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THE HEATS OF COMBUSTION AND STRAIN ENERGIES OF SOME CYCLOPHANES

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Abstract—Heats of combustion and vapor pressure curves have been determined for 2,2-metacyclophane (II), 3,3-paracyclophane (III), 2,2-metaparacyclophane (IV), 1,8-paracyclophane (V), 6,6-paracyclophane (VI), 2,2-perhydroparacyclophane (VII). From these data, values have been derived for the heats of combustion and formation of both the solid and gaseous compounds. Heats of crystal transition, and of fusion, have been measured for II, III, and IV. Measurements have also been made of the heat capacities of 2,2-paracyclphane, II, III, and IV at 300°K and 318°K. Experimental strain energies at 298°K and in a motionless state are derived from the heats of formation by comparisons with group contributions and also by comparison of heats of strain relieving reactions with reference reactions. The crystal and gaseous heats of formation and experimental room temperature strain energies are respectively (in kcal mole^{-1}): II, 18·7 ± 1·5, 40·7 ± 1·9, 12; III 6·24 ± 0·63, 30·92 ± 0·88, 12; IV, 31·26 ± 0·51, 52·18 ± 0·73, 24; V, −19·6 ± 1·7, 6·9 ± 2·2, 2; VI, −46·0 ± 2·3, −18·5 ± 2·8, −7; VII, −58·4 ± 3·1, −37·4 ± 3·6, 26. The structure, strain energy and thermodynamic functions of VII have been calculated by energy minimization using a set of transferable potential functions.

INTRODUCTION

THE cyclophanes are an interesting group of strained ring compounds and have been the subject of extensive study. X-ray diffraction analysis[1, 2] of 2,2-paracyclophane (I) shows distortion of the aromatic rings and the heat of combustion[3] demonstrates the presence of considerable strain energy due to ring distortion as well as interring repulsion. 2,2-metacyclophane (II) and 3,3-paracyclophane (III) have also been the subject of X-ray diffraction analysis.[4, 5] In the present work, we have determined the heats of combustion of the latter two in order to obtain experimental values of their strain energies. We have also determined the heats of combustion of 2,2-metaparacyclophane[6] (IV) and 1,8 and 6,6-paracyclophanes[7, 8] (V and VI).

The perhydro analog of 2,2-paracyclophane (2,2-perhydroparacyclophane, (VII) has been prepared[9] and is a very interesting molecule because of the extreme hydrogen crowding between the cyclohexane rings. We have determined its heat of combustion also.

In the interpretation of the strain energy and geometry of such molecules, the use of transferable valence force potentials for bond stretching, bending and torsion in the calculation of the conformation of minimum energy is a powerful tool. In a separate paper,[10] we have illustrated the use of a minimization procedure with calculations of

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strain energies, conformations and thermodynamic functions of four of the cyclophanes (I, II, III, IV). In the present work, we have also predicted by such calculation a structure of the perhydro compound (VII).

DISCUSSION

Although one could attempt to interpret the heats of formation directly in terms of structure, the concept of strain energy has a ready interpretative value and has been widely used. Experimental strain energies may be derived from the heats of formation in several ways. It is desirable, however, to use a method that is compatible with energy minimization calculations. The latter type of calculation implies that there is a set of intrinsic transferable bond energies (of any degree of dependence on neighboring groups) and a set of transferable potential functions for bond stretching, bending, and twisting as well as a set of non-bonded potentials. There are two points to make about such a model. First, it is appropriate to a molecule with neither thermal or zero point vibrational energy, a state which we shall refer to as the hypothetical motionless state. Highly successful bond energy or group contribution schemes have been worked out for unstrained molecules which inherently include the vibrational and thermal effects and can be used for defining strain energies at finite temperatures by comparison of experimental and predicted heats of formation. However, it is known that strain energies defined in this way are temperature dependent and can be significantly different in the hypothetical motionless state.[11, 12] Fortunately, this problem can be handled satisfactorily for we feel that adequately reliable gas-phase thermodynamic functions ($H^\circ_T - H^\circ_0$, in this case) and zero point energies can be calculated for the conformation of minimum energy as part of the overall energy minimization calculation.[10]

The second point about the model has to do with the handling of non-bonded contributions in the definition of strain energies. In a model where these are used, the "unstrained" molecules will have appreciable energy beyond the intrinsic bond energies and, furthermore, it will not appear only as non-bonded energy, the minimization of energy will cause it to be also distributed among bond deformations. Thus, a set of group contributions must be worked out for both the total atomization and the intrinsic bond energies in unstrained molecules if strain energies in other molecules are to be defined. Our procedure for strain energy calculations is outlined below.

We assume that the calculated *energy* of atomization in the hypothetical motionless state (indicated by *) is given by

$$E^*_a(\text{calc.}) = \Sigma E^*_i - (DE + NB) \tag{1}$$

where E^*_i are a set of intrinsic bond or group contributions to the energy of atomization, DE is the deformation energy (bond stretching, bending, and twisting) and NB is the non-bonded energy contribution. $DE + NB$ is calculated by energy minimization using transferable potential functions. The experimental energy of atomization of a hydrocarbon of formula, $C_n H_m$, is given in terms of the experimental heat of formation at 298°K by,

$$\begin{aligned} E^*_a(\text{exp}) = & -\Delta H^\circ_f(\text{exp, } 298^\circ\text{K}) + n(170{\cdot}890) \\ & + m(52{\cdot}090) + (H^\circ_{298^\circ\text{K}} - H^\circ_0) + ZPE \\ & - 5/2\,(n + m)\,RT_{298^\circ\text{K}} \end{aligned} \tag{2}$$

where the heats of atomization of C (graphite) and H_2 (g) at 298°K have been taken from Stull and Sinke[13] and $H^\circ_{298^\circ\mathrm{C}} - H^\circ_0$ and ZPE are the enthalpy and zero point energy of the compound. The calculated strain energy in the motionless state is defined by

$$-SE^*(\text{calc.}) = E_a^*(\text{calc.}) - \Sigma E_a^*(\text{group}) \tag{3}$$

where ΣE_a^* (group) is the sum of group (or bond) contributions to the total atomization energy appropriate for unstrained molecules. These latter group contributions include both the intrinsic bond energies and deformation and non-bonded energies in the unstrained molecules. The experimental strain energy in the hypothetical motionless state is given by,

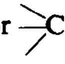
$$-SE^*(\text{exp.}) = E_a^*(\text{exp.}) - \Sigma E_a^*(\text{group}). \tag{4}$$

For the strain energy at room temperature it is more convenient to work with heats of formation and we have used the traditional definition of

$$SE(\text{exp.})_{298^\circ\mathrm{C}} = \Delta H_f^\circ(\text{exp.}, 298^\circ\mathrm{K}) - \Sigma\Delta H_f(\text{group}), \tag{5}$$

where the right-hand term is the predicted heat of formation based on group contributions derived from unstrained molecules. For numerical values, we have used the scheme of Franklin tabulated by Janz.[14,*] For the calculated strain energy at room temperature, we have used the analogy of Eqn. (2) with E_0^* (exp.) replaced by E_a^*(calc.) to define ΔH_f° (calc, 298°K) and, thus, obtain

$$\begin{aligned} SE\,(\text{calc})_{298^\circ\mathrm{C}} &= \Delta H_f^\circ(\text{calc}, 298^\circ\mathrm{K}) - \Sigma\Delta H_f(\text{group}) \\ &= -\Sigma E_i^* + NB + DE + n(170{\cdot}890) + m(52{\cdot}090) \\ &\quad + (H^\circ_{298^\circ\mathrm{C}} - \mathrm{H}^\circ_0) + ZPE - 5/2\,(n+m)\,RT_{298^\circ\mathrm{C}} \\ &\qquad - \Sigma\Delta H_f\,(\text{group}). \end{aligned} \tag{6}$$

In the calculations[10] on compounds I, II, III, and IV, the only non-bonded interaction included was aC···C repulsion between aromatic rings, an interaction not present in unstrained compounds. Therefore, the intrinsic bond contributions become equal to the total atomization energy bond contributions ($\Sigma E_i^* = \Sigma E_a^*$(group)) and SE^*(calc) becomes equal to $DE + NB$. A group contribution to the total atomization energy in the motionless state for  is derived in Table 1 using group contributions for E_a^* for CH, —CH_2— and —CH_3 derived from alkanes in other work. Benzene and toluene are included for completeness.

Using the group contributions of Table 1 and the DE + NB of reference (10) in Eqn (6), the room temperature strain energies may be theoretically calculated for compounds I–IV. They are summarized in Table 2 along with experimental strain energies of V and VI. The latter were considered too complicated for energy minimization calculations.

We have also repeated the calculations of reference (10) using the non-bonded potential functions for C··· C, C···H, and H···H derived by Williams[15] from

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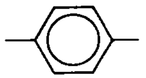
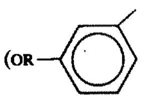
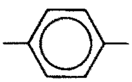
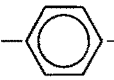
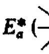
[*] 24·3 kcal mole^{-1} was used for  .

TABLE 1. DERIVATION OF GROUP CONTRIBUTION (kcal mole^{-1}) OF  (OR )[a] TO THE ENERGY OF ATOMIZATION IN THE HYPOTHETICAL MOTIONLESS STATE

Compound	$\Delta H_f^\circ(298)$	$H_{298}^\circ - H_0^\circ$ [b,c]	ZPE[b]	$\Delta E_a^*(\text{exp.})$[d]
Benzene	19·51	3·42 (calc) 3·40 (API)	65·25	1369·26
Toluene	11·96	4·28 (calc) 4·31 (API)	82·15	1665·20
p-xylene	4·30	5·14 (calc) 5·36 (API)	99·02	1961·22

 = CH$_3$—  —CH$_3$ − 2(—CH$_3$) = 1250·68

(E_a^* (—CH$_2$—) = 293·81 kcal mole^{-1}, E_a^* (—CH$_3$) = 355·27 kcal mole^{-1}, and

E_a^* ( CH) = 233·41 kcal mole^{-1})[e]

[a] taken to be the same as para group.

[b] calculated value is found using the methods and potential functions of reference (10). —CH$_3$ group was considered a free rotator in the thermodynamic calculation.

[c] API is the value from F. D. Rossini, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, Pa. (1953) and is shown for comparison.

[d] Heat of atomization in hypothetical vibrationless state (kcal mole^{-1}).

[e] From alkanes.

crystalline hydrocarbon structures for the non-bonded interactions between the aromatic rings. Results very similar to those of ref. 10 for the geometries and strain energies were obtained. In view of the wider generality of the potentials of ref. 15, they are probably to be preferred to the C···C potential derived and used by us previously.[10] The use of Williams' potentials make the calculations on the cyclophanes completely *a priori*.

Another approach to definition of strain energy is based on the comparison of strain relieving reactions with similar reactions in unstrained systems. For example, the difference between

$$\Delta H \text{ for 2,2-paracyclophane (g)} + 2H_2(g) \rightarrow 2\ p\text{-xylene (g)} \qquad (7)$$

and

$$2\,C_{a+b}\,(n\text{-alkane}) + 2H_2 \rightarrow 2C_a\,(\text{n-alkane}) + 2C_b\,(\text{n-alkane}) \qquad (8)$$

can be defined as the strain energy. Table 3 lists strain energies defined this way both at 298°K and in the hypothetical motionless state.

It is to be noticed that, although there is a definite tendency for the values of SE^* in Tables 2 and 3 to be larger than $SE_{298^\circ\text{C}}$, the difference is not particularly significant. This is in contrast to the cyclic alkanes where differences of several kilocalories are observed.[11, 12]

TABLE 2. EXPERIMENTAL AND CALCULATED STRAIN ENERGIES[a] OF CYCLOPHANES (KCAL MOLE^{-1}) FROM INTRINSIC GROUP CONTRIBUTION APPROACH

Cyclophane	$DE^b + NB$	$H^\circ_{298^\circ K} - H^{\circ c}_0$	ZPE^c	$E^*_a(\text{exp})^d$	ΣE^{*e-}_a	SE^* (exp)	SE^* (calc)	$SE_{298^\circ K}$ (exp.)	$SE_{298^\circ K}$ (calc.)
2,2-para	35·1	8·32	176·49	3645·20	3676·60	31·4	35·1	30·9	34·6
2,2-meta	20·9	8·06	177·05	3664·70	3676·60	11·9	20·9	11·9	20·8
2,2-metapara	27·3	8·00	177·33	3653·42	3676·60	23·2	27·3	23·4	27·5
3,3-para	10·2	9·70	212·23	4252·57	4264·22	11·7	10·2	11·9	10·4
1,8-para								2·7	
6,6-para								−8·0	

[a] SE^* refers to strain energy in a hypothetical motionless state, exp. and calc. values are defined in Eqs. 3 and 4 of the text.

[b] Deformation energy due to bond stretching, bending and twisting calculated in ref. 10.

[c] Enthalpy and zero point energy calculated in ref. 10.

[d] Energy of atomization in hypothetical motionless state, Eqn. (2) of text.

[e] Sum of group contributions (Table 1) to atomization energy in hypothetical motionless state.

The various deformations and distribution of strain energies among the deformations has already been discussed[10] for compounds I–IV. Although no calculations were made for compounds V and VI, the small strain energy of 1,8-paracyclophane appears to be consistent with molecular models. The substantial negative strain energy (stabilization) of 6,6-paracyclophane is probably the result of SE_{298° being somewhat smaller than SE^* and also perhaps due to some stabilization due to Van der Waals attraction in such a large globular molecule that is not accounted for by the group increments from n-alkanes. The latter effect appears to be real for 2,2-perhydroparacyclophane as discussed below.

TABLE 3. EXPERIMENTAL STRAIN ENERGIES OF CYCLOPHANES (kcal mole^{-1}) BASED ON COMPARISON OF HEATS OF STRAIN RELIEVING HYDROGENATIONS WITH THOSE OF *n*-ALKANES[a]

Cyclophane	Hydrogenation products	ΔH(298°)	ΔH^*	SE_{298°	SE^*
2,2-*para*	2(*p*-xylene)	−51·5	−58·2	31·5	32·6
2,2-*meta*	2(*m*-xylene)	−32·4	−39·1	12·4	13·5
2,2-*metapara*	*m*-xylene and *p*-xylene	−43·7	−50·1	23·7	24·5
3,3-*para*	2(1-Me-4Et-benzene)	−31·7	−37·3	11·7	11·7
1,8-*para*[b]	*p*-xylene, toluene and *n*-hexane	−30·6		1·7	
6.6-*para*	2(*p*-xylene) and 2(*n*-butane)	−33·2		−6·8	

[a] The reference heat of hydrogenation of one n-alkane bond was taken to be 10·0 kcal mole^{-1} at 298°K and 12·8 kcal mole^{-1} in the hypothetical vibrationless state. The latter is based on enthalpy functions in the API tables (see Table 1) and derived from the frequencies of alkanes tabulated by R. G. Snyder and J. H. Schachtschneider, *Spectrochim Acta* **21**, 169 (1965) and enthalpy function and zero point energy of H_2 of 2·02 and 6·28 kcal mole^{-1} respectively.

[b] The reference bonds here were taken to 2 n-alkane bonds and the pendant carbon–carbon bond in toluene.

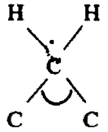
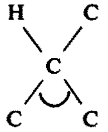
2,2-perhydroparacyclophane is a very complex molecule, and the problem of calculation of its structure by energy minimization is formidable. However, investigations with molecular models indicated that, due to hydrogen crowding, there are few structures that are not highly strained. Fisher–Taylor–Hirshfelder models could not be made to close. Leybold Stuart–Briegleb models could be assembled in one relatively distinct conformation. Using this conformation as a starting structure, a converging structure could be calculated. The potential functions used were those adopted in other work yet to be reported by us for saturated hydrocarbons. These functions differ from the ones used for compounds I–IV in that non-bonded functions are used between *all* pairs of atoms except those mutually involved in bond stretching and bending. These non-bonded functions are a slight modification of those of Williams[15] and were chosen to represent both the effects of substitution on bond torsion and steric interaction between non-bonded atoms. The potential function constants are tabulated in Table 4.

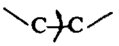
TABLE 4. POTENTIAL FUNCTION CONSTANTS FOR SATURATED HYDROCARBONS USED FOR 2,2-PERHYDROPARACYCLOPHANE[a]

Bond stretching

	k_r	$R^\circ(A^\circ)$
C—H	4·55	1·09
C—C	4·40	1·53

Bond bending

	k_θ	θ°
	0·80	111·0°
	0·75	111·0°
	0·608	109·5
	0·508	107·9



Bond torsion (cosine potential)

Uo = 0·0146

Non-bonded and torsion (all pairs of atoms not in same bond angle interaction)

$$V = A \exp(-BR) - B/R^6$$

	A	B	C
C···C	104·0	3·09	4·45
C···H	30·0	3·415	0·96
H···H	18·4	3·74	0·19

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[a] All units are such that energies are in units of 10^{-11} ergs and distances in Ångstroms. Bond stretching and bending potentials are harmonic with the force constants and natural length and angles given. (To convert ergs molecule^{-1} to kcal mole^{-1} multiply by 144·0).

TABLE 5. STRAIN ENERGY[a] AND STRAIN ENERGY DISTRIBUTION IN 2,2-PERHYDROPARACYCLOPHANE (kcal mole^{-1})

$DE + NB$[b]	$H^\circ_{298^\circ} - H^\circ_0$[c]	ZPE[c]	E^*_a (exp.)[d]	ΣE^*_a (group)[d]	ΣE^*_i[e]	SE^* (exp.)	SE^* (calc.)	SE_{298° (exp.)	SE_{298° (calc.)
44·69 (42·76)	9·92 (9·77)	253·55 (254·57)	4428·4	4459·36	4466·72	31·0 (30·1)	37·3 (35·4)	26·1	32·1 (31·0)

		Strain energy distribution			
Bond stretching	Torsional strain	C—C—C— bending	C—C—H and H—C—H bending	Non-bonded	Total
2·3 (2·2)	4·8 (ring 1, carbons 1–6) (4·9) 5·6 (ring 2, carbons 9–14) (5·7) 5·9 (linkages thru 7, 8 and 15, 16) (5·4)	6·9 (5·8)	5·4 (3·9)	13·8 (14·9)	44·7 (42·8)

[a] The strain energies in the last four columns are defined in eqs (3–6) of text. Values in parentheses are for the structure of Figure 2. The others are for the structure of Figure 1.

[b] Deformation and non-bonded energy.

[c] Enthalpy and zero-point energy calculated from vibrational analysis of final structure, see Table 7.

[d] Energy of atomization in hypothetical motionless state, experimental and from group contributions (Eq. (2) and Table 1 respectively.

[e] Sum of group contributions to intrinsic (excluding non-bonded and deformation energy in unstrained molecules) bonded energy, CH_3— = 355·74, —CH_2— = 294·13, —CH = 234·19.

TABLE 6. SOME CALCULATED GEOMETRICAL PARAMETERS OF 2,2-PERHYDROPARACYCLOPHANE

$ijkl$ interaction[a]	ϕ_{ijkl} (torsional angle)	θ_{ijk} (bond angle)
1, 2, 3, 4	54·9 (64·9) degrees	111·6 (112·0) degrees'
2, 3, 4, 5	64·9 (28·9)	108·8 (108·6)
3, 4, 5, 6	17·4 (26·0)	110·8 (114·8)
4, 5, 6, 1	37·0 (47·4)	114·2 (116·3)
5, 6, 1, 2	46·8 (11·9)	112·8 (112·0)
6, 1, 2, 3	0·4 (43·8)	114·5 (114·3)
1, 6, 7, 8	30·8 (104·6)	116·6 (113·9)
6, 7, 8, 9	119·9 (145·3)	117·5 (116·0)
7, 8, 9, 10	178·1 (177·3)	116·5 (116·4)
8, 9, 10, 11	67·0 (61·3)	110·7 (110·2)
9, 10, 11, 12	56·3 (44·8)	111·6 (111·9)
10, 11, 12, 13	6·5 (11·1)	113·3 (114·1)
11, 12, 13, 14	35·3 (47·1)	113·3 (112·0)
12, 13, 14, 9	28·2 (26·0)	118·1 (116·4)
13, 14, 9, 10	19·9 (29·0)	115·6 (114·8)
11, 12, 15, 16	114·0 (103·8)	112·8 (113·9)
12, 15, 16, 3	58·5 (144·9)	118·8 (116·0)
15, 16, 3, 4	156·5 (60·4)	113·3 (116·3)

Some C···H and H···H distances[b]							
C····H[b]		C····H[c]		H····H[b]		H····H[c]	
i, j	r_{ij}(Å)	i, j	r_{ij}(Å)	i, j	r_{ij}(Å)	i, j	r_{ij}(Å)
				19, 38	2·32	17, 26	2·18
9, 21	2·68	4, 30	2·46	21, 30	1·99	18, 28	2·19
6, 21	2·61	5, 30	2·60	21, 39	1·93	22, 30	2·00
8, 21	2·40	7, 18	2·60	22, 43	2·32	22, 42	2·11
13, 21	2·60	8, 44	2·52	25, 28	2·22	26, 27	2·20
14, 21	2·33	13, 44	2·60	30, 34	2·10	28, 39	2·10
12, 21	2·66	14, 44	2·46	34, 42	2·19	30, 44	2·02
11, 30	2·69	15, 35	2·60	38, 43	2·20	34, 36	2·18
		16, 30	2·53	18, 30	2·30	35, 42	2·20

[a] See Fig. 1 for atom numbering. Torsional angle ϕ is measured relative to the eclipsed configuration as zero. Values in parentheses are for structure of Figure 2.

[b] All C···H distances less than 2·70 Å and all H···H distances less than 2·40 Å for the structure of Figure 1.

[c] All C···H distances of 2·60 Å or less and all H···H distances of 2·20 Å or less for the structure of Figure 2.

TABLE 7. GAS-PHASE THERMODYNAMIC FUNCTIONS OF 2,2-PERHYDROPARACYCLOPHANE[a] (cal degree^{-1} mole^{-1})

T(°K)	$-(F^\circ - H^\circ_0)/T$	$(H^\circ_T - H^\circ_0)/T$	S°	C_p°
298·16	132·07 (145·16)	33·26 (32·73)	165·34 (177·88)	66·22 (65·35)
300	132·28 (145·36)	33·47 (32·93)	165·75 (178·29)	66·69 (65·86)
400	143·46 (156·37)	44·91 (44·29)	188·37 (200·66)	91·55 (90·70)
500	154·74 (167·51)	56·61 (55·95)	211·35 (223·46)	114·36 (113·60)

Zero Point Energy = 253·55 kcal mole^{-1} (254·57)

[a] Calculated by method of Ref 10 using parameters of Table 4.

Values in parentheses are for the structure of Figure 2, other are for the structure of Figure 1.

The structure was refined to an RMS deviation of 0·01 Å and required five iterations. All 964 bond stretching, bending, torsional and non-bonded interactions were included in the calculation. Leaving out non-bonded interactions greater than 4 Å apart (~450 total interactions) raised the calculated deformation and non-bonded energy by 5 kcal mole^{-1}. It seems likely that there is a stabilization due to Van der Waals attraction in large globular molecules of this type that somewhat greater than are accounted for by group contributions based on smaller molecules. The final

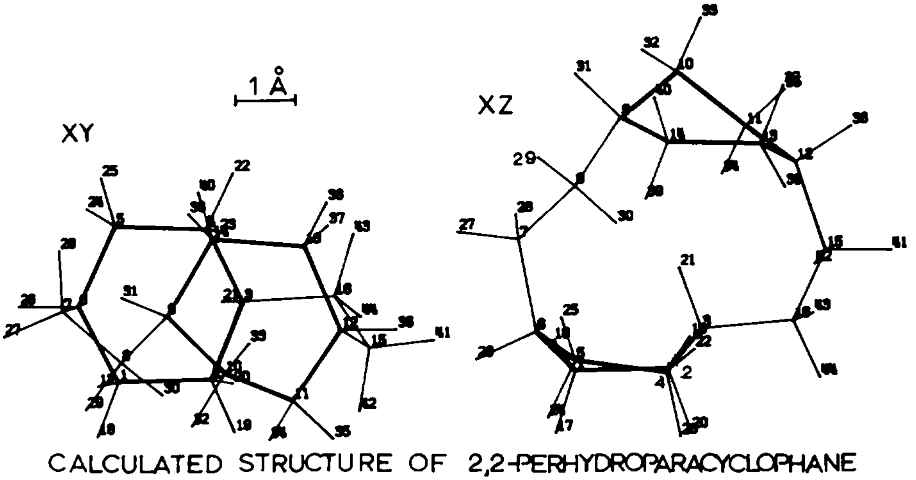

FIG. 1 XY and XZ plane projections of the calculated structure of 2,2-perhydro-paracyclophane. Carbon atoms in the cyclohexane rings (shown darker) are numbered 1–6 and 9–14. Hydrogens are numbered 17–44 and are placed consecutively on carbons 1–16.

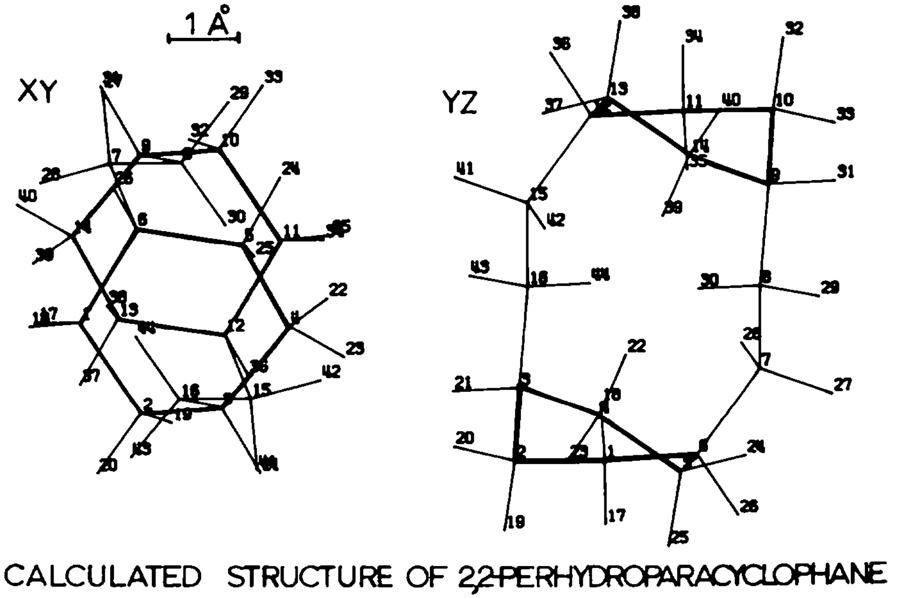

FIG. 2 XY and YZ plane projections of an alternate calculated structure of 2,2-perhydro-paracyclophane. Bonds at the junctures of the cyclohexane rings are *cis* with respect to each other in both rings in contrast to the structure of Fig. 1 where one ring (9–14) is connected *cis* and the other (1–6) is connected *trans*.

structure is illustrated in Fig. 1 and the strain energy and its distribution are summarized in Table 5. Some geometrical parameters are listed in Table 6. The calculated thermodynamic functions are tabulated in Table 7.

Since non-bonded interactions were included between all appropriate pairs of atoms, in contrast to the calculations on compounds I–IV, it is necessary to use a set of intrinsic group energy contributions distinct from the group contributions to the total atomization energy to arrive at E_a^*(calc) from Eq. (1) in order to calculate the strain energy in Eq. (3)' These group contributions, derived in other work by us, are listed in Table 3 also.

It is to be noticed that the strain energy in the hypothetical motionless state is significantly higher (5 Kcal mole^{-1}) than at room temperature and illustrates the importance of taking this effect into account in strain energy calculation by energy minimization. The strain energy of the structure calculated is close enough to the measured strain energy that, in view of very large numbers of interactions and the difficulty in finding a reasonable structure, we feel that the predicted structure has a reasonable chance of being near the actual one.*

EXPERIMENTAL

The samples of compounds III, IV, V, VI, and VII were very kindly furnished to us by Prof. D. J. Cram. A sample of II was given us by Prof. V. C. Boekelheide and was supplemented by our syntheses of additional compound by his method.[16] The samples were purified by multiple-pass zone refining followed by sublimation.

The heats of combustion were determined with a calorimeter and techniques which have been previously described[17] except that a G2 Mueller resistance bridge (Leeds and Northrup 8069-B) was used. A typical set of results is given in Table 8. The vapor pressures were determined by an effusion cell technique,[17] and were fitted by least squares to the equation,

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

Values for the constants A and B, such that P is in mm and T in °K, are given in Table 9. The heats of vaporization were calculated from the Clausius–Clapeyron equation as:

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

TABLE 8. ENERGY OF COMBUSTION AT 298°K OF 2,2-METAPARACYCLOPHANE

M_s	M_f	$^{\ominus}R$	Q_f	Q_i	Q_{std}	$-^{\ominus}E_c^{\circ}$
0·182643	0·002186	0·203290	9·15	0·67	1·01	9996·75
0·182912	0·002228	0·203502	9·32	0·67	1·01	9991·60
0·183300	0·002227	0·203974	9·32	0·67	1·01	9993·71
0·183042	0·002235	0·203663	9·35	0·67	1·01	9992·29
0·183305	0·002190	0·203959	9·16	0·67	1·01	9993·57
0·182455	0·002260	0·203075	9·46	0·67	1·01	9994·72

M_s = Weight of sample (g. in air vs. SS)
M_f = Weight of fuse (g. in air vs. SS)
ΔR = Corrected temperature rise (ohms)
Q_f = Heat from combustion of fuse. (calories)
Q_i = Energy of Ignition. (calories)
Q_{std} = Heat correction to standard states (Washburn) (cal. g^{-1} air vs. SS)
$-\Delta E_c^{\circ} = (\varepsilon\Delta R - Q_f - Q_i - Q_{std})/M_s$, where ε, the energy equivalent calorimeter = 9034·72 ± 1·59 cal. ohm^{-1}

mean = 9993·77 ± 1·49
mean = 9986·56 ± 1·49
when weights are corrected to vacuum

TABLE 9. VALUES OF CONSTANTS A AND B FROM VAPOR PRESSURE CURVES

	A	B
2,2-Metacyclophane	−4791	12·43
2,2-Metaparacyclophane	−4524	11·88
2,2-Perhydroparacyclophane	−4450	11·25
3,3-Paracyclophane	−5109	12·75
1,8-Paracyclophane	−5480	12·81
6,6-Paracyclophane	−5681	12·82

$\log P(\text{mm}) = A/T(°\text{K}) + B$

TABLE 10. HEAT CAPACITIES, IN cal /K^{-1} mole^{-1} OF SOME CYCLOPJANES

	300°K	318°K
2,2-Metacyclophane	57·5 ± 1·4	69·3 ± 1·8
2,2-Metaparacyclophane	62·5 ± 2·0	Crystal transition
2,2-Paracyclophane	59·3 ± 1·7	61·7 ± 0·6
3,3-Paracyclophane	77·5 ± 1·9	81·1 ± 2·1

As the vapor pressure measurements were made above 298°K, it was necessary to correct the heats of vaporization to this temperature using the expression:

$$\Delta H_{vap}^{298°C} = \Delta H_{vap} - \Delta Cp(T°K - 298).$$

where T°K is the midpoint of the temperature range of bapor pressure measurements, and $^{\Theta}$Cp is the difference: $(Cp)_{vap} - (Cp)_{solid}$. In some cases, the correction was estimated, but in others, the heat capacities of the solids were measured, using a differential scanning calorimeter (Perkin–Elmer DSC-1B). In these cases, the vapor heat capacity used was that calculated by Boyd,[10] from empirical balence-force potentials. The measured heat capacities are given in Table 10. Some further data on purity and heats of transition and fusion were also obtained with the differential scanning calorimeter, and these are given in Table 11. Crystal transitions were discovered in the middle of the vapor pressure ranges in 2,2-metaparacyclophane and 3,3-paracyclophane after the vapor pressures had been determined. For the former, the heat of transition

TABLE 11. PURITY (mole%), HEATS OF CRYSTAL TRANSITION, AND HEATS OF FUSION, (kcal mole^{-1}) OF SOME CYCLOPHANES

	Purity	Transition I	Transition II	Fusion
2,2-Metacyclophane	99·90	—	—	5·12 ± 0·05 at 404°K
2,2-Metaparacyclophane	99·94	0·210 ± 0·002 at 315°K		3·05 ± 0·05 at 354°K
3,3-Paracyclophane	99·78	1·76 ± 0·03 at 332°K	0·110 ± 0·002 at 351°K	2·81 ± 0·04 at 377°K

Note added in proof: Prof. N. L. Allinger has commented that in the calculated structure of Fig. 1, the bonds 6,7 and 3,16 are *trans* with respect to ring 1–6 in contrast to ring 9–14 where the juncture is *cis* and has speculated that a structure with both junctures *cis* would be more stable. We have been able to calculate such a structure and find it to be slightly more stable than the one in Fig. 1. It is shown in Fig. 2 and the energetic and structural results are included in Tables 5,6 and 7 in parentheses. The second structure is probably also more compatible with some preliminary X-ray diffraction results from Prof. K. N. Trueblood's laboratory.

TABLE 12. SUMMARY OF THERMOCHEMICAL DATA IN kcal mole^{-1} AT 298°K FOR CYCLOPHANES[a]

		ΔH_c°	ΔH_{vap}	ΔH_f°
2,2-Metacyclophane	(c)	$-2070·1 \pm 1·5$	$21·9 \pm 0·3$ (308–332°K)	$18·7 \pm 1·5$
	(g)	$-2092·1 \pm 1·9$	$22·0 \pm 0·4$ (298°K)	$40·7 \pm 1·9$
2,2-Metaparacyclophane	(c)	$-2082·63 \pm 0·31$	$20·70 \pm 0·20$ (310·8–328·2°K)	$31·26 \pm 0·51$
	(g)	$-2103·55 \pm 0·53$	$20·92 \pm 0·22$ (298°K)	$52·18 \pm 0·73$
2,2-Perhydroparacyclophane	(c)	$-2402·9 \pm 3·1$	$20·4 \pm 0·3$ (316–338°K)	$-58·4 \pm 3·1$
	(g)	$-2423·9 \pm 3·6$	$21·9 \pm 0·5$ (298°K est.)	$-37·4 \pm 3·6$
3,3-Paracyclophane	(c)	$-2382·35 \pm 0·43$	$23·37 \pm 0·20$ (321·6–343·2°K)	$6·25 \pm 0·63$
	(g)	$-2406·23 \pm 0·68$	$24·70 \pm 0·25$ (298°K est.)	$30·92 \pm 0·88$
1,8-Paracyclophane	(c)	$-2843·6 \pm 1·7$	$25·1 \pm 0·3$ (354–376°K)	$-19·6 \pm 1·7$
	(g)	$-2870·1 \pm 2·2$	$26·5 \pm 0·5$ (298°K est.)	$6·9 \pm 2·2$
6,6-Paracyclophane	(c)	$-3304·2 \pm 2·3$	$26·0 \pm 0·2$ (352–371°K)	$-46·0 \pm 2·3$
	(g)	$-3331·7 \pm 2·8$	$27·5 \pm 0·5$ (298°K, est.)	$-18·5 \pm 2·8$

[a] In calculating uncertainties, the conventions suggested by F. D. Rossini employing the double standard deviation of the mean, have been followed. *Chem. Rev.* **18**, 233 (1936).

has negligible effect. For the latter no deviation from a straight line plot of log P *versus* $1/T$ was observed and ΔH_{vap} for this compound is assumed to be an average of the two crystal forms with the low temperature form being assigned a value of half the heat of transition higher than the average. The heats of formation are summarized in Table 12.

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