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Conformations and Strain Energy of Cyclopentane and its Derivatives

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Earlier calculations of the conformation and strain energy of cyclopentane are refined by the addition of terms for the election correlation energy of non-bonded but nearby atoms and for the zero point vibrational energy. The agreement with observed properties of cyclopentane is substantially improved. It is shown that substitution of the cyclopentane will ordinarily yield a barrier to the pseudo-rotation of ring puckering and that the energy minimum will in some cases correspond to C_2 symmetry and in other cases to C_S symmetry. It is shown that certain of the parameters evaluated for cyclopentane may be transferred to derivatives and that strain energies may becalculated for the derivatives if potential barrier values are available for the appropriate open chain model compounds.

In 1941 Aston, Schumann, Fink and Doty[1] showed that the cyclopentane ring was puckered. The torsional forces associated with the single C–C bonds are undoubtedly responsible for this puckering and semi-quantitative calculations of the strain energy and of the detailed equilibrium conformation have been presented.[2–4] While the quantitative comparison of these results with the experimental heat of combustion value[5] was only partially satisfactory, a significant qualitative result emerged from the Kilpatrick, Pitzer and Spitzer[3] investigations, namely, "that the puckering of the ring is not of a definite type but that the angle of maximum puckering rotates around the ring." While certain authors[6–8] have been reluctant to accept this pseudo-rotation of the puckering and the consequent indefiniteness of the cyclopentane conformation, McCullough[9] has reported more precise heat capacity measurements for cyclopentane which definitely confirm the free pseudo-rotation.

It is the purpose of this paper to present: first, new and improved calculations of the total strain energy of cyclopentane and of the equilibrium degree of puckering, and second, a discussion of the expected equilibrium conformation of cyclopentane derivatives where, in general, the substitution will introduce a potential barrier restricting the pseudo-rotation.

Strain Energy of Cyclopentane.—Previous strain energy calculations for cyclopentane considered only the torsional energy associated with the rotation of C–C single bonds and the strain of bending C–C–C bond angles below the tetrahedral value. The force constant for the latter effect was taken from the normal vibration analysis of cyclohexane and open chain hydrocarbons, while the torsional potential was estimated from that of ethane and other simple hydrocarbons. These two terms do not yield any explanation of the difference in energy between such paraffin isomers as *n*-butane and isobutane or *n*-pentane and neopentane. Consequently the lack of quantitative agreement for the strain energy of cyclopentane was not too surprising.

Recently calculations for the paraffins were improved[10] by the addition of terms for the zero point vibration energy and for the interaction energy of nearby but non-bonded electron clouds. The correlation of the motion of these electrons yields an attractive force and an energy decrease which may be treated by the method used by F. London for attractive van der Waals forces between nonpolar molecules. These calculations for the paraffin isomerization energies yielded quite good agreement and we now extend the same method to cyclopentane and cyclohexane.

The numerical constants of previous investigations were retained.[3,10] The London or correlation energy is given by the formula

$$\Delta E_C = -[22.6\Sigma R_{CC}^{-6} + 8.68\Sigma R_{CH}^{-6} + 3.42\Sigma R_{HH}^{-6}] \times 10^{-60} \text{ ergs} \quad (1)$$

where the sums are over all non-bonded interatomic distances of the types indicated. Bond distances are taken as C–C, 1.54 Å.; C–H, 1.10 Å. The C–C–C bending constant was taken as 0.8×10^{-11} erg/radian^2 and the torsional potential barrier as a cosine function of 2800 cal./mole height.

The puckering in cyclopentane is described by the formula

$$z_j = \sqrt{\frac{2}{5}}\, q \cos 2\left(\frac{2\pi}{5} j + \varphi\right) \quad (2)$$

where z_j is the displacement of the j^{th} atom perpendicular to the plane of the unpuckered ring, q measures the amplitude, and φ the phase angle of the puckering.

The calculations follow the method of Kilpatrick, *et al.*[3]; additional details are given in the Appendix. The results for cyclopentane are given in Table I for six values of the parameter q. The bond energies, C–H, 102.4 and C–C, 80.2 kcal./mole, which were obtained in the corresponding treatment of the paraffins, together with the dissociation energies of the elements yield the term $-\Delta H_{\text{bond}} = 59.0$ kcal./mole. The zero point vibrational energy was calculated from the assignment of Miller and Inskeep.[6]

A plot (Fig. 1) of the heat of formation $-\Delta H_f°$

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[1] J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, THIS JOURNAL, **63**, 2029 (1941); J. G. Aston, H. L. Fink and S. C. Schumann, *ibid.*, **65**, 341 (1943).

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

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

[4] R. Spitzer and H. M. Huffman, *ibid.*, **69**, 211 (1947).

[5] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh (1953 and subsequent supplements).

[6] F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

[7] C. G. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, 3549 (1956); *Chemistry and Industry*, 54 (1956).

[8] B. Curnutte and W. F. Shaffer, *J. Mol. Spectroscopy*, **1**, 239 (1957).

[9] J. P. McCullough, *J. Chem. Phys.*, **29**, 966 (1958).

[10] K. S. Pitzer and E. Catalano, THIS JOURNAL, **78**, 4844 (1956).

TABLE I

ENERGY OF CYCLOPENTANE AT 0°K.

q, Å.	0.00	0.236	0.308	0.40	0.50	0.60
$-E_C$, kcal./mole	44.49	44.57	44.67	44.94	45.72	47.03
E_{torsion}, kcal./mole	14.00	11.48	9.99	8.05	6.18	4.95
$E_{\text{C–C–C}}$, kcal./mole	0.08	0.62	1.10	2.19	4.26	7.72
$-\Delta H_{\text{bond}}$, kcal./mole	59.0	59.0	59.0	59.0	59.0	59.0
$\Sigma {}^1/_2 h\nu$, kcal./mole	85.26	85.26	85.26	85.26	85.26	85.26
$-\Delta H_f^0$, kcal./mole	4.2	6.2	7.3	8.4	9.0	8.1

vs. q yields a minimum of 9.0 kcal./mole at 0.50 Å. These values may be compared with the experimental $-\Delta H_f° = 10.7$ kcal./mole[5] and the value of $q_0 = 0.47$ Å. which fits the experimental entropy.[11] The agreement for q_0 is excellent and for $\Delta H_f°$ reasonably satisfactory but not within experimental error.

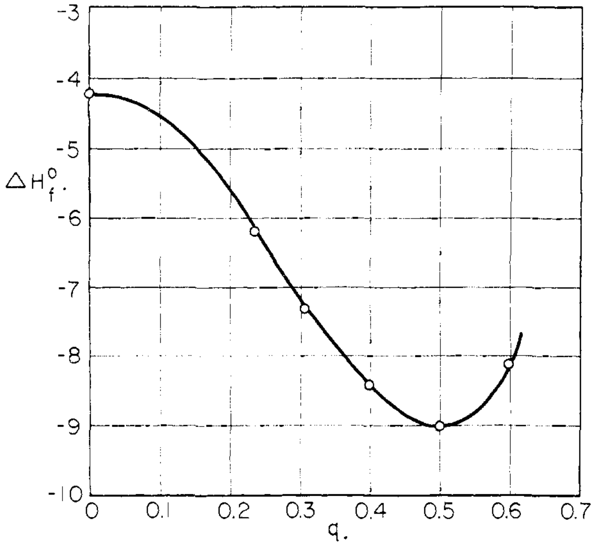

Fig. 1.—The calculated heat of formation (in kcal./mole) of cyclopentane as a function of the amplitude of puckering q in Å.

The calculations reported in Table I were made for cyclopentane in the conformation of C_S symmetry, *i.e.*, with $\varphi = 0$ or any integral multiple of $\pi/10$ in equation 2. The various terms were also calculated for the C_2 conformation which may be obtained on substitution of any odd integral multiple of $\pi/20$ for φ. The simplest case is $\varphi = -3\pi/20$ which yields $z_1 = 0$ and thus places atom one on the symmetry axis. A near equilibrium value 0.48 Å. was taken for q and the following values were obtained: $-E_C = 45.0$, $E_{\text{torsion}} = 6.5$, $E_{\text{C–C–C}} = 3.77$, $-\Delta H_f° = 8.5$ kcal./mole. The torsional and bond bending strain energies are very close to the comparable values for $q = 0.48$ interpolated from Table I. The electron correlation energy and the net heat of formation differ by about one-half kilocalorie from the values for the C_S form; we are not sure whether this difference is significant or not (see Appendix). It may be concluded, nevertheless, that the calculated energy difference between C_2 and C_S forms is small and thus in practical agreement with experiment[9] and with the earlier calculation.[3]

The second derivative of the energy with respect to q gives the restoring force for the vibration (283 cm.$^{-1}$) in which the amplitude of puckering varies. The effective mass for this vibration was calculated only approximately and interaction with other vibrations was neglected. The resulting spectroscopic force constant, $k = 1.3 \times 10^5$ dynes/cm., agrees as well as could be expected with that obtained from the plot of the values of Table I, *ca.* 1.1×10^5.

While the 1.7 kcal./mole difference in $\Delta H_f°$ indicates that some further improvement in the theory of the energy is needed, the present results are qualitatively correct in all respects and yield as close a quantitative agreement as can be expected for a relatively simple theory.

A similar calculation for cyclohexane, where there is no torsional or C–C–C angle strain, yields $-\Delta H_f° = 19.5$ kcal./mole at 0°K. in excellent agreement with the experimental value of 20.0 kcal./mole. In this calculation the zero point energy was obtained from the frequency assignment of Beckett, *et al.*[12]

Cyclopentane Derivatives and Related Five-membered Ring Compounds.—If cyclopentane is substituted in such a manner as to change significantly one or more of the torsional potential barriers, then the cancellation of forces that yield the free pseudo-rotation will no longer be as exact and a potential restricting the pseudo-rotation is to be expected. An example is thiacyclopentane where Hubbard, *et al.*,[13] found a potential barrier of 2800 cal./mole from their interpretation of spectroscopic and thermodynamic data.

An exact calculation of the potential barrier for the pseudo-rotation would require the readjustment of the puckering to minimize the energy for each phase angle between the puckering maximum and the substituted atom. However, we may obtain approximate results by assuming that the bond twist angles remain the same as in cyclopentane itself. These are shown for the two symmetrical conformations[14] in Fig. 2 and Table II for $q_0 = 0.48$ Å. The extreme difference in energy for a single substitution is obtained by placing the substituent in the unique position in each case (position one in Fig. 1). There are, of course, inter-

TABLE II

TORSIONAL ANGLES IN CYCLOPENTANE

	C_S	C_2
$\theta_{12} = \theta_{51}$	46.1°	15.15°
$\theta_{23} = \theta_{45}$	28.6°	39.45°
θ_{34}	0.0°	48.1°
$1 + \cos 3\theta_{12}$	0.25	1.70
$1 + \cos 3\theta_{23}$	1.07	0.52
${}^1/_2(1 + \cos 3\theta_{34})$	1.00	0.09

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[11] The original calculation of Kilpatrick, Pitzer and Spitzer[3] used an erroneous symmetry number of 5 instead of 10. Correction of this error doubles the value of q_0. See THIS JOURNAL, **80**, 6697 (1958).

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

[13] W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 6025 (1952).

[14] The names *envelope* and *half chair* have been suggested for the C_S and C_2 forms, respectively, by Brutcher (private communication). These terms seem to the writer to be appropriate if descriptive names are desired in addition to the symmetry symbols.

mediate conformations between C_2 and C_S which have the same energy in cyclopentane and smoothly varying energy in substituted molecules. Also conformations obtained by placing the substituent in an unsymmetrical position in the C_2 and C_S forms are also real but of intermediate energy.

The last three lines in Table II give the coefficients of the potential barriers $V_{12} = V_{51}$, $V_{23} = V_{45}$ and V_{34}, respectively, in the torsional strain energy. If we wish only the energy difference ΔV_C for the conformation change $C_S \rightarrow C_2$, we obtain

$$\Delta V_C = 1.45 V_{12} - 0.55 V_{23} - 0.91 V_{34} \qquad (3)$$

This torsional energy difference may be taken as a good approximation to the net difference in total energy unless some special complication such as a repulsive steric hindrance is present. If all potential barriers are the same, the result is zero within computational error as stated above.

Let us now consider in particular the case where substitution has occurred at position one in cyclopentane. The barriers are 2800 cal./mole except for $V_{12} = V_{51}$ which may be different. Then

$$\Delta V_C = 1.45(V_{12} - 2800) \text{ cal./mole} \qquad (4)$$

where the change is $C_S \rightarrow C_2$ as before. Table III contains values of V_{12} taken from appropriate model molecules and the resulting ΔV_C values for several substituted cyclopentanes and related compounds containing saturated five-membered rings.

It should be emphasized that the ΔV_C values in Table III are potential barriers to the pseudo-rotation which is restricted in these cases. A positive value of ΔV_C indicates that the lowest energy phase angle of puckering is the symmetrical C_S form; a negative value indicates that the lowest energy phase angle is the symmetrical C_2 form. One may assume that a simple cosine function yields a good approximation for the energy of all intermediate values of the phase angle. Thus ΔV_C is *not* the energy difference between separate potential minima such as the equatorial and axial conformations of methylcyclohexane but is the height of the energy barrier restricting the rotation of the phase of puckering.

TABLE III

POTENTIAL BARRIERS TO PSEUDO-ROTATION IN CYCLOPENTANE DERIVATIVES

Substance	V_{12}	ΔV_C
Methylcyclopentane	3.40[a]	0.9
Fluorocyclopentane	3.30[b]	0.7
Methylenecyclopentane	1.98[c]	−1.2
Cyclopentanone	1.15[d]	−2.4
Pyrrolidine	1.90[e]	−1.3
Tetrahydrofuran	1.07[f]	−2.5
Thiacyclopentane	0.71[g]	−3.0

[a] Propane: K. S. Pitzer, *J. Chem. Phys.*, **12**, 310 (1944). [b] Ethyl fluoride: D. Herschbach, *ibid.*, **25**, 358 (1956). [c] Propylene: D. R. Lide, Jr., and D. E. Mann, *ibid.*, **27**, 868 (1957). [d] Acetaldehyde: R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957). [e] Methylamine: D. R. Lide, Jr., *ibid.*, **22**, 1613 (1954); Shimoda, Nishikawa and Itoh, *J. Phys. Soc. Japan*, **9**, 947 (1954). [f] Methanol: E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **21**, 1804 (1953); J. D. Swalen, *ibid.*, **23**, 1739 (1955). [g] Methanethiol: R. W. Kilb, *ibid.*, **23**, 1736 (1955).

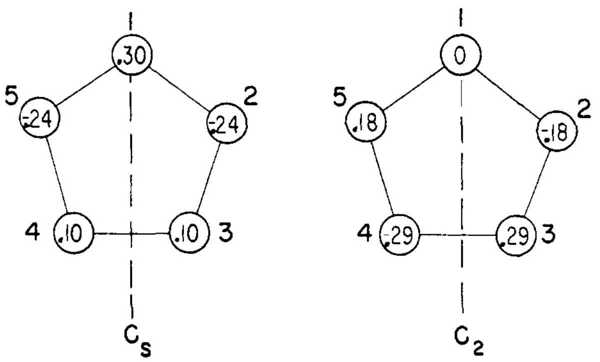


Fig. 2.—The two symmetrical conformations of cyclopentane. Figures inside the circles show equilibrium displacements perpendicular to plane of the paper in Å.; figures outside the circles indicate the numbering adopted for the carbon atoms.

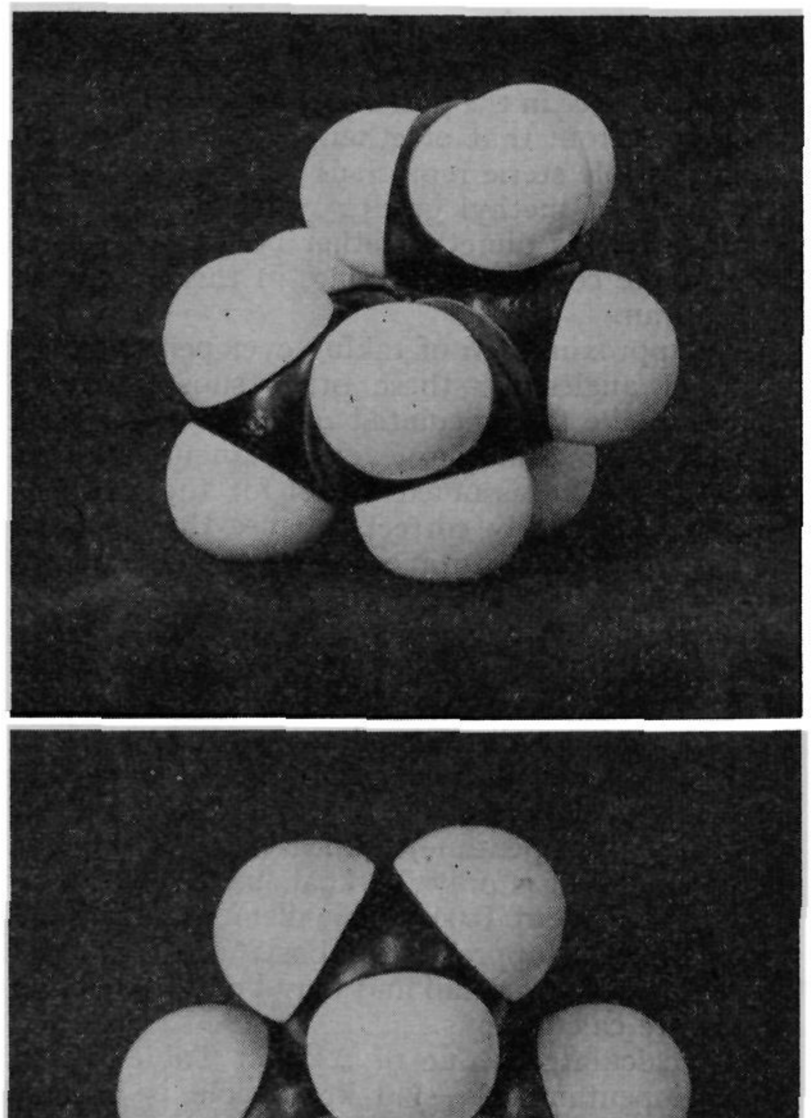
The model compounds chosen for obtaining V_{12} values are given in the footnotes to Table III. It should be remembered that the essential quantity is the difference in the potential barrier of the model compound from that of ethane. Also we wish to avoid possible steric repulsions between the hydrogen atoms of methyl groups which arise in compounds such as dimethyl ether but which do not arise in the corresponding ring, in this case tetrahydrofuran.

The approximation of taking cyclopentane bond torsional angles for these other substances will tend to make the calculated ΔV_C values too large. Consider, for example, cyclopentanone with its small V_{12}. The assumed model for the stable C_2 form will be nearly correct because the reduction of V_{12} from cyclopentane to cyclopentanone will tend only to reduce θ_{12} which is already small. However, in the high energy C_S form θ_{12} is larger than optimum for the low V_{12} of cyclopentanone. Reduction in the puckering parameter reduces the C–C–C angle strain at moderate cost in torsional strain. A quantitative calculation for the C_S form of cyclopentanone (assuming still the E_C values of cyclopentane) indicates that the corrected potential is only 0.2 kcal./mole lower (at a value of q_0 about 0.04 Å. smaller) than was obtained on the approximate basis of Table III. Thus this effect is small and may be ignored in approximate calculations.

The calculated value of ΔV_C in Table III for thiacyclopentane of −3.0 kcal./mole is in good agreement with the experimental value ±2.8 kcal./mole obtained by Hubbard, *et al.*[13] The thermodynamic method used in their work determines the magnitude but not the sign of the potential barrier. McCullough[9] reports that the value for pyrrolidine is small without indicating an upper limit. The calculated value of −1.3 kcal./mole is certainly much smaller than that for thiacyclopentane and may be small enough to yield agreement with experiment.

Discussion

The data presented in Tables II and III provide the basis for estimates of strain energies for many five-membered ring systems. For maximum accuracy one should readjust all of the molecular parameters in order to minimize the strain energy for each individual case. A few exploratory calculations indicated, however, that useful estimates of strain energy differences may be obtained in many cases by retaining the geometry of cyclopentane but recognizing the difference in torsional potential barriers caused by the substitution. In making such calculations it is essential to select the conformation of cyclopentane which will be most stable in the substituted molecule. Thus a single substituent which raises the two adjacent barriers ($V_{12} = V_{51}$) stabilizes the symmetrical C_S form whereas if a single substituent lowers the adjacent barriers the symmetrical C_2 form becomes the most stable. One may then calculate torsional strain energy differences by multiplying the appropriate value of $(1 + \cos 3\theta_{12})$ in Table II by the difference in potential barrier height V_{12}. If two molecules are to be compared which have different stable conformations, then one must compare each with cyclopentane and sum the two differences. A case of this type will be illustrated below.



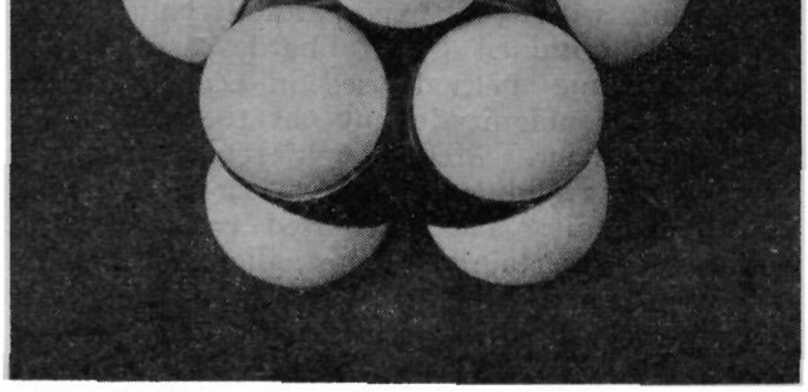


Fig. 3.—Two views of methylcyclopentane with the methyl group in the most axial conformation. The absence of steric repulsions analogous to axial methylcyclohexane is apparent.

The possibility of steric repulsions analogous to those of axial substituents in cyclohexane must also be considered. Examination of appropriate models (Fig. 3) shows no large interference in the cyclopentane case for the methyl group or any smaller group. An approximate quantitative value for the axial–equatorial energy difference can be obtained from the heat of formation values[5] found for *cis*- and *trans*-1,3-dimethylcyclohexanes which are −22.19 and −21.65 kcal./mole, respectively, at 0°K. The *cis* isomer has a di-equatorial conformation while the *trans* is axial–equatorial. Hence the energy difference of 0.54 kcal./mole may be ascribed to the extra strain of the axial methyl group. The corresponding value for the cyclohexane system is, of course, much larger (*ca.* 1.9 kcal./mole).

The terms axial and equatorial are descriptive only for that portion of the cyclopentane ring where the C–C bonds are in a nearly staggered orientation. We see from Table II that the 1,2- and 5,1-bonds in the C_S form are nearly staggered, hence the three successive positions 5, 1 and 2 qualify. In 1,3-dimethylcyclopentanes the methyl groups would be expected to be in positions 5 and 2 of the Table II numbering for the C_S form.

Since the e–a energy difference is small, the value $\Delta V_C = 0.9$ kcal./mole in Table III for methylcyclopentane may be interpreted as a good approximation to the net barrier to pseudo-rotation in that molecule. This agrees well with the value selected by Kilpatrick, *et al.*,[15] 0.75 kcal./mole which is consistent with the entropy of methylcyclopentane.[5] Conversely one may regard the agreement just cited as confirming the low e–a energy difference in methylcyclopentane.

Cases of axial conformation of groups larger than methyl or of conformations which are di-axial on the same side of the ring may have large strain but need individual consideration.

Let us now consider particular data of several types which relate to the strain of saturated five-membered rings. The heats of hydrogenation measured by Turner and Garner[16] for methylenecyclopentane (−26.9 kcal./mole) and methylenecyclohexane (−27.8 kcal./mole) may be interpreted to yield the difference in strain energy of methylcyclopentane and methylenecyclopentane. If all thermal energy terms are assumed to cancel and both cyclohexane compounds are strain free,[16a] then one assigns the difference of 0.9 kcal./mole to an increased amount of strain in methylcyclopentane over that in methylenecyclopentane.

(15) J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947).

(16) R. B. Turner and R. H. Garner, THIS JOURNAL, **79**, 253 (1957); **80**, 1424 (1958).

(16a) H. C. Brown, J. H. Brewster, and H. Shechter, THIS JOURNAL, **76**, 467 (1954), assume that the introduction of an exo double bond into cyclohexane introduces strain. The structural explanation proposed was strain associated with the opposed orientation of the double bond relative to the C–H bonds of adjacent ring methylene groups. Recent microwave studies (ref. *d* of Table III and D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.*, **28**, 728 (1958)) have shown that this opposed orientation is the stable orientation, hence there is no basis for expecting appreciable strain in methylenecyclohexane or cyclohexanone.

The equilibrium conformations will be C_S for methylcyclopentane and C_2 for methylenecyclopentane. The values of $(1 + \cos 3\theta_{12})$ in Table II then yield for the difference in torsional strain

$$\Delta E_{\text{tors}} = 0.25(3.40 - 2.80) + 1.70(2.80 - 1.98) = 1.54 \text{ kcal./mole}$$

where the first term is the increase in torsional strain of methylcyclopentane over cyclopentane and the second term the decrease of methylenecyclopentane below cyclopentane.

The unstrained H–C–H bond angle in ethylene[17] is larger than tetrahedral (117°) although the force constant is somewhat smaller (0.7 instead of 0.8×10^{-11} erg/radian^2). The ring angles were readjusted approximately to minimize the strain under these new conditions and the result indicated an increase in C–C–C bond angle strain of about 0.9 kcal./mole in methylenecyclopentane above that in cyclopentane or in methylcyclopentane.

The net result (1.54 − 0.9) is the calculated strain energy difference of 0.64 kcal./mole which may be compared to Turner and Garner's experimental difference of 0.9 kcal./mole. This is as good agreement as can be expected in view of the approximations made and the omission of differences in electron correlation energies.

A somewhat similar argument may be applied to the data on the reaction of cyclic cyanohydrins to form the cyclic ketone and hydrogen cyanide. Prelog and Kobelt[18] report the standard free energy of dissociation to be 2.4 and 4.2 kcal./mole, respectively, for the cyclopentane and cyclohexane systems in 96% alcohol at 22–23°. The difference of 1.8 kcal./mole may be attributed to the appropriate difference in strain free energies.

Cyclohexanone is unstrained. The corresponding cyanohydrin may have either the OH or the CN group axial with the other in the equatorial position. Various investigations of cyclohexanol[19] indicate that the strain free energy of an axial OH group is 0.6 ± 0.2 kcal./mole. Such knowledge as we have of the van der Waals repulsive contour of the CN group indicates that it will be less hindered in the axial position than the OH group.

At this point we must note that it is strain free energy which we are estimating for the cyanohydrin, whereas it was strain energies (or enthalpies) in earlier examples. If the cyanohydrin were purely a-CN, e-OH and the a-CN were strain free, there would still be a strain free energy of $RT \ln 2$ (or 0.4 kcal./mole at 300°K.) because the elimination of the e-CN, a-OH conformation has reduced the entropy. In this case the 0.6 kcal./mole strain of a-OH will not eliminate the a-OH conformation; also the a-CN conformation may have a few tenths kcal. strain. Hence an exact calculation is not possible but the estimate of 0.5 ± 0.2 kcal./mole for the strain free energy of the cyclohexanone cyanohydrin seems reliable.

The strain free energy in the cyclopentane system is, therefore, 2.3 kcal./mole greater in the cyanohydrin than in the ketone. The calculations follow closely the method explained above for methylenecyclopentane and methylcyclopentane. One readily calculates that the torsional strain energy of cyclopentanone is less than that of cyclopentane by 1.70(2.80 − 1.15) = 2.8 kcal./mole. The additional C–C–C bond angle strain in cyclopentanone must be very nearly the same as that in methylenecyclopentane, hence we take the same value of 0.9 kcal./mole.

There do not appear to be any serious steric hindrance effects in the cyclopentanone cyanohydrin, but the torsional potential barriers are presumably somewhat greater than in cyclopentane. Barrow[20] gives 3.3 kcal./mole for the barrier to methyl rotation in ethanol. The substitution of the CN group might be expected to increase this value somewhat but we have no basis for an accurate estimate. Fortunately the coefficient from Table II for the C_S form is only 0.25, hence a crude estimate will suffice. We take 4.0 kcal./mole for the barrier adjacent to the C(OH)CN group and obtain 0.25(4.0 − 2.8) = 0.3 kcal./mole for the excess torsional strain over that of cyclopentane.

Since the pseudo-rotation of the cyclopentane ring is substantially restricted for both the ketone and the cyanohydrin, the entropy effects should approximately cancel and we find from the terms previously discussed 0.3 + 2.8 − 0.9 = 1.2 kcal./mole for the excess strain in the cyanohydrin over that of the ketone. The agreement of this figure with the experimental value to 0.1 kcal./mole is, of course, fortuitous, since the calculation could easily err by 0.5 kcal./mole. Nevertheless, the results indicate that the important effects are adequately considered in these simple calculations.[21]

Fused rings offer a wide variety of situations; only one will be mentioned here in concluding this discussion. The hydrindanes were considered by Dauben and Pitzer[22] who emphasized the effects on the six-membered ring. We may now add that the ring fusion will also restrict the conformation of the five-membered ring. Since the shared C–C bond is staggered ($\theta = 60°$) in the normal chair conformation of cyclohexane, the five-membered ring will tend to place its most nearly staggered bond in that location. Table II shows that this is bond 3–4 in the C_2 conformation. Thus the five-membered ring in hydrindane will take the C_2 conformation with the unique CH_2 group (1 in Fig. 2) in the 8-position. We note, however, from Table II that $\theta_{12} = \theta_{51}$ for the C_S conformation is only 2° less than θ_{34} in C_2. The difference in energy

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[17] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957); H. C. Allen and E. K. Plyler, THIS JOURNAL, **80**, 2673 (1958).

[18] V. Prelog and M. Kobelt, *Helv. Chim. Acta*, **32**, 1187 (1949).

[19] E. L. Eliel and C. A. Lukach, THIS JOURNAL, **79**, 5986 (1957); S. Winstein and N. J. Holmes, *ibid.*, **77**, 5562 (1955); R. A. Pickering and C. C. Price, *ibid.*, **80**, 4931 (1958).

[20] G. M. Barrow, *J. Chem. Phys.*, **20**, 1739 (1952).

[21] The heat of hydrogenation values for the cyclic ketones may also be discussed in a similar fashion. Unfortunately the large difference in heat of hydrogenation of cyclohexanone (−15.42) from those of acetone (−13.41) and methyl ethyl ketone (−13.19) remains unexplained. The value for cyclopentanone is calculated to be about 2.0 kcal./mole smaller than that of an unstrained ketone, hence the observed value of −12.50 kcal./mole is reasonable but no more can be said. The measurements are by M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938); J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *ibid.*, **61**, 1868 (1939).

[22] "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 37.

for this 2° change is very small, consequently substitution of hydrindane could easily introduce forces which would shift the conformation somewhat.

Appendix

The mathematical procedure in calculating atomic positions in a puckered cyclopentane (sym. C_S) is described briefly. First consider the carbon atoms; going clockwise around cyclopentane, the odd C-atom is given the number 1 and the position of each atom denoted by (x_i, y_i, z_i). z_i is given from equation 2 as a certain fraction of q, which is a measure of the puckering. All the x_i, y_i are unknowns except x_1 and y_1 which are set at zero.

$$(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 = (1.54)^2 \tag{A-1}$$

$$(x_3 - x_2)^2 + (y_3 - y_2)^2 + (z_3 - z_2)^2 = (1.54)^2 \tag{A-2}$$

$$x_3 = -x_4 = 0.77 \tag{A-3}$$

$$x_5 = -x_2 \tag{A-4}$$

$$y_3 = y_4 \tag{A-5}$$

$$y_2 = y_5 \tag{A-6}$$

$$y_1 = x_1 = 0 \tag{A-7}$$

$$z_1 = 0.63q \tag{A-8}$$

$$z_2 = z_5 = -0.51q \tag{A-9}$$

$$z_4 = z_3 = 0.20q \tag{A-10}$$

The scalar products of bond vectors yield

$$(1.54)^2 \cos \omega_1 = -x_2^2 + y_2^2 + (z_2 - z_1)^2 \tag{A-11}$$

$$(1.54)^2 \cos \omega_2 = x_2(x_2 - 0.77) + y_2(y_2 - y_3) + (z_2 - z_1)(z_2 - z_3) \tag{A-12}$$

Kilpatrick, Pitzer and Spitzer[3] found that the potential energy minimum lies very close to the configuration given by $\omega_1 = \omega_2$. We adopt this relation, which simplifies the calculations, and equate (A-11) and (A-12) which yields equation A-15. Equation A-1 may be reduced to A-13 and (A-2) to (A-14); thus we have three equations for x_2, y_2 and y_3 which must be solved simultaneously

$$x_2 = [(1.54)^2 - (1.14q)^2 - y_2^2]^{1/2} \tag{A-13}$$

$$y_3 - y_2 = [(1.54)^2 - (0.71q)^2 - (0.77 - x_2)^2]^{1/2} \tag{A-14}$$

$$y_2 y_3 = 2x_2^2 - 0.77x_2 - (1.14q)(0.43q) \tag{A-15}$$

After several iterations have yielded a solution for x_2, y_2 and y_3 (which must be exact for A-13 and A-14 but may be only approximate for A-15), equations A-11 and A-12 may be solved for $\cos \omega_1$ and $\cos \omega_2$. $\cos \omega_3$ is given by

$$1.54 \cos \omega_3 = 0.77 - x_2 \tag{A-16}$$

The torsion angles are given by the equations

$$\cos \theta_{12} = \frac{\cos \omega_2(\cos \omega_1 - 1) - \sin {}^1/_2\omega_1(1 - 2 \sin {}^1/_2\omega_1)}{\sin \omega_1 \sin \omega_2} \tag{A-17}$$

$$\cos \theta_{23} = \frac{\cos \omega_2 \cos \omega_3 + \sin {}^1/_2\omega_1}{\sin \omega_2 \sin \omega_3} \tag{A-18}$$

$$\cos \theta_{34} = 1 \tag{A-19}$$

The above equations suffice for the calculation of torsional and C–C–C angle strain energies.

The hydrogen atom positions are determined in the following way: first define the vector

$$\mathbf{R}_i = 2\mathbf{r}_i - \mathbf{r}_{i-1} - \mathbf{r}_{i+1} \tag{A-20}$$

where the $\mathbf{r}_i$ are the vectors to the carbon atoms; then let

$$\mathbf{s}_i = \mathbf{R}_i/|\mathbf{R}_i| \tag{A-21}$$

Also let

$$\mathbf{T}_i = (\mathbf{r}_i - \mathbf{r}_{i+1}) \times (\mathbf{r}_i - \mathbf{r}_{i-1}) \tag{A-22}$$

and

$$\mathbf{t}_i = \mathbf{T}_i/|\mathbf{T}_i| \tag{A-23}$$

The two hydrogen atom positions on the ith CH_2 are now given by

$$\mathbf{h}_i = \mathbf{r}_i + 1.10\left[\sqrt{\frac{1}{3}}\,\mathbf{s}_1 + \sqrt{\frac{2}{3}}\,\mathbf{t}_i\right] \tag{A-24}$$

$$\mathbf{h}'_i = + 1.10\left[\sqrt{\frac{1}{3}}\,\mathbf{s}_1 - \sqrt{\frac{2}{3}}\,\mathbf{t}_i\right] \tag{A-25}$$

This treatment assumes a tetrahedral H–C–H angle and places the H atoms symmetrically with respect to the adjacent C–C bonds. It remains to calculate all of the interatomic distances and sum their inverse sixth powers in accordance with equation 1. This last calculation involves many steps and corresponding opportunities for error. Several calculations were made for C_S forms with increasing q values which gave an opportunity to check the trend of each interatomic distance and thereby identify errors. Since only one calculation was made for a C_2 form, it must be regarded as less reliable although it was carefully checked.

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