whereas the M06-2X density functional generates considerable deviations from the G3 and G4 data: ~ 20 kJ mol⁻¹ for compound **1** and ~ 15 kJ mol⁻¹ for **2**. While considering cyclopropane, one can see that the heat of HDR, average over three measurements, $\Delta_r H^\circ = -116.1 \pm 0.7$ kJ mol⁻¹ is equal in magnitude and opposite in sign to the ring strain energy $E_s = 115.7 \pm 0.4$ kJ mol⁻¹ calculated using the experimental enthalpies of formation of HDR participants.

Therefore, in this study, all calculations were carried out by the G3¹² and G4¹³ methods, which showed high convergence to experimental data. The calculations were carried out using the cluster supercomputer of the Ufa Institute of Chemistry, Ufa Federal Research Center, RAS, and the Gaussian 09, Revision C01, software package.¹⁴ The calculation results were visualized in the ChemCraft software.¹⁵

Results and Discussion

We will consider the application of the authors' homodesmotic method in relation to bicyclobutane (**7**). The group composition and the type of bonding of the thermochemical groups in the molecule correspond to graph **A** and to the connection matrix for internal groups **B** (Fig. 1).

The matrix is symmetric with respect to the main diagonal; therefore, only the first half of the matrix can be considered. The selection of HDRs implies zeroing of any number of units in matrix **B**, which transforms it into another matrix or a set of smaller matrices. These matrices correspond to HDR products. The algorithm for constructing the complete set of HDRs was described in more detail previously.^{6,8} For compound **7**, there are 13 independent ways to transform matrix **B**, which corresponds to a complete set of HDRs comprising 13 formal equations (Scheme 1).

Only HDRs that have no cyclic products were selected for the calculation of E_s (**7**), that is, altogether 10 reactions. The heats were determined for each formal reaction, and the results are summarized in Table 2. The other cyclic compounds of the set were analyzed in a similar way (see Table 2).

The heats of all presented HDRs differ from zero, which is due to the lack of compensation of the ring strain energy in the HDR products. For the simplest cyclopropene and cyclopropane structures, the scatter in the $\Delta_r H^\circ$ values does not exceed 3 kJ mol⁻¹, which is within the expected calculation error. However, for more complex compounds, the results are highly scattered (up to ~ 15 kJ mol⁻¹), which is unacceptable for this type of

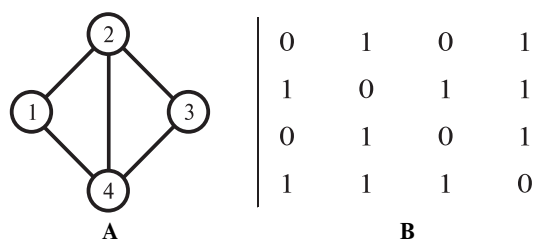


Fig. 1. Graph **A** and bond matrix of the internal groups **B** of compound **7**.

Table 1. Enthalpies of formation ($\Delta_f H^\circ$) and standard enthalpies (H°) for the test cyclopropane and cyclopropene derivatives and reference compounds

Com- pound	Structural formula	$\Delta_f H^\circ$ /kJ mol ⁻¹	H° (Hartree)		Com- pound	Structural formula	$\Delta_f H^\circ$ /kJ mol ⁻¹	H° (Hartree)	
			(G3)	(G4)				(G3)	(G4)
1		277	-116.512199	-116.534088	33		-176.4	-236.800439	-236.844391
2		53.3	-117.763248	-117.785821	34		—	-273.631865	-273.681738
3		201	-155.808853	-155.837815	35		—	-273.631149	-273.681229
4		244	-155.785502	-155.814516	36		—	-273.648824	-273.699315
5		292	-193.867404	-193.903295	37		—	-273.650911	-273.701404
6		127	-195.096133	-195.132641	38		—	-273.650643	-273.701097
7		217.0	-155.795929	-155.826118	39		—	-274.858699	-274.909336
8		23.0	-157.036101	-157.065749	40		—	-274.858479	-274.909094
9		185.1	-195.073169	-195.110018	41		-174.3	-236.799457	-236.843173
10		-4.2	-196.309055	-196.345878	42		-171.6	-236.798420	-236.842220
11		-8.2	-196.311303	-196.348159	43		-185.6	-236.803671	-236.847492
12		130.0	-234.353477	-234.397772	44		-167.1	-236.797195	-236.840900
13	MeMe	-84.0	-79.718910	-79.733661	45		-202.1	-276.072003	-276.122959
14		20.41	-117.777073	-117.798805	46		-206.2	-276.073327	-276.124552
15		-104.7	-118.988316	-119.010256	47		-194.7	-276.068300	-276.119386
16		-134.2	-158.260983	-158.290334	48		-201.5	-276.071079	-276.122088
17		0.63	-157.046169	-157.075059	49		-215.0	-315.340296	-315.398499
18		-10.8	-157.050305	-157.079280	50		-220.1	-315.340738	-315.399200
19		-125.6	-158.257936	-158.287099	51		-219.4	-315.340744	-315.398953
20		-17.9	-157.052522	-157.081679	52		-213.2	-315.337295	-315.395348
21		-167.9	-197.535841	-197.571947	53		-213.0	-315.336426	-315.394625
22		-153.7	-197.529798	-197.566342	54		-236.2	-354.610147	-354.675574
23		136.4	-195.091262	-195.126802	55		-232.2	-354.608733	-354.673865
24		106.3	-195.103956	-195.139714	56		-241.2	-354.603004	-354.676005
25		-35.5	-196.321004	-196.357269					
26		-41.5	-196.323169	-196.359527					
27		-146.8	-197.527548	-197.563944					
28		-56.1	-235.589929	-235.633077					
29		—	-234.361588	-234.404297					
30		74	-234.377558	-234.420572					
31		85	-234.373789	-234.416835					
32		—	-235.588738	-235.632153					

(to be continued)

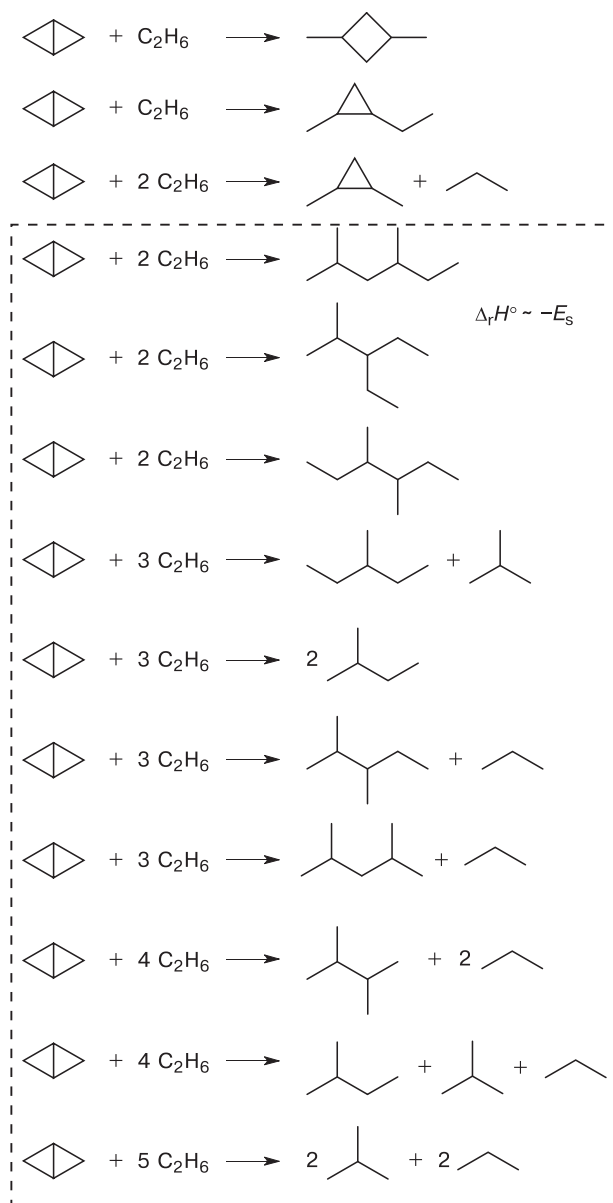
Table 1 (continued)

Compound	Structural formula	$\Delta_f H^\circ$ /kJ mol ⁻¹	H° (G3) H° (G4)	
			Hartree	
57		-254.8	-393.876078	-393.948863
58		-252.3	-393.874983	-393.947573
59		-249.7	-393.874141	-393.946414
60		-213.9	-315.338016	-315.396420
61		-233.8	-354.606238	-354.671602
62		-231.2	-354.605112	-354.670517
63		—	-233.139578	-233.182003
64		—	-312.901550	-312.958699
65		—	-312.900962	-312.958200
66		—	-273.631238	-273.681192

estimates. The seeming lack of reproducibility of the calculation results can be easily explained. Evidently, all unaccounted interactions make contributions to $\Delta_r H^\circ$; therefore, scatter of the calculated HDR heats for complex compounds is caused by one more unbalanced interaction that is present in the reaction products, but is absent in the reactants, namely, 1,4-steric interaction of hydrocarbons, which is known as the *gauche*-effect. In this case, E_s will be equal in magnitude to the HDR heat $\Delta_r H^\circ$ minus the *gauche*-interaction energy E_{gauche} . Note that the numbers of these interactions are different for different HDRs. If additivity is assumed for E_{gauche} , as in Benton's method, it is obvious that $\Delta_r H^\circ$ will follow a linear dependence on the number of interactions n in the HDR products (see Table 2, the right column), as shown in Fig. 2.

The linear dependence of $\Delta_r H^\circ$ on n for compound 7 actually holds with the correlation coefficient of 0.95 and higher. Extrapolation of this dependence to $n = 0$ gave the E_s value, and the average *gauche*-effect energy E_{gauche}

Scheme 1



was determined from the slope of this straight line. The E_s values for other compounds were calculated in a similar way (with exceptions described below) (Table 3). As expected, E_{gauche} was the same for all cyclopropanes (2.1 ± 0.2 kJ mol⁻¹). Note that in the decomposition products of compound 7, *gauche*-interactions are possible only for carbon atoms in the sp^3 hybridization state. In the general case, for the given set of cyclic compounds, 1,4-interactions may be of both sp^3-sp^3 and sp^3-sp^2 types in alkenes and sp^3-sp type in alkynes.

Analysis of the data for cyclic compounds containing multiple bonds leads to a number of conclusions about consideration of the *gauche*-interactions involving sp - and sp^2 -hybridized carbon atoms. First, only sp^3-sp^3 type *gauche*-interactions are present in methylenecyclohexane 3;

Table 2. Heats of homodesmotic reactions

Compound	Reaction	$\Delta_r H^\circ / \text{kJ mol}^{-1}$			<i>n</i>
		Calculation from published data ^{10,11}	G3	G4	
Cyclopropene	1 + 14 → 30	—	-231.8	-230.2	0
	1 + 2 14 → 18 + 24	—	-230.8	-229.2	0
Cyclopropane	2 + 13 → 27	-116.1	-119.2	-116.7	0
	2 + 2 13 → 15 + 19	-115.6	-118.6	-116.1	0
	2 + 3 13 → 3 15	-115.4	-118.1	-115.4	0
Methylenecyclopropane	3 + 13 → 28	—	-163.2	-161.7	2
	3 + 14 → 38	—	-165.1	-164.6	1
	3 + 2 14 → 31 + 20	—	-166.2	-165.6	0
	3 + 13 + 14 → 17 + 25	—	-163.7	-162.9	1
	3 + 13 + 2 14 → 2 17 + 20	—	-165.3	-164.6	0
1-Methylcyclopropene	4 + 14 → 37	—	-231.9	-231.3	1
	4 + 14 → 36	—	-231.2	-230.5	0
	4 + 2 14 → 24 + 26	—	-229.7	-228.7	0
Ethylenecyclopropane	5 + 13 → 34	—	-119.6	-117.6	2
	5 + 13 → 35	—	-117.7	-116.2	2
	5 + 2 13 → 19 + 23	—	-115.5	-113.6	0
	5 + 2 13 → 15 + 29	—	-117.3	-115.4	1
	5 + 3 13 → 15 + 23	—	-114.9	-113.0	0
Vinylcyclopropane	6 + 13 → 39	—	-114.6	-113.0	2
	6 + 13 → 40	—	-114.0	-112.4	1
	6 + 2 13 → 15 + 32	—	-113.2	-111.4	1
	6 + 2 13 → 19 + 25	—	-118.1	-116.6	0
	6 + 3 13 → 2 15 + 25	—	-117.6	-115.9	0
Bicyclobutane	7 + 2 13 → 51	-268.4	-280.9	-277.0	3
	7 + 2 13 → 52	-260.2	-271.9	-267.6	6
	7 + 2 13 → 53	-262.0	-269.6	-265.7	6
	7 + 3 13 → 45 + 15	-271.8	-282.7	-278.6	2
	7 + 3 13 → 42 + 16	-270.8	-280.3	-276.9	2
	7 + 3 13 → 2 22	-272.4	-280.8	-277.2	1
	7 + 3 13 → 47 + 15	-268.9	-272.9	-269.2	5
	7 + 4 13 → 22 + 16 + 15	-273.6	-282.3	-278.7	1
	7 + 4 13 → 33 + 2 15	-268.2	-277.0	-273.4	4
	7 + 5 13 → 2 15 + 2 16	-274.8	-283.9	-280.3	0
Methylcyclopropane	8 + 13 → 41	-113.3	-116.7	-114.9	1
	8 + 13 → 42	-110.6	-114.0	-112.4	2
	8 + 2 13 → 15 + 22	-113.4	-116.0	-114.3	1
	8 + 2 13 → 16 + 19	-114.8	-118.1	-116.5	0
	8 + 3 13 → 2 15 + 16	-114.6	-117.6	-115.8	0
Spiropentane	9 + 2 13 → 54	-253.3	-260.3	-257.9	6
	9 + 2 13 → 55	-249.4	-256.6	-253.4	8
	9 + 2 13 → 56	-258.3	-241.6	-259.0	4
	9 + 3 13 → 49 + 15	-252.8	-259.2	-256.7	6
	9 + 3 13 → 50 + 15	-257.9	-260.3	-258.5	4
	9 + 3 13 → 46 + 19	-260.2	-260.2	-257.8	2
	9 + 3 13 → 48 + 19	-264.9	-260.2	-257.8	4
	9 + 4 13 → 48 + 2 15	-260.0	-259.7	-257.1	4
	9 + 4 13 → 43 + 19 + 15	-265.0	-265.5	-263.0	2
	9 + 4 13 → 46 + 2 15	-264.7	-265.6	-263.6	2
	9 + 4 13 → 21 + 2 19	-268.2	-270.2	-266.4	0
	9 + 5 13 → 43 + 3 15	-264.8	-264.9	-262.4	2
	9 + 5 13 → 21 + 2 15 + 19	-268.0	-269.6	-265.8	0
	9 + 6 13 → 21 + 4 15	-267.8	-269.1	-265.1	0

(to be continued)

Table 2 (continued)

Compound	Reaction	$\Delta_r H^\circ / \text{kJ mol}^{-1}$			<i>n</i>
		Calculation from published data ^{10,11}	G3	G4	
1,2-Dimethylcyclopropane	10 + 13 → 47	-115.2	-105.9	-104.6	5
	10 + 13 → 45	-118.1	-115.6	-114.0	2
	10 + 2 13 → 33 + 15	-114.5	-110.0	-108.8	4
	10 + 2 13 → 22 + 16	-119.9	-115.3	-114.1	1
	5 + 3 8 → 9 + 2 10	-121.1	-116.8	-115.7	0
1,1-Dimethylcyclopropane	11 + 13 → 46	-114.0	-113.2	-112.2	2
	11 + 13 → 48	-109.3	-107.3	-105.7	4
	11 + 2 13 → 19 + 21	-117.3	-117.2	-114.4	0
	11 + 2 13 → 15 + 43	-114.1	-112.5	-111.0	2
1,1'-Bicyclopropyl	11 + 3 13 → 2 15 + 21	-117.1	-116.7	-113.7	0
	12 + 2 13 → 57	-216.8	-222.6	-219.9	6
	12 + 2 13 → 58	-214.3	-219.7	-216.5	7
	12 + 2 13 → 59	-211.7	-217.5	-213.5	8
	12 + 3 13 → 2 41	-226.6	-232.9	-230.0	2
	12 + 3 13 → 42 + 41	-223.9	-230.2	-227.5	3
	12 + 3 13 → 2 42	-221.2	-227.5	-225.0	4
	12 + 3 13 → 60 + 19	-217.5	-225.1	-222.5	5
	12 + 3 13 → 52 + 19	-216.8	-223.2	-219.7	6
	12 + 3 13 → 61 + 15	-216.5	-221.5	-218.2	6
	12 + 3 13 → 62 + 15	-213.9	-218.5	-215.3	7
	12 + 4 13 → 41 + 16 + 19	-228.1	-234.3	-231.5	1
	12 + 4 13 → 42 + 16 + 19	-225.4	-231.6	-229.0	2
	12 + 4 13 → 41 + 22 + 15	-226.7	-232.2	-229.4	2
	12 + 4 13 → 42 + 22 + 15	-224.0	-229.5	-226.8	3
	12 + 4 13 → 33 + 2 19	-221.6	-228.9	-226.2	4
	12 + 4 13 → 60 + 2 15	-217.3	-224.6	-221.9	5
	12 + 4 13 → 47 + 19 + 15	-219.0	-224.3	-221.4	5
	12 + 4 13 → 52 + 2 15	-216.6	-222.7	-219.1	6
	12 + 4 13 → 53 + 2 15	-216.4	-220.4	-217.2	6
	12 + 5 13 → 2 16 + 2 19	-229.6	-235.8	-233.1	0
	12 + 5 13 → 41 + 16 + 2 15	-227.9	-233.8	-230.9	1
	12 + 5 13 → 22 + 16 + 15 + 19	-228.2	-233.7	-230.9	1
	12 + 5 13 → 42 + 16 + 2 15	-225.2	-231.1	-228.4	2
	12 + 5 13 → 2 22 + 2 15	-226.8	-231.6	-228.7	2
	12 + 5 13 → 33 + 19 + 2 15	-221.4	-228.4	-225.6	4
	12 + 5 13 → 47 + 3 15	-218.8	-223.7	-220.7	5
	12 + 6 13 → 19 + 2 15 + 2 16	-229.4	-235.2	-232.5	0
	12 + 6 13 → 22 + 3 15 + 16	-228.0	-233.1	-230.3	1
	12 + 6 13 → 33 + 4 15	-221.2	-227.8	-224.9	4
12 + 7 13 → 2 16 + 4 15	-229.2	-234.7	-231.8	0	
Ethylnylcyclobutane	63 + 13 → 64	—	-113.06	-112.99	2
	63 + 13 → 65	—	-111.52	-111.68	1
	63 + 2 13 → 34 + 15	—	-112.33	-112.03	2
	63 + 2 13 → 23 + 27	—	-108.73	-108.75	0
	63 + 13 → 15 + 66	—	-110.68	-110.59	1
	63 + 2 13 → 19 + 29	—	-110.60	-110.46	1
	63 + 3 13 → 2 15 + 29	—	-110.04	-109.81	1
	63 + 3 13 → 15 + 19 + 23	—	-108.19	-108.09	0
	63 + 4 13 → 3 15 + 23	—	-107.62	-107.44	0

Note: *n* is the number of *gauche*-interactions in the HDR products.

therefore, the above-described procedure for data processing in the $\Delta_r H^\circ - n$ coordinates was applied to compound 3. Second, for methylcyclopropane 4 and vinylcyclopropane 6, no dependence of the reaction heat on the number of $\text{sp}^3 - \text{sp}^2$ *gauche*-interactions can be reliably traced. In this

situation, the E_s value was determined using HDRs whose products were devoid of *gauche*-interactions. Third, an unexpected result was obtained for ethylnylcyclopropane 5 where the dependence of $\Delta_r H^\circ$ on $n(\text{sp}^3 - \text{sp})$ is fulfilled with a high correlation coefficient, but with a negative slope.

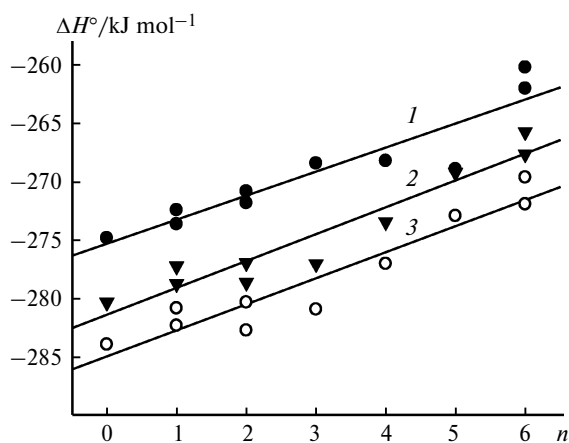


Fig. 2. Heats of HDRs for bicyclobutane vs. the number of *gauche*-interactions in the products of formal reactions: (1) calculations using the published enthalpies of formation of HDR participants, (2) G4 calculation, (3) G3 calculation.

Presumably, the *gauche* states of unsaturated compounds are stabilized by weak interactions of the π -electrons with spatially proximate atoms. Indeed, the conformational potential of pent-1-ene and pent-1-yne studied by the B3LYP/GTBas3 method (Fig. 3) has similar energies for *gauche* and antiperiplanar conformations of an unsaturated compound. The correction of energies for conformationally stable states by G4 calculations demonstrates that more favorable *gauche*-conformation of the alkene has excess energy of only $\Delta H^\circ = 0.2 \text{ kJ mol}^{-1}$ (2.8 kJ mol^{-1} for another *gauche*-conformer). In the case of alkyne, the *gauche*-conformation is even more stable than the *ap*-isomer, although the difference between the energies of these states is moderate: 0.2 kJ mol^{-1} . Meanwhile, neither the natural bond orbitals (NBO) nor Bader's method (AIM) revealed any significant stabilizing effects in the *gauche*-conformers of unsaturated compounds.

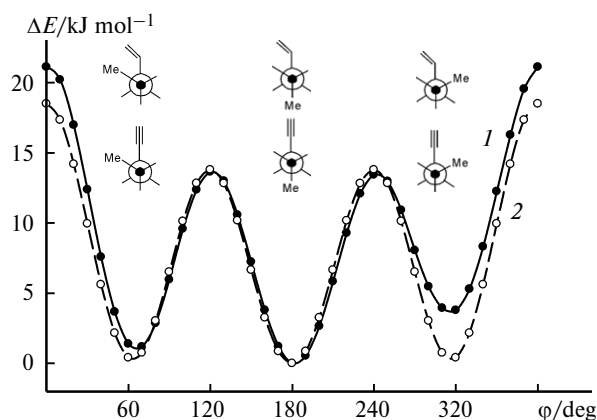


Fig. 3. Conformational potential of pent-1-ene (1) and pent-1-yne (2) for rotation about the C(2)–C(3) bond. The calculation was carried out in the B3LYP/GTBas3 approximation (the theory level for geometry optimization used in the composite G4 method).

To validate the data obtained for compound **5**, we studied its homologue, ethynylcyclobutane **63**, which obeys a similar $\Delta_r H^\circ - n(\text{sp}^3 - \text{sp})$ dependence with the slope of the same sign and magnitude: -2 kJ mol^{-1} (Fig. 4). The reason for the much more pronounced extra-stabilization of the *gauche* states in compounds **29**, **34**, **35**, and **64–66** (products of HDRs of ethynylcycloalkanes) compared with pent-1-yne is currently unclear and apparently requires additional studies. However, from the practical standpoint, this does not interfere with determination of the ring strain energy for **5** and **63** (see Table 3).

Generally, analysis of the data of Table 3 leads to the following conclusions. First, for saturated cyclopropane derivatives, data on the enthalpies of formation are available for all HDR participants and thus the E_s value can be calculated from equations presented in Table 2. The results of these calculations are in good agreement with the data of composite calculations of E_s . The mean absolute de-

Table 3. Ring strain energy E_s and energy of *gauche*-interactions E_{gauche} (kJ mol^{-1}) for cyclopropane and cyclopropene derivatives

Compound	E_s			E_{gauche} (G4)
	Calculation from published data ¹⁰	G3	G4	
Cyclopropene	225*	231.3±0.7	229.7±0.7	—
Cyclopropane	115.7±0.4	118.6±0.6	116.1±0.7	—
Methylenecyclopropane	—	165.7±0.5	165.2±0.2	1.7±0.4
1-Methylcyclopropane	—	230.9±1.2	230.1±1.1	—
Ethynylcyclopropane	—	115.2±0.2	113.3±0.2	-2.1±0.2
Vinylcyclopropane	—	117.8±0.4	116.3±0.5	—
Methylcyclopropane	114.9±0.3	118.0±0.3	116.2±0.3	2.0±0.3
1,2-Dimethylcyclopropane	117.5±0.4	117.8±1.2	116.6±1.0	2.1±0.1
1,1-Dimethylcyclopropane	117.4±0.3	117.2±0.4	114.5±0.8	1.9±0.2
1,1'-Bicyclopropyl	230.2±0.2	235.7±0.4	233.1±0.4	2.3±0.1
Spiropentane	268.9±0.4	265.0±0.7	268.0±0.9	2.5±0.1
Bicyclobutane	275.7±0.4	284.9±0.9	281.4±0.9	2.2±0.1
Ethynylcyclobutane	110*	108.3±0.3	108.2±0.4	-2.2±0.3

* Ring strain correction according to Benson.⁹

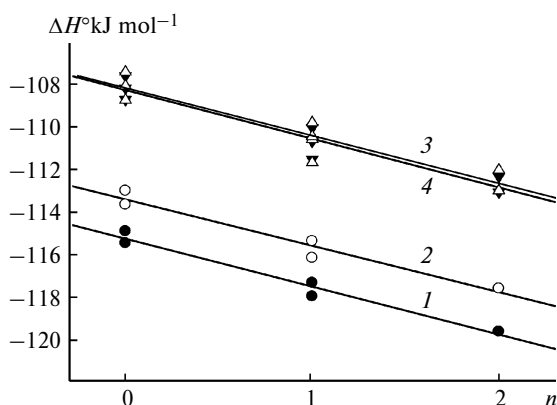


Fig. 4. Heats of HDRs for ethynylcycloalkanes **5** and **63** vs. the number of sp³–sp interactions in the products of formal reactions: (1, 2) ethynylcyclopropane, G3 and G4 calculations, respectively; (3, 4) the same for ethynylcyclobutane.

viation (MAD) for seven compounds is 2.1 kJ mol⁻¹ for the G4 method and 3.6 kJ mol⁻¹ for G3. Thus, the used levels of theory are applicable for reliable quantitative determination of E_s and, in a wider sense, for the calculation of the non-valence energies by the HDR method. Second, comparison of the results of composite calculations indicates that, with only one exception, the G3 method leads to somewhat overestimated values by, on average, 1.7 kJ mol⁻¹ than G4. Generally, the G4 method should be recognized as preferable, all other factors being the same. Third, the methyl, vinyl, and ethynyl substituents have a slight effect on E_s . Conversely, in the case of methyl-encyclopropane **3**, E_s sharply increases (by ~40 kJ mol⁻¹) in comparison with cyclopropane, which is evidently caused by the presence of sp²-hybridized carbon atom in the three-membered ring. If the ring contains two sp² carbon atoms, the ring strain energy increases by additional 65 kJ mol⁻¹. A clear trend of E_s variation is observed for the studied bicyclic compounds. If the E_s value in 1,1'-bicyclopentane **12** is additive, *i.e.*, it is equal to twice the ring strain energy of cyclopropane, then the presence of one carbon atom common to both rings in spirocyclopentane **9** increases E_s by 35 kJ mol⁻¹. In the annulated bicyclic compound **7**, the energy of the cage structure increases by additional 13 kJ mol⁻¹.

Among the set of compounds, bicyclobutane **7** has the highest E_s of 281.4 kJ mol⁻¹ (G4); the estimate based on the enthalpies of formation differs from the calculated value only by 2%, with MAD = 5.7 kJ mol⁻¹. We suggest that the relatively large MAD value may be due to the error of experimental determination of $\Delta_f H^\circ$ of compound **7**. In particular, according to a database,¹⁰ this value was calculated from the enthalpy of combustion without using the Washburn correction, *i.e.*, without converting the results of calorimetric measurements to normal conditions.

All calculations were carried out using the equipment of the Center for Collective Use "Chemistry", of the Ufa Institute of Chemistry, Ufa Federal Research Center, RAS.

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