Tetrahedron, 1966, Vol. 22, pp. 119 to 122. Pergamon Press Ltd. Printed in Northern Ireland

# THE HEAT OF COMBUSTION AND STRAIN ENERGY OF 2,2-PARACYCLOPHANE

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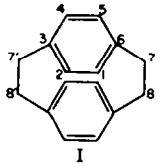
(*Received* 17 *June* 1965)

**Abstract**—The heat of combustion and vapor pressure curve of solid 2,2-paracyclophane have been determined and used to derive the heats of combustion and formation of both the solid and gaseous compound. Comparison of the experimental heat of formation with that expected for an unstrained reference structure indicates a strain energy of 31 kcal mole$^{-1}$. The division of the strain energy among several contributions is discussed.

## INTRODUCTION

2,2-PARACYCLOPHANE (I) is an interesting strained ring system.[1] Planarity of the




I

benzene rings and the *para* substituent carbon atoms along with accommodation of the $\pi$ electron clouds between the rings would not be possible without excessive strain in the bridging ethylene groups. x-Ray diffraction analysis[2,3] shows that the actual conformation is one in which the aromatic rings are deformed out of planarity. Further, the Lonsdale structure[3] shows appreciable stretching of the $C_7$–$C_8$ with slight bending of the $C_6$–$C_7$ bond whereas the Brown structure shows more bending of $C_6$–$C_7$ and less stretching of $C_7$–$C_8$. The overall strain manifests itself in such effects as perturbation of the portion of the electronic absorption spectrum characteristic of the benzene rings.[4–6] It is of interest to have a quantitative thermochemical measure of the strain energy and it was the purpose of the present research to undertake a determination of this.

## EXPERIMENTAL

The heat of combustion was determined with a calorimeter and techniques that have been described.[7] The results are listed in Table 1. The vapor pressures (Table 2) were determined by an effusion cell technique[7] and were fitted by least-squares to the equation,

$$\log P = A/T + B.$$

The heat of vaporization was calculated from the Clausius-Clapeyron equation as

$$\Delta H_{vap} = -2{\cdot}303\,RA.$$

This equation is accurate only in the range of the measurements (343–383°K) which lies outside of

[1] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.* **73**, 5691 (1951).
[2] C. J. Brown, *J. Chem. Soc.* 3265 (1953).
[3] K. Lonsdale, H. J. Milledge, and K. V. Krishna Rao, *Proc. Roy. Soc.* **A255**, 82 (1960).
[4] D. J. Cram, N. L. Allinger and H. Steinberg, *J. Amer. Chem. Soc.* **76**, 6132 (1954).
[5] D. S. McClure, *Canad. J. Chem.* **36**, 48 (1958).
[6] A. Ron and O. Schnepp, *J. Chem. Phys.* **37**, 2540 (1962).
[7] R. H. Boyd, R. L. Christensen and R. Pua, *J. Amer. Chem. Soc.* **87**, 3554 (1965).

TABLE 1. ENERGY OF COMBUSTION OF 2,2 PARACYCLOPHANE, 25°

| M | $M_F$ | ΔR | ΔR′ | $q_1$ | $q_2$ | $q_3$ | $-\Delta E_c°$(cal/gm air vs SS) |
|---|---|---|---|---|---|---|---|
| 0·175818 | 0·002328 | 0·197676 | 0·196600 | 0·84 | 0·93 | 0·80 | 10,018·1 |
| 0·179705 | 0·001998 | 0·201774 | 0·200850 | 0·80 | 0·80 | 0·80 | 10,014·6 |
| 0·177252 | 0·002430 | 0·199442 | 0·198315 | 0·73 | 0·82 | 0·80 | 10,025·1 |
| 0·179127 | 0·002265 | 0·201451 | 0·200404 | 0·97 | 0·58 | 0·80 | 10,024·8 |
| 0·164951 | 0·001910 | 0·185409 | 0·184526 | 0·87 | 0·79 | 0·80 | 10,023·2 |
| 0·177095 | 0·002305 | 0·199114 | 0·198048 | 0·95 | 0·89 | 0·80 | 10,019·9 |
| 0·176867 | 0·002275 | 0·198857 | 0·197805 | 0·95 | 0·65 | 0·80 | 10,021·9 |
| | | | | | | | 10,021·1 Av. |
| | | | | | | | $\sigma = 3·5$ |
| | | | | | | | 10,014·3 cal/gm-vac |

M = Sample wt. (in air vs SS)
$M_F$ = Wt. fuse (in air vs SS)
ΔR = Corrected temp rise (ohms)
ΔR′ = ΔR − $M_F$ (0·4624)
$q_1$ = Electrical energy correction
$q_2$ = Nitric acid correction
$q_3$ = Correction to standard states, "Washburn correction"
$\Delta E_c°$ = Heat of combustion, 25° corrected to standard states

$$-\Delta E_c° = \frac{\varepsilon \Delta R' - q_1 - q_2 - q_3}{M}$$

ε = energy equivalent of calorimeter
= 8972·2 ± 2·8 cal/ohm (first four combustions)
= 8973·2 ± 2·8 cal/ohm (last three combustions)

298°K. An estimated adjustment to 298°K was made. The thermochemical data are summarized in Table 3.

The sample of 2,2-paracyclophane used was furnished to us by Professor D. J. Cram. It was purified twice by sublimation.

The sample wt. was reduced to *vacuo* using a density[8] of 1·229 gm ml.$^{-1}$.

## DISCUSSION

The strain energy can be derived by comparison of the experimental heat of combustion or formation with that of an unstrained reference structure. The latter can be

TABLE 2. VAPOR PRESSURE OF 2,2-PARACYLOPHANE

| T°C | P (microns) |
|---|---|
| 70·21 | 0·534 |
| 80·37 | 1·32 |
| 90·11 | 3·22 |
| 99·95 | 6·41 |
| 110·41 | 16·8 |

log P(microns) = 13·843–4,849/T(°K)

TABLE 3. SUMMARY OF THERMOCHEMICAL DATA, 25° 2,2-PARACYCLOPHANE

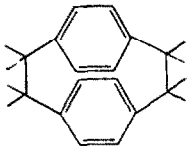
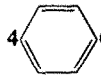
| | $\Delta H_c°$ (kcal mole$^{-1}$) | ΔH (vaporization) (kcal mole$^{-1}$) | $\Delta H_f°$ (kcal mole$^{-1}$) |
|---|---|---|---|
| Solid | −2088·2 ± 0·9[a] | 22·2 ± 0·2 (343–383°K) | 36·9 ± 0·9 |
| | | 23·0 ± 1·0 (298°K, estimated) | |
| Gas | −2111·2 ± 1·9[b] | | 59·9 ± 1·9 |

[a] Uncertainty is $\pm\sigma\Delta H_c°$, where $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$ and $\sigma_1$ and $\sigma_2$ are relative standard deviations of calibration runs and sample runs respectively.

[b] Uncertainty is summed uncertainty of $\Delta H_c°$ and $\Delta H_{vap}$.

conveniently obtained from a group contribution scheme. The strain energy arrived at in this manner is listed in Table 4: Another equivalent way is by direct comparison of experimental data for two reactions, one that relieves the strain in the compound of interest and a similar one for an unstrained compound. This approach leads to another interesting and unexpected consideration. If hydrogenation of the $—CH_2—$

TABLE 4. STRAIN ENERGY OF 2,2 PARACYCLOPHANE
(all units are kcal mole$^{-1}$)

| (Literature Refs for data used) | | (1) $\Delta H_f°$ (Ref. structure)[a] | (2) $\Delta H_f°$ (exp) | Strain energy (2)-(1) | Strain energy A-B | |
|---|---|---|---|---|---|---|
| | | 29·0 | 59·9 | 31 | | |
| *b* | A |  | $+ 2H_2 \longrightarrow 2CH_3$  $—CH_3$ | | | |
| | | | $\Delta H° = -51.5$ | | | |
| *b,c* | B. 2  $—CH_2$-$CH_2$  | | $+ 2H_2 \longrightarrow 4$  $CH_3$ | | | 37 |
| | | | $\Delta H° = -14.6$ | | | |
| *b* | B′ 2 $R_1—CH_2—CH_2—R_2$ | | $+ 2H_2$ | $2\ R_1—CH_3 + 2R_2—CH_3$ | | 31 |
| | | | $\Delta H° = -20$ | | | |

[a] Calculated from group contributions, J. L. Franklin, *Ind. Eng. Chem.* **41**, 1070 (1949).
[b] F. D. Rossini, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*. Carnegie Press, Pittsburgh, Pennsylvania (1953).
[c] See Ref. 8.

$CH_2—$ bonds is selected as the strain relieving reaction, hydrogenation of the central bond in bibenzyl would be the obvious comparison reaction. However, according to the available experimental data,[8] bibenzyl is an unusually stable compound possessing

[8] There are two modern values of the heat of combustion (and the derived heat of formation) of bibenzyl in good agreement, $\Delta H_f° = 10·53$ kcal mole$^{-1}$, (G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine *J. Amer. Chem. Soc.* **68**, 2524 (1946)) and $\Delta H_f° = 11·6$ kcal mole$^{-1}$ (J. Coops, D. Mulder, J. W. Dienske and J. Smittenberg, *Rec. Trav. Chim.* **72**, 785 (1953)). Unfortunately, as is often the case with heats of vaporization derived from vapor pressure curves at low pressures, the agreement here is not as good. There are three values: $\Delta H_{vap} = 17·3$ kcal mole$^{-1}$ (N. F. H. Bright, *J. Chem. Soc.* 624 (1951); 17·5 kcal mole$^{-1}$ (K. L. Wolf and H. Weghofer, *Z. Phys. Chem.* **B39**, 194 (1938)); and 20·07 kcal mole$^{-1}$ (A. Aihara, *Bull. Chem. Soc. Japan* **32**, 1242(1959)). We have selected Aihara's value since it is the highest and leads to the smallest extra thermochemical resonance energy for bibenzyl. Use of the other two values would raise this to 6 kcal mole$^{-1}$. Clearly, in view of the theoretical importance of this effect, the thermochemical data for this compound, especially the heat of vaporization, should be established unequivocally on a sample of established purity.

a thermochemical resonance energy 3–4 kcal mole$^{-1}$ in excess of toluene or benzene.[9] Thus using the central bond in bibenzyl as the model, (reactions A. and B., Table 4) the strain in 2-2-paracyclophane appears to be $\sim$ 6 kcal mole$^{-1}$ larger than by either the group contribution method or by using a bond in an aliphatic hydrocarbon as the model (reactions A. and B'., Table 4). If true, the enhanced stability of bibenzyl is certainly surprising and its explanation presumably would require, in the valence bond description, contributions of the hyperconjugative type. Further evidence that this effect might be real comes from a rather accurate x-ray diffraction determination of the structure.[10] The central C—C bond appears to be slightly shortened, 1·51 A° vs. 1·54 A° for a normal —$CH_2$—$CH_2$— bond.

TABLE 5. STRAIN ENERGY CONTRIBUTIONS, KCAL MOLE$^{-1}$

| Out-of-plane deformation of aromatic rings[a] | Stretching of $C_7$–$C_8$ bond[b] | Eclipsed hydrogens ($C_7$, $C_8$; $C_7'$ $C_8'$) | Other angle strains[c] | Ring repulsion[d] |
|---|---|---|---|---|
| 15 | 5 | 4 | 1 | (6) |

[a] Calculated using a bond rotation angle of 15·6° calculated from the atomic coordinates of Ref 3 and a force constant of 0·18 × $10^5$ dynes/cm from Ref 13 for twisting of eight ring bonds.

[b] Using a force constant of 4·5 × $10^5$ dynes/cm (G. H. Herzberg, *Molecular Structure and Molecular Structure* Vol. II. van Nostrand, New York, N.Y. (1945) and a deformation of 0·09 A° (Ref 3).

[c] From the coordinates of Ref 3, the angle between the bond $C_6$–$C_7$ and plane $C_1$, $C_5$, $C_6$ is 2·8° and $C_6$, $C_7$, $C_8$ is strained $\sim$2°. We have estimated one kcal mole$^{-1}$ as the contribution from these.

[d] Difference between the sum of other terms and 31 kcal mole$^{-1}$ (the total strain energy).

It is of interest to interpret the overall strain energy in 2,2-paracyclophane in terms of the various deformations and repulsions. Trueblood[11] has made an *a priori* estimate of the strain energy of 33 kcal mole$^{-1}$. The principal contribution of 26 kcal mole$^{-1}$ (based on Brown's structure[2] and Whiffens'[12] spectroscopic force constant) is from the out-of-plane distortion of the aromatic rings. We have made a similar calculation based on the structure of Lonsdale[3] *et al.* and the force constant of Kakiuti and Shimanouchi[13] with similar but significantly different results. These calculations are summarized in Table 5. It is seen that according to our analysis there is inferred by difference an appreciable non-bonded replusion between the rings. This would include hydrogen repulsions as well as carbon.

*Acknowledgment*—The author is greatly indebted to the U.S. Army Research Office (Durham) for financial support of this work. He is also grateful to Professor D. J. Cram for furnishing the sample and for his interest.

[9] G. Wheland *Resonance in Organic Chemistry* Chap. 3. Wiley, New York, N.Y. (1955), reports the thermochemical resonance energy of bibenzyl as normal, i.e. twice that of benzene or toluene. His experimental vapor phase heat of combustion however is from F. Klages value (*Chem. Ber.* **82**, 358 (1949)) based on earlier thermochemical work and an estimated heat of vaporization.

[10] D. W. J. Cruickshank, *Acta Cryst.* **2**, 65 (1949).

[11] K. N. Trueblood, private communication.

[12] D. H. Whiffen, *Phil. Trans. Roy. Soc.* **A248**, 131 (1955).

[13] Y. Kakiuti and T. Shimanouchi, *J. Chem. Phys.* **25**, 1252 (1956).