in this paper for cyclopentane brings into agreement a number of previously unrelated facts, and that a final understanding of the broader problems will not essentially change this analysis.

Summary

The published data from electron diffraction, Raman and infrared spectra, entropy and specific heat measurements have been combined to develop as complete a picture of structure of the cyclopentane molecule as possible. Most striking is the result that the puckering of the ring is not of a definite type but that the angle of maximum puckering rotates around the ring. Other properties prove to be consistent with this conclusion. Among the results obtained are an assignment of vibration frequencies and tables of the thermodynamic functions, $-(F - H_0)/T$, S, $(H - H_0)/T$ and C_P for the range 298.16 to 1500° K.

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

The Thermodynamic Properties and Molecular Structure of Cyclohexane, Methylcyclohexane, Ethylcyclohexane and the Seven Dimethylcyclohexanes[1]

BY CHARLES W. BECKETT,[2] KENNETH S. PITZER[3] AND RALPH SPITZER[4]

This paper is a continuation of studies on the structural and thermodynamic properties of hydrocarbons. As compared to cyclopentane,[5] in which a large number of configurations with nearly equal stability result from the opposition of torsional forces about single bonds against forces tending to maintain tetrahedral angles, cyclohexane has one predominant stable configuration, the chair form, since it lies at the minimum in potential energy of each type. Other, higher energy tautomers exist in quite small amounts at room temperature. The energies of these, however, are low enough so that they may contribute to thermal properties. We[6] have recently measured the heat capacity of gaseous cyclohexane and methylcyclohexane and these data are compared with calculated values in the present paper.

In the course of our study very interesting effects of geometrical tautomerism in disubstituted cyclohexanes became apparent. These have been mentioned briefly in a communication to the editor,[6a] but further details are given in this paper.

These compounds are important as constituents of petroleum hence their properties should have considerable practical interest.

We shall first discuss the work on cyclohexane in some detail and then briefly describe the less detailed calculations on its derivatives.

Cyclohexane

Equilibrium Configuration.—Hassel and collaborators[7] have made an extensive study of cyclohexane by the electron diffraction method. They find that substantially all of it is in the more symmetrical chair (D_{3d}) form with a carbon–carbon distance of 1.54 Å. and approximately tetrahedral bond angles. They do not exclude a small percentage of the less symmetrical, boat form. If the staggered position is the potential minimum for the rotation about single bonds, then the chair form would be expected to have a lower energy since it maintains the staggered position throughout while the boat form twists two C–C bonds into an opposed configuration.[8]

Spectra and Vibration Frequencies.—Rasmussen[9] has very adequately summarized his own and previous spectroscopic work on cyclohexane and has shown that all lines can be explained on the chair (D_{3d}) model. This confirms the conclusion drawn from electron diffraction results. Since Rasmussen's work, the infrared spectrum has been investigated[10] further in the range 15–25μ. This later work shows that the frequency reported by Kettering and Sleator[11] at 673 cm.$^{-1}$ is spurious and that instead a band exists at 522 cm.$^{-1}$. Another weaker band at 459 cm.$^{-1}$ is also suggested.

A normal coördinate analysis has been carried out for the series of molecules cyclopropane, cyclobutane, cyclopentane and cyclohexane by Dr. C. S. Lu and certain of the present authors which will be published separately.[12] This analysis,

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[1] This research was supported by Project 44 of the American Petroleum Institute with headquarters at the National Bureau of Standards.

[2] Research Associate, Project 44 of the American Petroleum Institute.

[3] Associate Supervisor, Project 44 of the American Petroleum Institute and Professor of Chemistry at the University of California.

[4] National Research Council Fellow in Chemistry, 1945–1946. Present address: Department of Chemistry, Oregon State College, Corvallis, Oregon.

[5] J. E. Kilpatrick, K. S. Pitzer and Ralph Spitzer, THIS JOURNAL, **69**, 2483 (1947).

[6] R. Spitzer and K. S. Pitzer, THIS JOURNAL, **68**, 2537 (1946).

[6a] K. S. Pitzer and C. W. Beckett, *ibid.*, **69**, 977 (1947). See also F. D. Rossini and K. S. Pitzer, *Science*, **106**, 647 (1947).

[7] O. Hassel, *Tids. Kjemi Bergvesen*, **3**, 32 (1943); O. Hassel and B. Ottar, *Arch. Math. Naturvidenskab.* **46**, No. 10, 1-7 (1942), and earlier papers there cited.

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

[9] R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943).

[10] Dr. R. Halford, private communication; American Petroleum Institute Research Project 44, "Catalog of Infrared Spectrograms," Serial No. 466 contributed by the Radiometry Section, National Bureau of Standards.

[11] C. F. Kettering and W. W. Sleator, *Physics*, **4**, 39 (1933).

[12] C. S. Lu, C. W. Beckett and K. S. Pitzer, to be published.

while uncertain at some points, indicates that the vibration frequencies listed in Table I for cyclohexane are substantially correct. At least the remaining errors should not be serious for the thermodynamic calculations we have made. The frequency at 231 cm.$^{-1}$ is not observed since it is forbidden in the Raman effect and the infrared has not been investigated in this region. The value was selected to fit the experimental entropy of cyclohexane.

The A_{1g} frequency at 1443 and the E_g frequency at 802 cm.$^{-1}$ were calculated to be near these values which are those of stronger lines in different symmetry classes. Presumably these lines are buried under the stronger lines. There is a resonance between the E_u frequency at 1030 cm.$^{-1}$ and 231 + 802 = 1033 (also E_u) leading to the pair of bands observed.

TABLE I

THE VIBRATION FREQUENCIES OF CYCLOHEXANE

Symbol class	Type of motion	Frequency	Source
A_{1g}	C–C bending	382	R (p)
	C–C stretching	802	R (p)
	CH_2 wagging	1155	R (p)
	CH_2 bending	1443	Calcd.[a]
A_{1u}	C–C stretching	1030	Calcd.
	CH_2 wagging	1176	Calcd.
	CH_2 twisting	1375	Calcd.
A_{2g}	CH_2 wagging	1185	Calcd.
	CH_2 twisting	1308	Calcd.
A_{2u}	C–C bending	522	I. R.
	CH_2 rocking	903	I. R.
	CH_2 bending	1456	I. R.
E_g	C–C bending	426	R (d)
	C–C stretching	1028	R (d)
	CH_2 rocking	802	Calcd.[a]
	CH_2 wagging	1266	R (d)
	CH_2 twisting	1346	R (d)
	CH_2 bending	1443	R (d)
E_u	C–C bending	231	Calcd.
	C–C stretching	864	I. R.
	CH_2 rocking	1030	I. R.[a]
	CH_2 wagging	1261	I. R.
	CH_2 twisting	1348	I. R.
	CH_2 bending	1456	I. R.

[a] See text discussion. C–H stretching (12 degrees of freedom) not analyzed in detail, 2950 cm.$^{-1}$ taken as average value.

A study of the motions of the 231 and 382 cm.$^{-1}$ frequencies indicates that they may be rather anharmonic. The 382 cm.$^{-1}$ motion eventually moves the molecule through the planar (D_{6h}) configuration at which point the potential energy is at a maximum. This was estimated to be 31 kcal. above the minimum. A better estimate of the anharmonicity comes from the overtone observed by Langseth and Bak[13] which gives an anharmonicity coefficient, X = 3.0 cm.$^{-1}$. The 231 cm.$^{-1}$ motion passes over a lower potential maximum at about 14 kcal. and then down to the boat form. Thus greater anharmonicity may be expected here. Since we have no value from the spectrum, X = 4.0 cm.$^{-1}$ was selected primarily to give the best fit with the heat capacity of the gas.

The equation (3) of Wagman, Kilpatrick, Pitzer and Rossini[14] was employed in calculating the effect of anharmonicity on the thermodynamic properties. No corrections for interaction between vibrations, for anharmonicities of higher frequencies, for interaction between vibration and rotation, or for rotational stretching were included because the last two were estimated to be negligible and no information was available for the first two. However, the effect of anharmonicity upon thermal properties decreases rapidly with increasing frequency so that no serious error can be involved.

Geometrical Tautomerism.—The chair and boat forms have already been mentioned. We assume that a tautomeric equilibrium exists between these forms. While we shall find the fraction in the boat form at room temperature to be small, it increases rapidly with the temperature. Since the conversion absorbs considerable heat this contributes a very appreciable term to the heat capacity. Indeed it would be difficult to fit the observed data without this term. Velocity of sound measurements might determine the rate of the tautomerism reaction because of this effect.

We have assumed that the energy difference is twice the internal rotation potential barrier in ethane[15] or 5.6 kcal. because the change from chair to boat twists two carbon–carbons bonds from their potential minima to their maxima. Also, since the symmetry number of the boat form is only 2 as compared to 6 for the chair form, we assign an entropy R ln 3 greater to the boat form. This assumes that apart from symmetry number, the sum of rotational and vibrational entropies of the two forms is the same. The usual thermodynamic equations then permit the calculations of the various properties desired.

Thermodynamic Properties.—The entropy and related properties of the ideal gas were calculated by the usual statistical methods. The physical constants and working formulas of Wagman, Kilpatrick, Taylor, Pitzer and Rossini[16] were used. Taking 1.54 and 1.09 Å., respectively, for the carbon–carbon and carbon–hydrogen bond distances and tetrahedral angles one obtains 12,583 × 10^{-117} g.^{3} cm.^{6} for the product of moments of inertia. Vibration frequencies and other parameters have already been discussed. Table II shows the magnitude of the various contributions to the heat capacity at 500°K. and the

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[13] A. Langseth and B. Bak, *J. Chem. Phys.*, **8**, 403 (1940).

[14] D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 467 (1945).

[15] K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

[16] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

entropy at 298.16°K. and also gives experimental values. The first experimental entropy (R. H.–A. P. I.) is obtained by adding the entropy of vaporization selected by Project 44 of the American Petroleum Institute[17] to the entropy of the liquid given by Ruehrwein and Huffman.[18]

TABLE II

CONTRIBUTIONS TO THERMAL PROPERTIES OF CYCLOHEXANE; COMPARISON OF CALCULATED AND OBSERVED VALUES; IDEAL GASEOUS STATE; CAL./DEG. MOLE

Calculated	$S^0_{(g)298.16}$	$C^0_{p500°\text{ K.}}$
Vibration, harmonic	9.111	36.268
Vibration, anharmonic	0.187	0.578
Chair to boat tautomerism	.005	.676
Translation and rotation	61.973	7.949
Total	71.28	45.47

Experimental:

$C^0_{p500°\text{ K.}}$ = 45.6 ± 0.5, Spitzer and Pitzer[6]
$S_{(\text{liq.})298.16}$ = 48.84 ± 0.10, Ruehrwein and Huffman[18]
$\Delta S^0_{(\text{vap.})298.16}$ = 22.43 A. P. I.[17]

$S^0_{(\text{gas})298.16}$ = 71.27 (R. H.–A. P. I.)
$S^0_{(\text{gas})298.16}$ = 71.42 ± 0.18, Aston, Szasz and Fink[19]

The value of the entropy of the gas given by Aston, Szasz and Fink[19] is also included.

Table III compares the calculated and experimental values for the heat capacity of the ideal gas over a range of temperature.[6,20]

Table IV gives the calculated values of S^0, $(F^0 - H^0_0)/T$, $(H^0 - H^0_0)/T$ and C^0 from 298.16 to 1500°K. Brickwedde, Moskow and Aston[21] have also presented values of these functions based on a crude vibrational assignment. Their calculated thermodynamic functions are, however, very similar to ours.

TABLE III

CALCULATED AND OBSERVED HEAT CAPACITIES OF CYCLOHEXANE IN THE IDEAL GASEOUS STATE, CAL./DEG. MOLE

Temp., °K.	C^0_p Calcd.	C^0_p Obs.	Reference
384	34.2	34.2 ± 0.3	Spitzer and Pitzer[6]
428	38.5	38.7 ± .4	Spitzer and Pitzer[6]
460	41.6	41.7 ± .4	Spitzer and Pitzer[6]
495	45.0	45.3 ± .5	Spitzer and Pitzer[6]
521	47.2	47.0 ± .5	Spitzer and Pitzer[6]
544	49.2	49.3 ± .5	Spitzer and Pitzer[6]
370	32.8	33.0	Montgomery and DeVries[20]
390	34.8	35.0	Montgomery and DeVries[20]
410	36.8	36.8	Montgomery and DeVries[20]

By employing the values in Table IV, a number of sources yield either the heat of hydrogenation of benzene to cyclohexane or the heat of formation of cyclohexane. Assuming the heat of formation of benzene[22] to be 24.000 kcal./mole at 0° K. one can calculate one quantity from the other. These values are listed in Table V. Comment is needed only on the values from the equilibrium studies of Burrows and Lucarini and of Zharkova and Frost. A value of ΔH^0_0 can be calculated from each equilibrium constant using the $(F_T - H_0)/T$ function for cyclohexane from Table IV and for hydrogen[16] and benzene.[22] These separate values of $\angle H^0_0$ were found to show no trend with temperature and were concordant within the average deviation shown in Table V.

TABLE IV

THERMODYNAMIC PROPERTIES OF CYCLOHEXANE IN THE IDEAL GASEOUS STATE, CAL./DEG. MOLE

Temp., °K.	C^0_p	$\frac{H^0 - H^0_0}{T}$	$-\frac{F^0 - H^0_0}{T}$	S^0
298.16	25.40	14.21	57.07	71.28
300	25.58	14.28	57.16	71.44
400	35.82	18.38	61.80	80.18
500	45.47	22.85	66.39	89.24
600	53.83	27.34	70.96	98.30
700	60.87	31.64	75.50	107.14
800	66.76	35.67	79.98	115.65
900	71.68	39.40	84.40	123.80
1000	75.80	42.85	88.74	131.59
1100	79.3	46.0	93.0	139.0
1200	82.2	48.9	97.1	146.0
1300	84.7	51.6	101.1	152.7
1400	86.8	54.0	105.0	159.0
1500	88.6	56.3	108.8	165.1

TABLE V

HEAT OF FORMATION AND OF DEHYDROGENATION OF CYCLOHEXANE AT 0°K.

(Dehydrogenation to benzene, all for ideal gas state in kcal./mole).

Ref.	Method	$-\Delta H^0_0$ formation	ΔH^0_0 dehydrogenation
23	Combustion, calorimetric	20.09 ± 0.2	44.09 ± 0.3
24	Combustion, calorimetric	20.02 ± .2	44.02 ± .3
25	Combustion, calorimetric	20.36 ± .4	44.36 ± .5
26	Hydrogenation, calorimetric	19.77 ± .2	43.77 ± .1
27	Hydrogenation, equilib.	20.3 ± .5	44.3 ± .4
28	Hydrogenation, equilib.	19.67 ± .3	43.67 ± .2

Alkyl Cyclohexanes

Tautomerism and Symmetry Effects.—As Hassel[7] has pointed out, the hydrogen atoms in cyclohexane may be divided into two types which

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[17] American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons," Table 7g.

[18] R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

[19] J. G. Aston, G. J. Szasz and H. L. Fink, *ibid.*, **65**, 1135 (1943).

[20] J. B. Montgomery and T. DeVries, *ibid.*, **64**, 2375 (1942).

[21] F. G. Brickwedde, M. Moskow and J. G. Aston, *J. Research Natl. Bur. Standards*, **37**, 263 (1946).

[22] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *ibid.*, **37**, 95 (1946).

[23] Recalculated from G. E. Moore, M. L. Renquist and G. S. Parks, THIS JOURNAL, **62**, 1505 (1940).

[24] E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Research, Natl. Bur. Standards*, **37**, 51 (1946).

[25] R. Spitzer and H. M. Huffman, THIS JOURNAL, **69**, 211 (1947).

[26] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **58**, 146 (1936).

[27] G. H. Burrows and C. Lucarini, *ibid.* ,**49**, 1157 (1927).

[28] V. R. Zharkova and A. V. Frost, *J. Gen. Chem., U. S. S. R.*, **2**, 534 (1932).

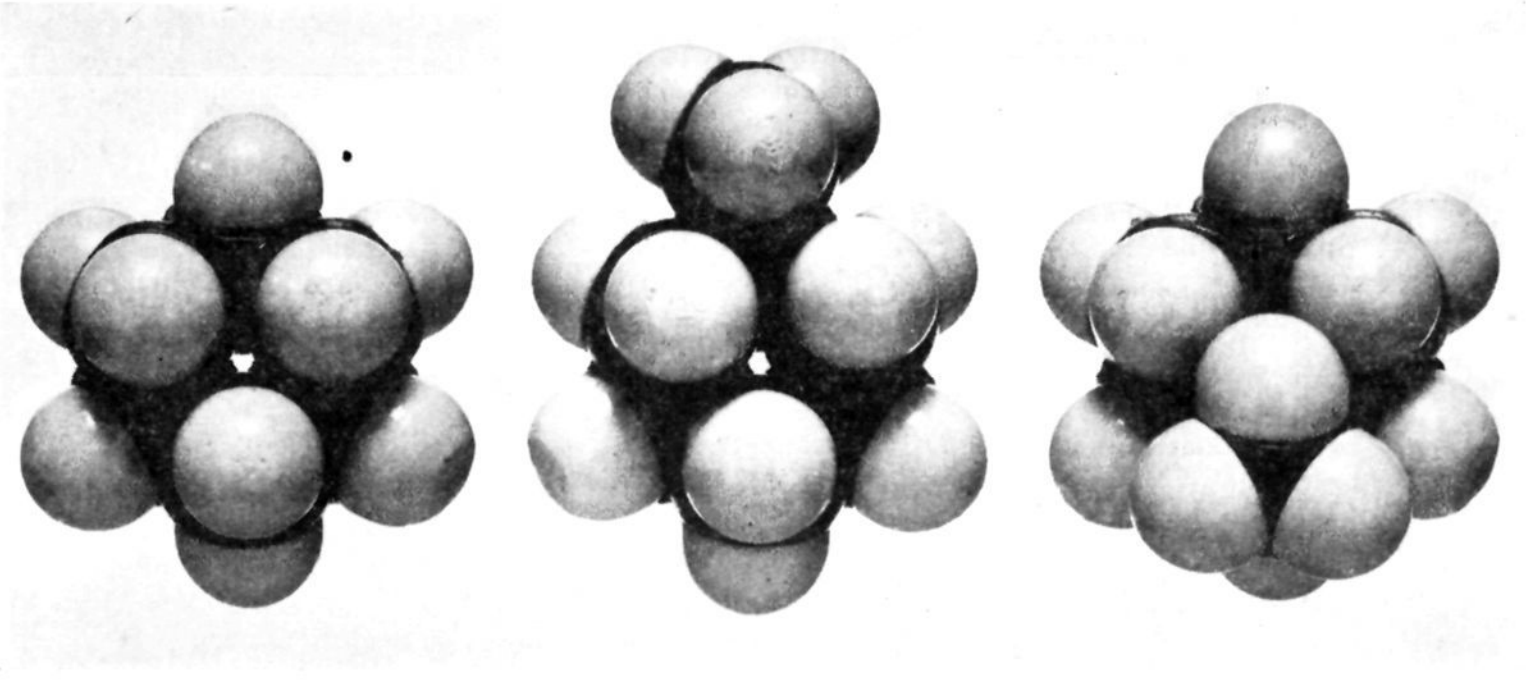

Fig. 1.—Cyclohexane (left), methylcyclohexane, equatorial (middle) and polar (right).

we shall call polar (p) and equatorial (e) (Hassel's ϵ and κ, respectively). If the carbon ring (in the chair configuration) be horizontal there are three polar hydrogens markedly above and three below the ring while six hydrogen atoms lie in an "equatorial" belt around the carbons. Of the two hydrogen atoms on each carbon, one is polar and one equatorial. If the six carbon atoms pass through a single plane over to the opposite chair configuration all hydrogens originally equatorial become polar and vice versa. So long as all are identical hydrogen atoms, nothing new is obtained, but with another group attached, tautomers become possible. Methylcyclohexane may have its methyl group in either a polar or an equatorial position. By studying a model of this molecule it is found that steric interactions arise which are similar to those of *n*-paraffins in their various configurations. One of us[29] has given a value of 0.8 kcal./mole for the strain energy, a, in *n*-butane twisted 120° about the central carbon–carbon bond as compared to the stable, planar configuration of that molecule. Polar methylcyclohexane has two similar interactions whereas the equatorial form has no strain of this type. Therefore, the energy of the former is greater than that of the latter by approximately twice the *n*-butane value. The assigned value, 1.8 kcal./mole, or $a = 0.9$ kcal./mole (together with the frequency assignment and potential barrier for the methyl rotation discussed below) appears to give the best agreement between calculated and observed entropies. However, other values from 1.6 to 2.4 kcal./mole will give agreement within experimental error.

Of the dimethylcyclohexanes, (1,1), (*cis*-1,2), (*trans*-1,3) and (*cis*-1,4) have one polar and one equatorial methyl and hence have only one tautomeric form of the type discussed above. The second and third, however, do have *d* and *l* configurations, which accounts for their double probability, since *d* and *l* forms have the same energy. In *cis*-1,2 the enantiomorphs are in tautomeric equilibrium while in *trans*-1,3 they are true isomers interconvertible only by inversion of two carbon atoms. The other dimethylcyclohexanes, (*trans*-1,2), (*cis*-1,3) and (*trans*-1,4) have two tautomers, one with both methyl groups polar and one with both methyl groups equatorial. The energy of the latter is lower in each case.

In the *trans*-1,4 compound the energy difference is clearly twice that in methylcyclohexane, $4a$ or 3.6 kcal./mole. In the *trans*-1,2 derivative there is one *n*-butane-like interaction in the equatorial form and four in the polar form giving an energy difference of $3a$ or 2.7 kcal./mole. For *cis*-1,3-dimethylcyclohexane the polar form encounters much worse steric interference because both methyl groups are on the same side of the plane. We have arbitrarily assigned an energy difference of $6a$ or 5.4 kcal./mole to this case. This value is so high that the polar form could be ignored at the lower temperatures.

The *trans*-1,2-dimethylcyclohexane has, further, *d* and *l* isomers with a symmetry number of 2 in each case so that no net change in the relative probability of this substance arises. It will be noted that in agreement with the simple theory, only *trans*-1,2 and *trans*-1,3 compounds can exist as long lived *d* or *l* isomers.

A previous publication[6a] has discussed these tautomers briefly and shown that, contrary to earlier suggestions, *trans*-1,3-dimethylcyclohexane is probably the higher boiling isomer.[29a]

In addition to the polar-equatorial tautomerism, the chair-boat tautomerism still exists in the

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(29) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

(29a) Added in proof: We have belatedly come upon the work of Mousseron and Granger (*Bull. soc. chim.*, **5**, 1618 (1938)) who prepared an optically active and therefore *trans*-1,3-dimethylcyclohexane. They found it to be the higher boiling isomer in agreement with our conclusion.

TABLE VI

TAUTOMERISM IN DIMETHYLCYCLOHEXANES

ΔS and ΔH are entropies and heats of isomerization from *cis* 1,4 for the gas state at 298.16°K. in cal./degree mole and kcal./mole, respectively.

Compd.	Config.	Tautomers description	Energy	Sum. no.	ΔS Calcd.	ΔS Obs.	ΔH Calcd.	ΔH Obs.
cis-1,2	e,p p,e	Enantiomorphs	3*a*	1	0.97	0.83[a]	0.9	1.13[a]
trans-1,2	e,e p,p	*d,l* isomers of each	*a* 4*a*	2 2	.11	.09	− .9	−0.83
cis-1,3	e,e p,p		0 6*a*	1 1	.00	.06[b]	−1.8	−1.94[b]
trans-1,3	e,p p,e	Tautomers identical *d,l* isomers	2*a*	1	1.38	1.10[c]	0.0	0.02[c]
cis-1,4	e,p p,e	Identical	2*a*	1	(0.0)	(0.0)	(.0)	(.0)
trans-1,4	e,e p,p		0 4*a*	2 2	−1.35	−1.58	−1.8	−1.91

[a] Estimated uncertainty: 0.2 in ΔS and 0.3 in ΔH for all compounds. [b] Isomer boiling at 120.1° formerly called *trans*. [c] Isomer boiling at 124.5° formerly called *cis*.

derivatives. Since the latter is less important, because of the greater energy difference, we have not attempted to study it in detail for each derivative. Rather we have assumed that the chair–boat tautomerism contributes the same amount to various properties of the derivatives as in cyclohexane itself.

Table VI summarizes various parameters arising from the tautomerism and symmetry of the dimethyl derivative. The entropies and heats of isomerism are given with *cis*-1,4 as a standard because that substance is free from tautomeric complications. The entropies are essentially those of symmetry and of mixing of tautomers, but they will be discussed in the next section. The calculated heats are merely the differences in energy, taking the lowest energy tautomer and giving *a* the value 0.9 kcal./mole mentioned above. (The use of the exact heat contents computed later would make a negligible difference.) The experimental heats of isomerization from Johnson, Prosen and Rossini[30] were received after all other calculations were complete. They agree remarkably well. While an *a* value of 0.97 kcal./mole would fit slightly better it did not appear worthwhile to repeat the calculations for this small change.

Indeed these heat of isomerization data afford a satisfying confirmation of the approximate value 0.8 kcal. originally assigned this *n*-butane interaction in the early and approximate work on the *n*-paraffins.[15]

In the earlier publication[6a] the present assignment of *cis* and *trans* configurations of 1,3-dimethylcyclohexanes was recommended on the basis of the entropy values and for other reasons given there. The excellent agreement of ΔH values in Table VI offers strong confirmation of that conclusion.

Thermodynamic Properties.—There were available experimental values, from the Third Law, of the entropy of methyl, ethyl and several dimethylcyclohexanes at 298.16°K. The values for the liquid state are from the work of Huffman and collaborators,[31] while the data for the entropy of vaporization are from various measurements at the National Bureau of Standards.[32] These experimental entropies for the ideal gas at 298.16°K. are listed in Table VII. We have also experimental values of the heat capacity of gaseous methylcyclohexane[6] which are shown in Table VIII.

TABLE VII

ENTROPIES OF THE ALKYLCYCLOHEXANES THROUGH C_8 AT 298.16° K.

Units: cal. per degree mole

	$S_{\text{liq.}}$[31]	$\Delta S_{\text{vap.}}$[32]	S^0_{gas} exptl.	S^0_{gas} calcd.
Methylcyclohexane	59.25	22.80	82.05	82.06
Ethylcyclohexane	67.14	24.32	91.46	91.44
1,1-Dimethylcyclohexane	63.88	23.35	87.23	87.24
cis-1,2-	65.53	23.95	89.48	89.51
trans-1,2-	65.30	23.45	88.75	88.65
cis-1,3-	65.16	23.56	88.72	88.54
trans-1,3-	65.82	23.93	89.75	89.92
cis-1,4-	64.83	23.84	88.67	88.54
trans-1,4-	63.70	23.39	87.09	87.19

TABLE VIII

THE HEAT CAPACITY OF METHYLCYCLOHEXANE

Values for ideal gas state in cal./deg. mole

T, °K.	C_p exptl.[6]	C_p calcd.
398	44.1 ± 0.4	44.1
439	48.6 ± .5	48.6
480	53.2 ± .5	53.0
527	57.8 ± .6	57.7

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(30) W. H. Johnson, E. J. Prosen and F. D. Rossini, unpublished data.

(31) H. M. Huffman, private communication and H. M. Huffman, THIS JOURNAL, **68**, 173 (1946).

(32) F. D. Rossini, private communication.

A study of the infrared and Raman spectra of these molecules indicated that it was not feasible to make detailed vibrational assignments from spectral data alone. Consequently we have assumed that each methyl group contributes the same increment to the sum of translational, rotational and vibrational entropy (or other function). The internal rotational contribution was taken to be that for a reduced moment of inertia of 5.3×10^{-40} g. cm.^{2} and for a 3.6 kcal./mole potential barrier to methyl rotation in all cases except 1,1 and *cis*-1,2-dimethylcyclohexanes where the two methyl groups interfere with one another. In these two cases the barriers were adjusted to fit the experimental entropies yielding 6.6 and 4.3 kcal./mole, respectively. The 3.6 kcal./mole value is rounded from that for isobutane[33] which seems the best analogy.

TABLE IX

VIBRATION FREQUENCIES OF METHYLCYCLOHEXANE

Units: cm^{-1}; values in parentheses indicate multiple weights. 153, 220, 307, 335, 403, 445, 520, 543, 768, 784, 843(2), 872, 910(2), 969, 1032(2), 1059, 1090, 1109, 1164, 1200, 1247(2), 1263(2), 1305(3), 1345(3), 1363, 1376, 1450(7), 2950(14).

The anharmonicity contribution in cyclohexane was assumed to apply here.

TABLE X

HEAT CAPACITIES OF METHYL CYCLOHEXANE, ETHYL CYCLOHEXANE AND THE SEVEN DIMETHYL CYCLOHEXANES IN THE IDEAL GASEOUS STATE

Temp., °K.	C_p^0, cal./deg. mole								
	Methyl-cyclo-hexane	Ethyl-cyclo-hexane	Dimethylcyclohexanes						
			1,1	*cis*-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3	*cis*-1,4	*trans*-1,4
298.16	32.27	37.9	36.9	37.4	38.0	37.6	37.6	37.6	37.7
300	32.51	38.2	37.2	37.7	38.3	37.9	37.9	37.9	38.0
400	44.35	51.6	50.7	51.1	51.9	51.2	51.1	51.1	51.6
500	55.21	63.8	63.3	63.5	64.2	63.6	63.4	63.4	64.0
600	64.46	74.1	74.1	74.0	74.6	74.2	73.8	73.8	74.6
700	72.23	82.8	83.2	82.8	83.3	83.1	82.5	82.5	83.3
800	78.74	90.1	90.7	90.1	90.5	90.5	89.8	89.8	90.6
900	84.20	96.2	97.0	96.3	96.6	96.7	95.9	95.9	96.8
1000	88.79	101.3	102.2	101.4	101.7	102.0	101.1	101.1	101.9
1100	92.7	105.7	106.6	105.8	106.0	106.4	105.5	105.5	106.2
1200	96.0	109.4	110.3	109.5	109.7	110.1	109.2	109.2	109.9
1300	98.8	112.5	113.5	112.7	112.8	113.3	112.4	112.4	113.0
1400	101.2	115.3	116.2	115.4	115.5	116.0	115.2	115.2	115.7
1500	103.2	117.6	118.4	117.7	117.8	118.3	117.5	117.5	118.0

This methyl increment was obtained by subtracting values for cyclohexane from those for methylcyclohexane without the polar-equatorial tautomerism. The latter were based on the best possible assignment of vibration frequencies for methylcyclohexane from the spectral data[34] making full use of analogies, to similar molecules. However, certain features were still uncertain and these were arbitrarily adjusted to give agreement with the various experimental, thermodynamic data mentioned above. Thus we may regard this vibrational assignment, listed in Table IX, as essentially an empirical representation of the thermodynamic data, but with the great advantage that it must extrapolate to approximately correct values at higher temperatures because the correct number of degrees of freedom are included and because all high frequencies are reasonably certain from the known regularities between similar molecules. The product of moments of inertia was calculated from the same distances and angles mentioned above to be $39{,}294 \times 10^{-117}$ g.^{3} cm.^{6}.

Table VI summarizes various parameters in the calculations of the entropies of the methyl derivatives and Tables VII and VIII compare the calculated entropy and heat capacity of gaseous methylcyclohexane with the experimental data. It should be noted that the entropies of methyl, *trans*-1,2, *cis* and *trans*-1,3 and *cis* and *trans*-1,4-dimethylcyclohexanes, six in all, have been fitted with a single adjusted quantity, the entropy increment per methyl group, together with the value of *a*, which is also known from other sources. This serves to confirm our general picture of the tautomeric equilibria and the assumption of a single increment for the methyl group. However, certain details within the methyl increment could be changed considerably without affecting its total value.

The more detailed calculations and experimental data for the methyl derivatives of benzene[35] indicate that the methyl increment method used here should be fairly satisfactory also for the gaseous heat capacity. However, there are no experimental values for the dimethylcyclohexanes to verify this.

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(33) K. S. Pitzer and J. E. Kilpatrick, *Chem. Rev.*, **39**, 435 (1946).

(34) Raman effect: H. Okazu, *J. Chem. Soc. Japan*, **60**, 559 (1939); Kohlrausch and Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936); J. Goubeau and E. Köhler, *Ber.*, **75A**, 65 (1942); Infrared: American Petroleum Institute Research Project 44, "Catalog of Infrared Spectrograms," Serial No. 258 and 369 contributed by the Universal Oil Products Co. and the Radiometry Section of the National Bureau of Standards, respectively.

(35) K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

TABLE XI

HEAT CONTENT FUNCTIONS OF METHYL CYCLOHEXANE, ETHYL CYCLOHEXANE AND THE SEVEN DIMETHYL CYCLOHEXANES IN THE IDEAL GASEOUS STATE

Temp., °K.	$(H^0 - H_0^0)/T$, cal./deg. mole								
	Methyl-cyclo-hexane	Ethyl-cyclo-hexane	Dimethylcyclohexanes						
			1,1	*cis*-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3	*cis*-1,4	*trans*-1,4
298.16	17.55	20.45	19.72	20.16	20.44	20.35	20.35	20.35	20.38
300	17.66	20.58	19.85	20.29	20.58	20.48	20.48	20.48	20.51
400	22.84	26.7	25.9	26.3	26.7	26.5	26.5	26.5	26.6
500	28.26	32.9	32.1	32.5	33.0	32.7	32.7	32.7	32.8
600	33.53	38.9	38.2	38.6	39.0	38.8	38.7	38.7	38.9
700	38.53	44.6	44.0	44.3	44.7	44.5	44.3	44.3	44.7
800	43.16	49.9	49.4	49.6	50.0	49.8	49.6	49.6	50.0
900	47.42	54.7	54.4	54.4	54.9	54.7	54.4	54.4	54.8
1000	51.33	59.1	58.9	58.9	59.3	59.1	58.8	58.8	59.3
1100	54.9	63.1	63.0	63.0	63.4	63.2	62.9	62.9	63.4
1200	58.2	66.8	66.8	66.7	67.1	67.0	66.6	66.6	67.1
1300	61.2	70.2	70.3	70.1	70.5	70.5	70.0	70.0	70.5
1400	64.0	73.3	73.5	73.3	73.6	73.6	73.1	73.1	73.6
1500	66.5	76.2	76.4	76.1	76.5	76.5	76.0	76.0	76.5

TABLE XII

ENTROPIES OF METHYL CYCLOHEXANE, ETHYL CYCLOHEXANE, AND THE SEVEN DIMETHYL CYCLOHEXANES IN THE IDEAL GASEOUS STATE

Temp., °K.	S^0, cal./deg. mole								
	Methyl-cyclo-hexane	Ethyl-cyclo-hexane	Dimethylcyclohexane						
			1,1	*cis*-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3	*cis*-1,4	*trans*-1,4
298.16	82.06	91.44	87.24	89.51	88.65	88.54	89.92	88.54	87.19
300	82.28	91.70	87.52	89.79	88.94	88.82	90.20	88.82	87.47
400	93.22	104.5	100.0	102.4	101.7	101.5	102.8	101.5	100.2
500	104.32	117.3	112.7	115.2	114.7	114.3	115.6	114.2	113.1
600	115.21	129.9	125.2	127.7	127.3	126.8	128.1	126.7	125.7
700	125.77	142.0	137.4	139.8	139.5	139.0	140.2	138.8	137.9
800	135.86	153.6	149.0	151.4	151.1	150.6	151.7	150.3	149.5
900	145.46	164.5	160.1	162.4	162.2	161.6	162.6	161.2	160.6
1000	154.57	174.9	170.6	172.8	172.6	172.1	173.0	171.6	171.1
1100	163.2	184.8	180.5	182.7	182.5	182.0	182.9	181.5	181.0
1200	171.4	194.2	189.9	192.0	191.9	191.4	192.2	190.8	190.3
1300	179.2	203.0	198.8	200.8	200.8	200.3	201.0	199.6	199.2
1400	186.6	211.4	207.3	209.3	209.2	208.8	209.4	208.0	207.7
1500	193.7	219.5	215.5	217.4	217.3	216.9	217.5	216.1	215.8

TABLE XIII

FREE ENERGY FUNCTIONS OF METHYL CYCLOHEXANE, ETHYL CYCLOHEXANE, AND THE SEVEN DIMETHYL CYCLOHEXANES IN THE IDEAL GASEOUS STATE

Temp., °K.	$-(F^0 - H_0^0)/T$, cal./deg. mole								
	Methyl-cyclo-hexane	Ethyl-cyclo-hexane	Dimethylcyclohexanes						
			1,1	*cis*-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3	*cis*-1,4	*trans*-1,4
298.16	64.51	70.99	67.52	69.35	68.21	68.19	69.57	68.19	66.81
300	64.62	71.12	67.67	69.49	68.36	68.34	69.72	68.34	66.96
400	70.38	77.8	74.1	76.1	75.1	75.0	76.4	75.0	73.6
500	76.06	84.5	80.6	82.6	81.7	81.6	83.0	81.6	80.2
600	81.68	91.0	87.0	89.1	88.3	88.1	89.4	88.1	86.7
700	87.24	97.4	93.3	95.5	94.7	94.5	95.8	94.5	93.2
800	92.70	103.7	99.6	101.8	101.1	100.8	102.1	100.8	99.6
900	98.04	109.9	105.7	107.9	107.3	107.0	108.3	106.9	105.7
1000	103.24	115.9	111.7	113.9	113.3	113.0	114.2	112.8	111.8
1100	108.3	121.7	117.5	119.7	119.1	118.8	120.0	118.6	117.6
1200	113.2	127.3	123.1	125.3	124.8	124.4	125.6	124.2	123.2
1300	118.0	132.8	128.5	130.7	130.2	129.9	131.0	129.6	128.7
1400	122.6	138.1	133.8	136.0	135.6	135.2	136.3	134.9	134.0
1500	127.1	143.3	139.1	141.3	140.8	140.4	141.5	140.1	139.3

The change from methyl to ethylcyclohexane is essentially similar to that from isobutane to isopentane, except for the symmetry number of three for isobutane. Consequently we have calculated the various thermodynamic functions for gaseous ethylcyclohexane from the equation

$$F(\text{ethylcyclohexane}) = F(\text{methylcyclohexane}) + F(\text{isopentane}) - F(\text{isobutane}) - R \ln 3$$

where F means C, S, $(H - H_0^0)/T$ or $-(F - H_0^0)/T$ and the $R \ln 3$ applies only to S and $-(F-H_0)/T$. This equation gives the value in Table VII.

By similar analogies one may offer equations for n-propyl and isopropylcyclohexane which may be of interest for making estimates.

$$F(n\text{-propylcyclohexane}) = F(\text{methylcyclohexane}) + F(\text{2-methylpentane}) - F(\text{isobutane}) - \text{R} \ln 3$$

$$F(\text{isopropylcyclohexane}) = F(\text{methylcyclohexane}) + F(\text{2,3-dimethylbutane}) - F(\text{isobutane}) - R \ln (3/2)$$

Again the $R \ln 3$ and $R \ln (3/2)$ terms apply only to the functions S and $-(F-H_0)/T$.

The values of several thermodynamic functions calculated by the various methods discussed above for a range of temperatures are listed in Tables X–XIII. Where values are given to the second decimal place, the error should not exceed 0.4, otherwise the error may be larger up to 1.0 or even more at the high temperatures.

These data of Tables X to XIII will be combined with the heat of formation values now being obtained by Rossini and collaborators in a later publication.

We wish to thank Dr. F. D. Rossini and Dr. H. M. Huffman for making available to us various data in advance of publication.

Summary

The data for cyclohexane from electron diffraction, Raman and infra-red spectra, and thermodynamic measurements were analyzed in various ways to give an assignment of vibration frequencies and calculated values of the heat capacity, entropy and heat and free energy functions for cyclohexane in the ideal gas state from 298.16 to 1500°K. It is concluded in agreement with others that at room temperature cyclohexane is predominantly in the chair form of symmetry D_{3d}. However, the heat capacity of gaseous cyclohexane definitely shows a contribution from conversion to the boat form which is approximately 5.6 kcal./mole higher in energy.

The possibilities of geometrical tautomerism in the methyl and dimethylcyclohexanes, mentioned in earlier publications, are discussed in greater detail. It is shown that the energy differences between these tautomers are related to the strain or steric energies in n-paraffins, and that there is good agreement between the corresponding energy quantity obtained from data on each series of compounds. The heats of isomerization confirm the assignment of the configuration *cis*-1,3-dimethylcyclohexane to the isomer boiling at 120.1° and *trans*-1,3 to the isomer boiling at 124.5°. The thermodynamic functions mentioned above were calculated also for methyl, ethyl and the seven dimethyl-cyclohexanes in the ideal gas state from 298.16 to 1500°K.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phosphorus Fluoroisocyanates and Difluoroisothiocyanate

BY HERBERT H. ANDERSON

Studies of mixed halides containing fluorine and isocyanate or isothiocyanate have been undertaken in this Laboratory; the silicon fluoroisocyanates[1] have been described. This paper in turn presents phosphorus fluorodiisocyanate, difluoroisocyanate and difluoroisothiocyanate.

Phosphorus Fluoroisocyanates

Preparation.—A mixture of powdered, sublimed antimony trifluoride and phosphorus isocyanate (free from benzene or chloroisocyanates[2,3]) was heated gently in a single-necked flask to start the uncatalyzed reaction. Manual agitation was used, since the antimony isocyanate that formed neither melted nor dissolved and so produced a somewhat viscous mixture. The method resembles that employed in two closely related fluorinations.[1,4] Table I shows the proportions of the reagents used to produce the two mixed halides.

TABLE I

PREPARATION OF PHOSPHORUS FLUOROISOCYANATES, USING 50 G. OF ANTIMONY TRIFLUORIDE

Run	Starting liquid, g.	Reflux temp., °C.	Press., mm.	PF_2-(NCO), g.	PF-$(NCO)_2$, g.	Effective fluorine transfer, %
1	145 $P(NCO)_3$	80–90	140	6	48	75
2	53 $P(NCO)_3$	36–40	140	2.5	28	30
3	70 $P(NCO)_3$	90–92	760	15	29	60
4	94 $PF(NCO)_2$	50–60[a]	760	50	..	55

[a] Reaction required two hours.

Phosphorus fluorodiisocyanate was purified, utilizing distillation columns similar to the one recommended by Rose,[5] yielded material of b. p. 98.9–99.1° at 771 mm.; no rearrangement to form products such as phosphorus trifluoride, difluoroisocyanate and isocyanate could be detected at this temperature.

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(1) Forbes and Anderson, THIS JOURNAL, **69**, 1241 (1947).

(2) Forbes and Anderson, *ibid.*, **62**, 761 (1940); **65**, 2271 (1943).

(3) Anderson, *ibid.*, **64**, 1757 (1942); **67**, 223, 2176 (1945).

(4) Schumb and Anderson, *ibid.*, **58**, 994 (1936).

(5) A. Rose, *Ind. Eng. Chem.*, **28**, 1210 (1936).