[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

# The Thermodynamic Properties and Molecular Structure of Cyclopentene and Cyclohexene[1]

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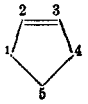
The molecules cyclopentene and cyclohexene have been studied by methods which followed naturally from earlier work on cyclopentane[5] and cyclohexane.[6] The potential energy relationships for bond bending and twisting (internal rotation) were transferred from the most analogous molecules where they are known and are used to deduce the equilibrium configurations of these slightly strained[7] ring molecules. With the aid of these results and the vibrational spectra the thermodynamic properties are correlated and extended by calculation to other functions and temperatures.

**Cyclopentene. Structure.**—The torsional forces about a double bond are so much larger than those about single bonds as to justify the assumption of planarity for four of the five carbon atoms of cyclopentene. These are atoms 1 to 4 in the diagram. However, if atom 5 is also in this plane, bonds 1–5 and 4–5 are at the maximum torsional energy since the methylene hydrogens are in opposed configuration. Therefore, we calculated the total potential or strain energy of cyclopentene as a function of the distance, $Z$, of carbon atom 5 from the plane of the other four. The C–C–C angles were adjusted to optimum values for each assumed value of Z.



The various potential constants employed are as follows: C–C–C and C═C–C angle bending, $k = 1.0 \times 10^{-11}$ ergs/radian$^2$ (a rounded average of values from various molecules); twist of 1–5 and 4–5 bonds, $V_0 = 2800$ cal./mole from ethane (and used for cyclopentane); twist of 1–2 and 3–4 bonds, $V_0 = 1950$ cal./mole from propylene.[8]

The final formula is, then, in kcal./mole

$$V = 0.022[2(\alpha_1 - 109.5)^2 + 2(\alpha_2 - 120)^2 + (\alpha_5 - 109.5)^2] + 1.95[1 - \cos 3\varphi_{12}] + 2.8[1 - \cos 3(\varphi_{15} - 60)] \quad (1)$$

where $\alpha_1$ is the skeletal bond angle at carbon 1, etc., and $\varphi_{12}$ and $\varphi_{15}$ are the twist angles about bonds 1-2 and 1-5. The latter are measured with respect to deviation from the planar configuration. It should be observed that in the planar structure the hydrogens about bond 1–2 are staggered, giving a potential minimum for torsion, whereas the hydrogens about bond 1–5 are opposed, giving a maximum. The difference in form of the terms in the potential function for these bonds is a consequence of this fact.

The symmetry of atoms 1 and 4 and of 2 and 3 is considered in the formula. The bond distances C–C, 1.54 Å. and C═C, 1.35 Å. were assumed.

Figure 1 shows the resulting potential energy as a function of $Z$. The various $\alpha$'s and $\varphi$'s were adjusted, so far as the geometry allows, to minimize the energy for each $Z$ value. Since there is some uncertainty as to the correctness of the potential constants, one should not regard the slight potential drop from $Z = 0$ to $Z = 0.22$ Å. as significant. However, one can conclude that, within the magnitude of thermal energy at room temperature, the potential energy of cyclopentene is unchanged by puckering atom 5 out of the plane by any amount up to about 0.3 Å. For the purpose of statistical mechanical calculation this potential function was expressed as

$$V(Z) = \begin{cases} O & |Z| < a \\ b(|Z| - a)^2 & |Z| > a \end{cases} \quad (2)$$

This function is shown dotted in Fig. 1 with $a = 0.277$ Å. and $b = 17.25$ kcal./mol Å$^2$., and is seen to approximate the solid curve rather well.

**Cyclopentene. Vibration Spectrum.**—The Raman spectrum of cyclopentene was taken from the work of Reitz,[9] which is in good agreement with earlier studies.

The infrared spectrum has been observed by several laboratories in the 3 to 15 micron range[10] and by the Shell Development Company from 15 to 24 microns.[11]

The various bands were assigned on the assumption of an average symmetry of $C_{2v}$ and with full consideration of the corresponding frequencies in related molecules. The result is given in Table I. While this assignment is far from certain in every detail, it seems probably correct for the

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[5] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, 9, 2483 (1947).

[6] C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947).

[7] K. S. Pitzer, *Science*, **101**, 672 (1945).

[8] Note that the *cis*-2-butene potential barrier value is not appropriate because hydrogen atoms on the two methyl groups interfere. In cyclopentene these hydrogens are absent and the bonds go instead to the third methylene group.

[9] A. W. Reitz, *Z. physik. Chem.*, **B33**, 179 (1936).

[10] Catalog of Infra-red Spectrograms issued by the American Petroleum Institute Research Project 44 at the National Bureau of Standards, Serial Nos. 200 and 456 from the Shell Development Company and 362 from the Socony-Vacuum Oil Company.

[11] Private communication from the Spectroscopic Department of the Shell Development Company.

Table I

Vibrational Spectrum of Cyclopentene

$C_{2v}$ symmetry assumed

Where values are given in parentheses, these are average observed or merely expected values. The second parenthesis gives the number of modes assumed to have this frequency.

| Sym. class | $A_1$ | $A_2$ | $B_1$ | $B_2$ |
|---|---|---|---|---|
| Selection rules | Ra., I. R. | Ra.$^-$ | Ra, IR | Ra, IR |
| Ring bending | 607 Ra, IR | 386 Ra$^-$ | [a] | 717—IR |
| C–H rocking | ......... | 1020 Ra$^-$ | 696—IR | ............ |
| $CH_2$ rocking | ......... | 935 Ra$^-$ | 1046—IR<br>1143—IR | ............ |
| C–C stretching | 900 Ra, IR<br>1104 Ra | ....... | ........ | 975—Ra, IR<br>1129—IR |
| C–H wagging | 1287 Ra, IR | ....... | ........ | 1352—IR |
| $CH_2$ wagging | 1208 ?, IR | ....... | ........ | 1201R ?<br>1300 ? IR |
| $CH_2$ twisting | ......... | (1330) (2) | (1330) (1) | ............ |
| $CH_2$ bending | 1437 Ra ?<br>1462 Ra, IR | ....... | ........ | 1445 ?, IR |
| C=C stretching | 1623 Ra, IR | ....... | ........ | ............ |
| C–H str. (olefinic) | 3060 Ra, IR | ....... | ........ | 3060 Ra, IR |
| C–H str. ($CH_2$) | (2950) (2) | (2950) | (2950) (2) | (2950) |

[a] This is the ring puckering motion whose potential is shown in Fig. 1.

thermodynamically important low frequencies and statistically correct for the higher frequencies.

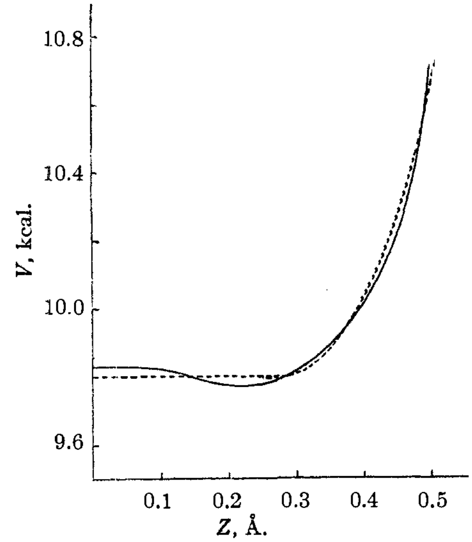

Fig. 1.—Total strain energy as a function of the out of plane distance of apical carbon atom. Solid line is calculated curve; dotted line, approximation employed for thermodynamic calculations.

**Cyclopentene. Thermodynamics.**—The entropy of cyclopentene, liquid, is 48.10 cal./deg. mole at 298.16°K. from the experiments of Huffman and collaborators,[12] while the entropy of vaporization[13] to the ideal gas at that temperature is 21.13 cal./deg. mole. This gives an experimental value for the ideal gas entropy of 69.23 cal./deg. mole at 298.16°K.

The moments of inertia of cyclopentene, with the dimensions given above, are 11.53, 11.87 and 21.80, all $\times 10^{-39}$ g. cm.$^2$.

Using these values, and the vibrational assignment given above, one calculates 65.13 cal./deg. mole for the entropy, excepting the peculiar ring puckering motion. This leaves 4.10 cal./deg. mole for that motion.

Thermodynamic functions are readily calculated (see Appendix I) for the potential energy of eqn. 2 on the classical mechanical basis. For heavy particles and a low effective frequency the quantum mechanical effects will be negligible. However, to make the entropy calculations entirely theoretical an effective reduced mass of the ring puckering motion is needed. Since the calculation of this mass would be quite laborious and would contribute relatively little in view of other approximations already made, we merely solved

Table II

Cyclopentene, Thermodynamic Functions

(Units: cal. per degree mole)

| $T$, °K. | $\frac{(H^0 - H_0^0)}{T}$ | $C^0$ | $-\frac{(F^0 - H_0^0)}{T}$ | $S^0$ |
|---|---|---|---|---|
| 200 | 9.97 | 12.33 | 53.37 | 63.34 |
| 298.16 | 11.61 | 17.95 | 57.62 | 69.23 |
| 300 | 11.65 | 18.08 | 57.69 | 69.34 |
| 400 | 14.12 | 25.08 | 61.37 | 75.49 |
| 500 | 16.98 | 31.62 | 64.82 | 81.80 |
| 600 | 19.90 | 37.19 | 68.18 | 88.08 |
| 700 | 22.71 | 41.86 | 71.46 | 94.17 |
| 800 | 25.36 | 45.78 | 74.67 | 100.03 |
| 900 | 27.82 | 49.11 | 77.80 | 105.62 |
| 1000 | 30.09 | 51.94 | 80.85 | 110.94 |
| 1100 | 32.19 | 54.37 | 83.81 | 116.00 |
| 1200 | 34.13 | 56.45 | 86.70 | 120.83 |
| 1300 | 35.92 | 58.24 | 89.50 | 125.42 |
| 1400 | 37.57 | 59.79 | 92.23 | 129.80 |
| 1500 | 39.10 | 61.13 | 94.87 | 133.97 |

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[12] H. M. Huffman, private communicaton.

[13] F. D. Rossini, private communication.

for the effective mass that gives agreement with the above entropy contribution. This gives 20.6 in atomic weight units which is not unreasonable for a methylene group type of motion.

Using all of the above data, the thermodynamic properties of cyclopentene in the ideal gas state were computed by the usual statistical mechanical formulas and are given in Table II. Although the second decimal place is given, the uncertainty is several tenths of a unit in these results.

**Cyclohexene. Structure.**—Cyclohexene, like cyclohexane,[6] probably has one predominant configuration and various higher energy forms which may affect thermal properties. The most stable form, as suggested earlier by Lister,[14] appears to be a configuration having $C_2$ symmetry and to be slightly strained.[7] Using bond distances, force constants, etc., described above for cyclopentene this strain energy was found to be about 1.6 kcal./mole; whereas the energy of another form, which resembles the cyclohexane boat, was calculated as 3.8 kcal./mole. Since these calculations are subject to considerable error we shall evaluate the exact potential energy difference, $\Delta V$, between the tautomers from the thermal data. Taking into account both symmetry numbers and also *d,l* forms, one obtains the equation

$$Q(\text{taut}) = 1 + \exp.\ (-\Delta V/RT)$$

for the tautomerism factor in the partition function. This is analogous to the chair-boat tautomerism of cyclohexane.[6]

**Cyclohexene. Vibration Spectrum.**—By comparing the observed Raman and infrared spectra[15] of cyclohexene with the spectra of cyclohexane[6] and of various olefins[16] a rough correspondence between the frequencies of these related compounds was observed. A tentative list of frequencies is given in Table III which is suitable for the estimation of thermal properties. The distribution of frequencies is approximately right. The list, however, has only a rather dubious plausibility as a detailed assignment.

**Cyclohexene. Thermodynamics.**—The entropy of cyclohexene in the liquid state has been measured by Huffman and co-workers[12] to be 51.67 cal./deg. mole at 298.16°K. while the entropy of vaporization to the ideal gas is given by Rossini[13] as 22.53 cal./deg. mole at 298.16°K. This yields the total, 74.20 cal./deg. mole, as the entropy of cyclohexene ideal gas at 298.16°K. In addition, the heat capacity of gaseous cyclohexene has been measured by Montgomery and DeVries[17] in the range near 400°K. The interpolated value from their data for 400°K. is 34.65 cal./deg. mole. Both of these quantities were calculated statistically for the low energy tautomer alone, using the value $11{,}260 \times 10^{-117}$ g.$^3$ cm.$^6$ for the product of the principal moments of inertia. The resulting entropy value, 74.16 cal./deg. mole, agrees well with experiment, but the heat capacity is at variance by 0.73 cal./deg. mole. When the tautomerism is introduced, it is found that a potential energy difference between the tautomers of 2700 cal./mole accounts for the discrepancy in the heat capacity without seriously disturbing the entropy agreement. Including tautomerism, with $\Delta V$ = 2700 cal./mole, the calculated entropy becomes 74.27 cal./deg. mole, and the heat capacity, 34.64 cal./deg. mole. While this $\Delta V$ is slightly higher than the estimate from strain considerations, it must be granted that the latter is only a rough approximation, and the difference is therefore of no importance.

TABLE III

CYCLOHEXENE VIBRATION FREQUENCY ASSIGNMENT

| Cyclohexene | | | Cyclo-hexane | *cis*-2-Butene |
|---|---|---|---|---|
| Raman | Infrared | Assigned | | |
| 190 | | 190 | 231 (2) | |
| 281 | | 281 | | |
| 394 | | 394 | 382 | |
| 451 | 456 | 456 | 426 (2) | |
| 492 | | 492 | | |
| 642 | 645 | 642 | 522 | |
| | 670 | 670 | | 673 |
| 715 | 719 | 715 | | |
| | 810 | 810 | 802 (3) | |
| 823 | | 823 | | |
| 875 | 876 | 875 | 864 (2) | |
| 904 | 904 | 904 | | |
| | 917 | 917 | 903 | |
| 966 | 966 | 966 | 1030 (5) | |
| | 1008 | 1008 | | |
| | 1037 | 1035 | | |
| 1047 | | 1047 | | |
| 1066 | 1062 | 1066 | | 1050 |
| 1138 | 1138 | 1138 | 1155 | |
| 1219 | 1220 | 1219 | 1176 | |
| | 1241 | 1241 | 1185 | |
| 1246 | | 1246 | 1261 (2) | |
| 1267 | 1266 | 1267 | 1266 (2) | 1267 |
| | 1307 | 1307 | 1308 | |
| | 1323 | 1323 | 1346 (2) | |
| | 1340 | 1340 | 1348 (2) | |
| 1350 | 1351 | 1351 | 1375 | |
| 1431 | 1437 | 1435 (2) | 1443 (3) | 1390 |
| 1454 | | 1454 (2) | 1456 (3) | |
| 1651 | 1649 | 1648 | | 1672 |
| | | 2950 (10) | | |

In Table IV are given the calculated values of various thermodynamic properties of cyclohexene in the ideal gas state and at various temperatures.

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[14] M. W. Lister, THIS JOURNAL, **63**, 143 (1941).

[15] K. W. F. Kohlrausch and R. Seka, *Ber.*, **69**, 729 (1936); F. F. Cleveland, *J. Chem. Physics*, **11**, 301 (1943); Catalog of Infrared Spectrograms issued by the American Petroleum Institute Research Project 44 at the National Bureau of Standards, Serial No. 201 from the Shell Development Company and No. 697 from the National Bureau of Standards, Radiometry Section. Also private communication from the Spectroscopic Department of the Shell Development Company.

[16] J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **37**, 163 (1946).

[17] J. B. Montgomery and T. DeVries, THIS JOURNAL, **64**, 2375 (1942).

As in Table II the uncertainty in these values is several tenths of a unit.

TABLE IV

CYCLOHEXENE, THERMODYNAMIC FUNCTIONS

(Units: cal./degree mole)

| $T$, °K. | $\frac{(H^0 - H_0^0)}{T}$ | $C^0p$ | $-\frac{(F^0 - H_0^0)}{T}$ | $S^0$ |
|---|---|---|---|---|
| 200 | 10.75 | 16.32 | 55.43 | 66.18 |
| 298.16 | 13.98 | 25.10 | 60.29 | 74.27 |
| 300 | 14.05 | 25.28 | 60.38 | 74.43 |
| 400 | 18.04 | 34.64 | 64.96 | 83.00 |
| 500 | 22.20 | 42.78 | 69.43 | 91.63 |
| 600 | 26.20 | 49.45 | 73.84 | 100.04 |
| 700 | 29.93 | 54.92 | 78.16 | 108.09 |
| 800 | 33.35 | 59.49 | 82.38 | 115.73 |
| 900 | 36.47 | 63.34 | 86.49 | 122.96 |
| 1000 | 39.33 | 66.62 | 90.48 | 129.81 |
| 1100 | 41.94 | 69.43 | 94.36 | 136.30 |
| 1200 | 44.34 | 71.85 | 98.12 | 142.46 |
| 1300 | 46.53 | 73.92 | 101.75 | 148.28 |
| 1400 | 48.55 | 75.72 | 105.27 | 153.82 |
| 1500 | 50.42 | 77.27 | 108.68 | 159.10 |

## Appendix I

In order to calculate thermodynamic functions for the mode of oscillation with potential energy given by equation (2) above, the partition function is needed

$$Q = \frac{(2\pi mkT)^{1/2}}{h} \int_{-\infty}^{+\infty} e^{-V(Z)/kT}\mathrm{d}Z \qquad (3)$$

On integration the result is

$$Q = \frac{(2\pi mkT)^{1/2}}{h} [2a + (\pi kT/b)^{1/2}) \qquad (4)$$

Let us define $y = 2a(b/\pi kT)^1/^2$, in terms of which the thermodynamic functions may be written as

$$\frac{-(F - H_0)}{T} = R\left[\ln\frac{2a(2\pi mk)^{1/2}}{h} + \frac{1}{2}\ln T + \ln\left(1 + \frac{1}{y}\right)\right]$$

$$\frac{H - H_0}{T} = \frac{R}{2}\left[\frac{2 + y}{1 + y}\right]$$

$$C = R\left[\frac{1}{2} + \frac{3}{4(1 + y)} - \frac{1}{4(1 + y)^2}\right]$$

## Summary

By the use of bond bending and bond twisting (internal rotation) potential constants from related molecules the potential or strain energy of cyclopentene and cyclohexene was calculated for various configurations. It was found that cyclopentene can pucker by moving the carbon opposite to the double bond out of the plane of the other four carbon atoms by about 0.3 Å. without significant change in energy from the planar configuration. Cyclohexene, by contrast, shows two tautomeric forms related to chair and boat cyclohexane which differ by about 2.7 kcal./mole.

The available Raman and infrared spectroscopic data are interpreted for cyclopentene and cyclohexene. With reasonable adjustments of otherwise somewhat uncertain parameters, agreement is obtained with the thermodynamic data for the two substances. The thermodynamic functions $(-(F^0 - H_0^0)/T, (H^0 - H_0^0)/T, S^0$ and $C_p^0)$ are then calculated for the ideal gas state from 200 to 1500°K.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Amine Exchange Reactions of Mannich Bases

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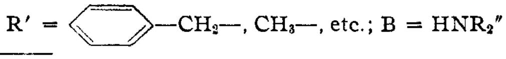
Amine exchange reactions occur when quaternary ammonium salts are heated with ammonia or primary or secondary amines[2] (eqn. A1). Similar reactions have been observed with Mannich bases of nitromethane[3] and of indole[4] (eqn. B1); the phenylhydrazones of ketonic Mannich bases form pyrazolines by internal amine exchange[5] (eqn. C).

Since these reactions appear to be similar in their mechanisms to the corresponding amine replacement reactions which occur in alkylations with quaternary salts of benzylamine[6,7,8] (eqn. A2), and with Mannich bases[4,8,9] (eqn. B2) and their quaternary salts[8,10] (eqn. A2), it seemed desirable to determine whether amine exchange reactions occur readily with ketonic and phenolic Mannich bases.

A. 1 $R'\text{—}\overset{+}{N}R_3 + :B \longrightarrow R'\overset{+}{B} + :NR_3$



$R' =$ —$CH_2$—, $CH_3$—, etc.; $B = HNR_2''$

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[2] Scholtz, *Ber.*, **24**, 2402 (1891); **31**, 414, 1700 (1898); von Braun and Zobel, *Ann.*, **445**, 247 (1925); *Ber.*, **59**, 1786 (1926); von Braun, Kuhn and Goll, *ibid.*, **59**, 2330 (1926); Hultquist, *et al.*, THIS JOURNAL, **70**, 23 (1948).

[3] Duden, Bock and Reid, *Ber.*, **38**, 2036 (1905).

[4] Howe, Zambito, Snyder and Tishler, THIS JOURNAL, **67**, 38 (1945).

[5] Mannich and Bauroth, *Ber.*, **57**, 1108 (1924); Nisbet and Gray, *J. Chem. Soc.*, 839 (1933); Levvy and Nisbet, *ibid.*, 1053, 1572 (1938); Nisbet, *ibid.*, 1237, 1568 (1938); 126 (1945); Harradence and Lions, *J. Proc. Roy. Soc. N. S. Wales*, **73**, 14 (1939) [*C. A.*, **33**, 8196 (1939)].

[6] von Meyer, *Abhandl. math.-phys. Klasse sächs. Akad. Wiss.*, **31**, 179 (1908) [*Chem. Zentr.*, **80**, II, 1800 (1909)].

[7] Snyder and Speck, THIS JOURNAL, **61**, 668, 2895 (1939).

[8] Snyder, Smith and Stewart, *ibid.*, **66**, 200 (1944).

[9] Mannich, Koch and Borkowsky, *Ber.*, **70**, 355 (1937); Reichert and Posemann, *Arch. Pharm.*, **275**, 67 (1937).

[10] duFeu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937).