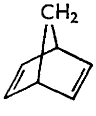
712. *Heats of Combustion and Molecular Structure. Part IX.* Bicyclo[2,2,1]heptane, 7-Oxabicyclo[2,2,1]heptane, and* exo- *and* endo-*2-Methyl-7-oxabicyclo[2,2,1]heptane.*

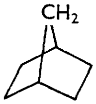
By A. F. BEDFORD, A. E. BEEZER, C. T. MORTIMER, and H. D. SPRINGALL.

The heats of combustion of the compounds mentioned in the title have been measured. The following heats of formation, $-\Delta H_f^\circ$, are derived: bicyclo[2,2,1]heptane (cryst.), 22·01 ± 0·65; 7-oxabicyclo[2,2,1]heptane (liq.), 53·51 ± 0·48; *exo*-, 60·67 ± 0·53; and *endo*-2-methyl-7-oxa-bicyclo-[2,2,1]heptane (liq.), 59·82 ± 0·51 kcal./mole. Strain energies of these compounds are related to their molecular structures.

THE five compounds, bicyclo[2,2,1]hepta-2,5-diene (I), bicyclo[2,2,1]heptane (II), 7-oxabicyclo[2,2,1]heptane (III), and *exo*- (IV) and *endo*-2-methyl-7-oxabicyclo[2,2,1]heptane (V) have in common a six-membered ring system of carbon atoms, bridged across the 1,4-position by a methylene group or an oxygen atom. In order to obtain information about the strain which this bridging causes in the molecules, the heats of combustion of the compounds (II—V) have been measured. Some thermochemical data are already available for the compound (I).



(I)



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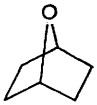

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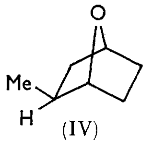

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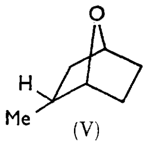

(V)

EXPERIMENTAL

Compounds.—Bicyclo[2,2,1]heptane, m. p. 84·0—84·8° (sealed capillary), 7-oxabicyclo-[2,2,1]heptane, b. p. 119·0—119·5°, n_D^{25} 1·4469, and *exo*-, b. p. 133·0—134·0°, n_D^{25} 1·4449, and *endo*-2-methyl-7-oxabicyclo[2,2,1]heptane, b. p. 138·5—140·0°, n_D^{25} 1·4497, were prepared[1] and supplied by Dr. H. K. Hall, jun., of E. I. du Pont de Nemours and Co., Wilmington, U.S.A. The samples had been purified by vapour-phase chromatography and were at least 99·9% pure.

Combustion Calorimetry.—Combustions were made in a twin-valve bomb (Parr Instrument Co., Moline, Illinois, U.S.A.) which, together with the subsidiary apparatus, has been described previously.[2] The liquid compounds were sealed in glass ampoules, and the solid bicycloheptane was compressed into pellets which were sealed in Melinex bags. A platinum baffle covered the crucible in which bicycloheptane pellets were burnt. The bomb was charged with 1 ml. of water and with oxygen at an initial pressure of 30 atm. Each sample was fired at 25°. All combustions were initiated by a platinum wire and cotton fuse. An additional fuse of oil was used to shatter the glass ampoules. After each combustion the bomb gases were analysed for carbon dioxide to an accuracy of ±0·02%.[3]

The energy equivalent of the calorimeter, E_s, was determined according to Prosen's method,[4] by combustion of a sample of benzoic acid having $-\Delta U_b = 6319·1 \pm 0·7$ kcal./g., standard deviation, $\bar{s}B$, ±0·012% ($E_s = 40180·3 \pm 5·5$ cal./ohm, standard deviation $\bar{s}E_s$, ±0·013%.) The heats evolved in the following ancillary processes were taken to have the values quoted: the formation of 0·1N-aqueous nitric acid from nitrogen, oxygen, and water, 13·81 kcal./mole;[4] the combustion of cotton fuse, 3·88 kcal./g.;[5] the combustion of Melinex,

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* Part VIII, *J.*, 1962, 3895.

[1] Wittbecker, Hall, and Campbell, *J. Amer. Chem. Soc.*, 1960, **82**, 1218.

[2] Fletcher, Mortimer, and Springall, *J.*, 1959, 580.

[3] Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 255.

[4] Prosen, "Experimental Thermochemistry," Vol. I, ed. Rossini, Interscience Publ., Inc., New York, 1956, Chap. 6.

[5] Coops, Jessup, and van Nes, "Experimental Thermochemistry," ed. Rossini, Interscience Publ., New York, 1956, Vol. I, Chap. 3.

TABLE 1.

Bicyclo[2,2,1]heptane (*M*, 96·174).

Expt.:	1	2	3	4	5
m^* (g.)	0·562668	0·482163	0·538816	0·450006	0·461616
m_i (g.)	0·006702	0·005084	0·005041	0·004803	0·004740
m_m (g.)	0·053794	0·055941	0·054752	0·059934	0·056325
ΔR_c (ohm)	0·16000	0·13842	0·15352	0·13028	0·13294
m_{CO_2} obs (g.)	1·93641	1·67988	1·85934	1·58622	1·61532
m_{CO_2} calc (g.)	1·93641	1·68084	1·85951	1·59651	1·61533
CO_2 obs′ : calc′ (%)	100·000	99·938	99·990	99·980	100·000
m' (g.)	0·562668	0·481864	0·538762	0·449916	0·461616
q_i (cal.)	26·07	19·73	19·56	18·64	18·40
q_m (cal.)	295·00	306·77	300·25	328·67	308·88
q_n (cal.)	0·97	0·83	0·41	0·41	0·41
q_w (cal.)	1·73	1·37	1·64	1·24	1·29
E_c (cal./ohm)	14·76	13·62	14·39	13·16	13·30
$-\Delta U_c°$ (kcal./mole)	1043·92	1044·83	1044·11	1044·74	1044·70

* Weight *in vacuo*: d_{20} 1·09 g./ml.

TABLE 2.

7-Oxabicyclo[2,2,1]heptane (*M*, 98·146).

Expt.:	1	2	3	4	5
m^* (g.)	0·964782	0·818279	0·728502	0·751659	0·934618
m_i (g.)	0·002101	0·001839	0·001788	0·001795	0·001842
m_o (g.)	0·028224	0·041441	0·026665	0·034380	0·024155
ΔR_c (ohm)	0·21625	0·18801	0·16452	0·17154	0·20823
m_{CO_2} obs (g.)	—	2·33376	2·04347	2·12966	2·59044
m_{CO_2} calc (g.)	—	2·33560	2·0472	2·13395	2·59391
CO_2 obs′ : calc′ (%)	—	99·921	99·816	99·799	99·866
m' (g.)	0·964782	0·817633	0·727162	0·750148	0·933366
q_i (cal.)	8·15	7·14	6·94	6·97	7·15
q_o (cal.)	310·56	455·18	292·88	377·62	265·31
q_n (cal.)	0·83	0·90	0·62	1·02	0·83
q_w (cal.)	3·54	2·57	2·34	2·45	3·51
E_c (cal./ohm)	9·30	7·99	7·05	7·32	8·98
$-\Delta U_c°$ (kcal./mole)	851·26	851·06	851·51	851·18	850·88

* d_{25} 0·9707 g./ml.

TABLE 3.

exo-2-Methyl-7-oxabicyclo[2,2,1]heptane (*M*, 112·173).

Expt.:	1	2	3	4	5
m^* (g.)	0·762423	0·680794	0·810118	0·817798	0·828493
m_i (g.)	0·002369	0·002836	0·002195	0·002339	0·002562
m_o (g.)	0·027948	0·057374	0·045137	0·038189	0·025098
ΔR_c (ohm)	0·17801	0·16793	0·19334	0·19324	0·19209
m_{CO_2} obs (g.)	2·18529	2·05566	2·37061	2·36947	2·35724
m_{CO_2} calc (g.)	2·18611	2·05574	2·37118	2·37053	2·35886
CO_2 obs′ : calc′ (%)	99·965	99·995	99·976	99·958	99·974
m' (g.)	0·762156	0·680760	0·809924	0·817455	0·828278
q_i (cal.)	9·19	11·01	8·52	9·08	9·94
q_o (cal.)	306·98	630·18	495·78	419·46	275·67
q_n (cal.)	0·0	0·13	0·0	1·19	1·06
q_w (cal.)	3·25	2·90	3·45	3·48	3·53
E_c (cal./ohm)	11·36	10·73	12·36	12·34	12·27
$-\Delta U_c°$ (kcal./mole)	1005·98	1005·97	1005·93	1006·34	1006·29

* d_{25} 0·941 g./ml.

$(C_{10}H_4O_4)_n/n$, 1052·9 kcal./mole;[6] and the combustion of oil of empirical formula $CH_{1·891}$, 10·9838 kcal./g. (this sample was supplied by Dr. J. P. McCullough, Bureau of Mines, Bartlesville, Oklahoma, and was designated U.S.B.M.-P3a.)

Units.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs.J. The atomic weights used are those recommended by the International Union in 1961, as listed by Wichers.[7] All weights used were calibrated against N.P.L. standards.

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[6] Evans and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 256.

[7] Wichers, *Nature*, 1962, **194**, 621.

Results.—The results of combustion experiments are given in Tables 1—4, in which the symbols have the same meanings as previously.[8] The following additional symbols are used: m_o = mass of oil; q_o = heat of combustion of oil. Where oil has been used in place of Melinex as fuse, these symbols, together with f_o = weight of CO_2/g. of oil = 3·1625 g., replace the quantities $f_m m_m$ and q_m in the equations [8] used in calculating $-\Delta U_c°$. The isothermal correction, E_c, for bicyclo[2,2,1]heptane (Table 1) includes a term for the heat absorbed by the platinum baffle during combustion. The $-\Delta U_c°$ terms are given by the expression [8]

TABLE 4.

endo-2-Methyl-7-oxabicyclo[2,2,1]heptane (M, 112·173).

Expt.:	1	2	3	4	5
m* (g.)	0·754209	0·779789	0·779507	0·771021	0·648561
m_i (g.)	0·002092	0·001870	0·002478	0·001964	0·002130
m_o (g.)	0·030870	0·029369	0·030833	0·033361	0·036404
ΔR_c (ohm)	0·17699	0·18226	0·18273	0·18149	0·15503
m_{CO_2} obs (g.)	2·16975	2·23499	2·24007	2·22489	1·89862
m_{CO_2} calc (g.)	2·17236	2·23751	2·24235	2·22620	1·89978
CO_2 obs′ : calc′ (%)	99·874	99·882	99·896	99·940	99·937
m' (g.)	0·753259	0·778869	0·778696	0·770558	0·648152
q_i (cal.)	8·12	7·26	9·66	7·62	8·27
q_o (cal.)	338·07	338·58	338·66	366·43	399·85
q_n (cal.)	1·44	1·33	1·35	1·42	1·13
q_w (cal.)	3·21	3·32	3·32	3·29	2·76
E_c (cal./ohm)	11·30	11·64	11·66	11·58	9·83
$-\Delta U_c°$ (kcal./ohm)	1007·08	1006·83	1007·11	1006·74	1007·01

* d_{25} 0·952 g./ml.

$$-\Delta U_c° = 10^{-3} \frac{M}{m'} [(E_s + E_c)\Delta R - (q_i + q_m + q_n + q_w - q_c)].$$

Data for the derivation of the enthalpy term, $-\Delta H_c°$, calculated from $-\Delta U_c°$, by using the expression $-\Delta H_c° = -\Delta U_c° - \Delta n\boldsymbol{RT}$, where Δn is the increase in number of moles of gas in the course of the reaction, are given in Table 5.

TABLE 5.

Bicyclo[2,2,1]-compound	$-\Delta U_c$ (mean) (kcal./mole)	Standard deviation of mean (kcal./mole)		$\Delta n\boldsymbol{RT}$ (kcal./mole)	Overall standard deviation $\bar{s}$* (%)	$-\Delta H_c°$ (kcal./mole)
			$(\bar{s}\Delta U_c°)$ (%)			
Heptane	1044·46	0·18	0·017	−1·78	0·025	1046·24 ± 0·52
oxa-Heptane	851·18	0·10	0·012	−1·19	0·022	852·37 ± 0·37
exo-Methyl-oxa-heptane	1006·10	0·09	0·009	−1·48	0·020	1007·58 ± 0·40
endo-Methyl-oxa-heptane	1006·95	0·07	0·070	−1·48	0·019	1008·43 ± 0·38

* Given by $\bar{s} = \sqrt{[(\bar{s}E)^2 + (\bar{s}B)^2 + (\bar{s}\Delta U_c°)^2]}$.

The combustions refer to the reactions:

$$C_7H_{12}(\text{cryst.}) + 10O_2(g) \longrightarrow 7CO_2(g) + 6H_2O(\text{liq.}),$$
$$C_6H_{10}O(\text{liq.}) + 8O_2(g) \longrightarrow 6CO_2(g) + 5H_2O(\text{liq.}),$$
$$C_7H_{12}O(\text{liq.}) + 9{\cdot}5O_2(g) \longrightarrow 7CO_2(g) + 6H_2O(\text{liq.}),$$

where $C_7H_{12}O$ is either the *exo*- or the *endo*-derivative.

Taking the $-\Delta H_f°$ values [9] at 25°, corrected [10] by using the 1961 atomic weights [7]—H_2O(liq.), 68·3149 ± 0·0096, and CO_2(g), 94·0517 ± 0·0108 kcal./mole—we calculate the $-\Delta H_f°$ values at 25° as follows: bicyclo[2,2,1]heptane (cryst.), 22·01 ± 0·65; 7-oxabicyclo[2,2,1]heptane (liq.), 53·51 ± 0·48; *exo*-2-methyl-7-oxabicyclo[2,2,1]heptane (liq.), 60·67 ± 0·53; and

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[8] Bedford, Carey, Millar, Mortimer, and Springall, *J.*, 1962, 3895.

[9] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

[10] Grundy, Head, and Lewis, *Trans. Faraday Soc.*, 1961, **58**, 1309.

endo-2-methyl-7-oxabicyclo[2,2,1]heptane (liq.), 59·82 ± 0·51 kcal./mole. The uncertainty interval associated with each of these terms is given by

$$2\bar{s} + x\bar{s}\Delta H_f^\circ(CO_2,g) + y\bar{s}\Delta H_f^\circ(H_2O,liq.),$$

where the $\bar{s}\Delta H_f^\circ$ terms are the uncertainties associated with the heats of formation of carbon dioxide and water, and x and y are the numbers of moles of these compounds produced in combustion of the heptane.

DISCUSSION

The heat of formation of bicyclo[2,2,1]hepta-2,5-diene (I), shown in Table 6, is calculated from an approximate heat of combustion $-\Delta H_c^\circ = 979·6 \pm 0·4$ kcal./mole, obtained by Skuratov and his colleagues[11] from two experiments on a specimen which had the characteristics, b. p. 89·4°/748 mm., d_{20} 0·9065 g./ml., n_D^{20} 1·4705. Differences, $-\Delta H$, between the heats of formation of the pairs of liquid compounds, $[-\Delta H_f^\circ(II) + \Delta H_f^\circ(I)$ etc., for the pairs II—I, III—II, IV—III, V—IV, are also shown in Table 6.

TABLE 6.

Compound (liquid)	I		II		III		IV		V
$-\Delta H_f^\circ$ (kcal./mole)	−48·0 ± 0·5		18·01 ± 0·65 *		53·51 ± 0·48		60·67 ± 0·53		59·82 ± 0·51
$-\Delta H$ (kcal./mole)		66·0 ± 1·1 †		35·50 ± 0·40 ‡		7·16 ± 0·28 ‡		−0·85 ± 0·22 ‡	
		(II—I)		(III—II)		(IV—III)		(V—IV)	

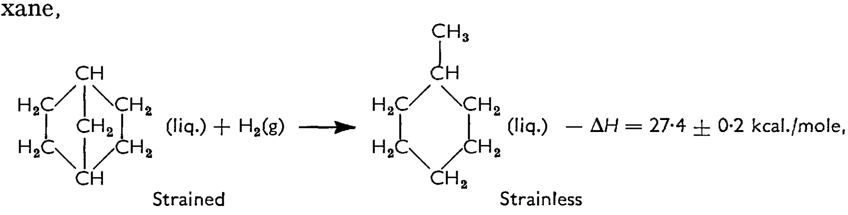
* The heat of fusion of bicyclo[2,2,1]heptane (II) is assumed to be 4·0 kcal./mole. † Uncertainty is the sum of the uncertainties associated with $-\Delta H_f^\circ$(I) and $-\Delta H_f^\circ$(II). ‡ The uncertainties associated with these values are given by

$$2\sqrt{[\{\bar{s}\Delta U_c^\circ(II)\}^2 + \{\bar{s}\Delta U_c^\circ(III)\}^2]}, \text{ etc.}$$

In the following discussion we have derived estimates of molecular strain from the comparison of the heats of formation, from standard-state elements, of similar pairs of compounds in the liquid phase, $-\Delta H_{f,1}{}^{st}$ terms, rather than from an analysis of atomic heats of formation, $-\Delta H_{f,a}$ terms.

The value $-\Delta H$(II—I) = 66·0 ± 1·1 kcal./mole corresponds to the heat of hydrogenation in the liquid phase of bicyclo[2,2,1]hepta-2,5-diene to bicyclo[2,2,1]heptane. It agrees quite well with Turner and Garner's value of 68·1 ± 0·1 kcal./mole, directly measured in acetic acid solution.[12] Turner and Garner have pointed out that the difference of 13·9 ± 0·3 kcal./mole between their heat of hydrogenation and twice the heat of hydrogenation[13] of cyclohexene to cyclohexane, in solution, $-\Delta H = 2(27·10 \pm 0·09)$ kcal./mole, probably reflects the angular strain in the bicycloheptadiene molecule, relative to that in bicycloheptane, caused by bridging the 1,4-positions with a methylene group.

There is, however, considerable strain in the bicycloheptane molecule itself because the hydrogen atoms are extensively eclipsed (as in cyclopentane, and in contrast to cyclohexane, where the strain can be relieved by the molecule's adopting either the chair or the boat conformation.) A measure of this interaction strain, together with any angular strain, in bicycloheptane, is given by the difference, $-\Delta H = 18·5 \pm 0·4$ kcal./mole, between the liquid-phase heats of hydrogenolysis of bicyclo[2,2,1]heptane to methylcyclohexane,



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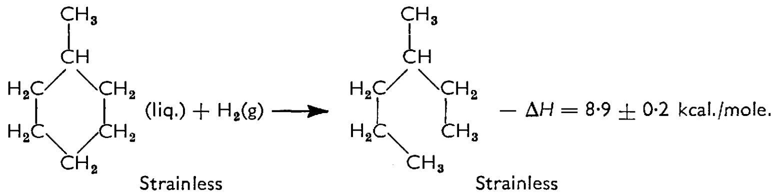
[11] Skuratov, Kozina, Shtecher, Preralova, Kamkina, and Zuko, *Bull. Chem. Thermodynamics*, 1958, **1**, 21; Skuratov, State University of Moscow, personal communication, 1963.

[12] Turner and Garner, *J. Amer. Chem. Soc.*, 1958, **80**, 1424.

[13] Turner and Meador, *J. Amer. Chem. Soc.*, 1957, **79**, 4133.

and of methylcyclohexane to 3-methylhexane



The values for these hypothetical reactions are calculated from the heats of formation, $-\Delta H_f^\circ$, of the liquid compounds:[14] methylcyclohexane, 45·45 ± 0·1, and 3-methylhexane, 54·35 ± 0·1 kcal./mole.

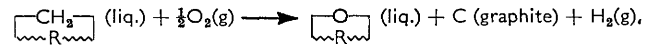
The difference between the $-\Delta H_f^\circ$ terms for liquid bicycloheptane and oxabicycloheptane $-\Delta H$(III—II), 35·5 ± 0·4 kcal./mole, is conveniently considered in relation to the corresponding differences between the $-\Delta H_f^\circ$ terms for the pairs cyclohexane (VI)–tetrahydropyran (VII), and cyclopentane (VIII)–tetrahydrofuran (IX) (Table 7).

TABLE 7.

	VI	VII	VIII	IX
$-\Delta H_f^\circ$ (liq.) (kcal./mole)...	37·34 ± 0·1 [14]	60·91 ± 0·4 [15]	25·46 ± 0·1 [14]	51·0 ± 0·3 [16]*
$-\Delta H$ (kcal./mole)	23·57 ± 0·5 (VII—VI)		25·5 ± 0·4 (IX—VIII)	

* Skuratov and his co-workers[17] have obtained a value of 51·8 kcal./mole for $-\Delta H_f^\circ$ (tetrahydrofuran).

The three $-\Delta H$ difference terms for these three pairs of substances are the $-\Delta H$ terms for the hypothetical general reaction.



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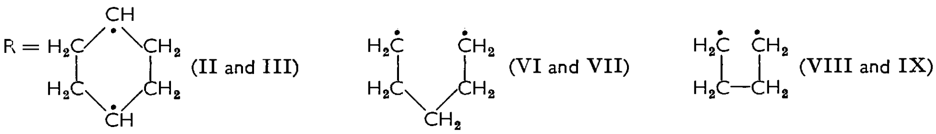

If we assume cyclohexane and tetrahydropyran to be unstrained, it appears that replacement of the bridging methylene group in bicycloheptane by an oxygen atom to give the oxabicycloheptane reduces the strain in the system to the extent of 12 kcal./mole. Since it is shown above that the total interaction and angular strain in bicycloheptane is 18·5 kcal./mole it follows that the total strain in the oxabicycloheptane is 6·5 kcal./mole. Replacement of a methylene group in cyclopentane by an oxygen atom to give tetrahydrofuran is accompanied by a relief of strain of only about 2 kcal./mole. When this is compared with the value of 12 kcal./mole for the corresponding replacement in the bicycloheptane compound a further indication is obtained of the high degree of strain operating in these bicyclo-compounds having two fused five-membered rings.

The difference, $-\Delta H$(IV—III) = 7·16 ± 0·28 kcal./mole, between the heats of formation of the bicycloheptane and the *exo*-2-methyl derivative is about 1·0 kcal./mole less

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[14] American Petroleum Institute Research Project 44, Carnegie Press, Pittsburg, Pa., 1952.

[15] Snelson and Skinner, *Trans. Faraday Soc.*, 1961, **57**, 2125; Skuratov and Kozina, *Doklady Akad. Nauk S.S.S.R.*, 1958, **122**, 109.

[16] Cass, Fletcher, Mortimer, Springall, and White, *J.*, 1958, 1406.

[17] Skuratov, Strepikheev, and Kozina, *Doklady Akad. Nauk. S.S.S.R.*, 1957, **117**, 452.

than the corresponding difference, $-\Delta H = 8{\cdot}11 \pm 0{\cdot}2$ kcal./mole, between the heats of formation of liquid cyclohexane and methylcyclohexane. These $-\Delta H$ difference terms are the $-\Delta H$ terms for the general reaction

$$\text{R–H (liq.)} + \text{C (graphite)} + \text{H}_2\text{(g)} \longrightarrow \text{R–CH}_3\text{ (liq.)}$$

It is possible that substitution of a hydrogen atom in the 2-position of the bicycloheptane by a methyl group introduced more strain, due to interaction, than a similar substitution does in cyclohexane.

The $-\Delta H$(V—IV) term, $-0{\cdot}85 \pm 0{\cdot}22$ kcal./mole, is the heat of *exo*→*endo* isomerisation for the two 2-methyl isomers and indicates that the *endo*-isomer is slightly more strained than the *exo*-isomer. This implies that there is more severe interaction between the hydrogen atoms on the 3-, 4-, 5-, and 6-carbon atoms and a 2-methyl group in the *endo*-conformation than is the case where this 2-methyl group is in the *exo*-conformation.

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