Thermochemical Studies on Double- and Triple-layered [2.2]Paracyclophanes. Estimation of Molecular Strain Energies.

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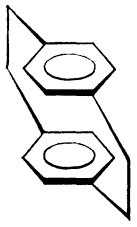
The measurements of enthalpies of combustion by use of precision oxygen-bomb combustion calorimeter together with the measurement of carbon dioxide recovery were made for double- and triple-layered [2.2]paracyclophanes. The enthalpies of sublimation were also determined by the measurement of temperature dependence of the vapor pressures for the two compounds. The following values are reported for the standard enthalpy of combustion ΔH_c°(298.15 K)/kJ mol^{-1} and standard enthalpy of sublimation ΔH_s°(298.15 K)/kJ mol^{-1}, respectively: double-layered [2.2]paracyclophane, 8729.48$\pm$1.80, 99.6$\pm$1.8; triple-layered [2.2]paracyclophane, 14230.87 $\pm$3.59, 125.9$\pm$2.5. From analyses of the derived standard enthalpy of formation in gaseous state the following two values for total strain energy U_s/kJ mol^{-1} of a molecule of triple-layered [2.2]paracyclophane were obtained: 251.9$\pm$5.6 with group method and 245.6$\pm$9.8 with chemical similarity method, respectively. These values are approximately twice the magnitudes of the corresponding quantities for double-layered [2.2]paracyclophane. From the analysis of the total strain energy by use of the result of Boyd's molecular mechanical calculation, the contribution from the twisting of the inner benzene ring to the total strain energy of triple-layered [2.2]paracyclophane was estimated to be almost twice that from one outer bent benzene ring.

Molecular and crystal structures of double-layered [2.2]paracyclophane (**1**) have been studied by X-ray diffraction method first by Brown,[1] and later reinvestigated by Lonsdale *et al.*,[2] by Bekoe *et al.*[3] and by Hope *et al.*[4] The various striking features in the molecular structure of **1** are as follows: (i) bent aromatic rings, (ii) short contact between aromatic rings, (iii) out-of-plane deformation of methylene carbon and aromatic hydrogen atoms from the plane defined by the nearest and next-nearest three aromatic carbon atoms, and (iv) eclipsing of bridge methylene groups. These features are considered to be resulted, directly or indirectly, from trans-annular π-electron repulsion in the molecule. Hope *et al.*[4] have shown that in the ordinary temperature phase of the crystal each molecule is statistically disordered to simulate a dynamic disorder that occurs by a twist of the aromatic rings with the amplitude of 3° in opposite directions about their common normal. Additional support for the twist can be found in spectroscopic[43] and thermal[28] results.



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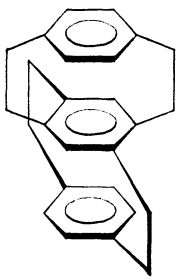

Compd. 2

Standard enthalpy of formation of **1** in the crystalline state has been reported by Boyd[5] and by Rodgers *et al.*[6] A significant difference of 9.4 kJ mol^{-1} has been found between these two values. Enthalpy of sublimation has been determined for this compound by Boyd[5] from the measurement of vapor pressure as a function of temperature. Strain energy has been estimated by Boyd[5] and by Rodgers *et al.*[6] from standard enthalpy of formation in gaseous state thus evaluated.

Boyd has also made calculation for this molecule based on a molecular mechanical method,[7] which enables simultaneous determination of molecular geometry, strain energy and thermodynamic quantities. Kao and Allinger[8] have applied a combined molecular orbital-molecular mechanics method to this molecule. They derived 199.2 kJ mol^{-1} for the standard enthalpy of formation in gaseous state which is significantly lower than both of the corresponding experimental values reported by Boyd[5] and by Rodgers *et al.*[6] and harboured a suspicion that the experimental results might be inaccurate. Lindner[9] also calculated standard enthalpy of formation for this compound in gaseous state by using a similar method.[10]

Molecular and crystal structures of triple-layered [2.2]paracyclophane (**2**) itself have not been reported. However, those for 1,4-bromo derivative of triple-layered [2.2]paracyclophane (**3**)[11] and for 4,4',7,7'-tetramethyl-substituted centrosymmetric quadruple-layered [2.2]paracyclophane (**4**)[12] have been studied by X-ray diffraction method. While outer aromatic rings in these molecules are boat-shaped, inner aromatic

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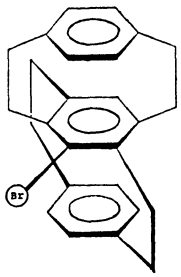

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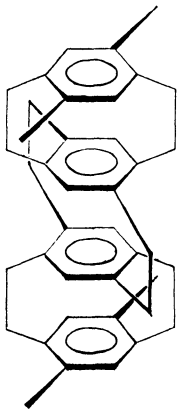

Compd. 4

rings are twisted by two upper and two lower methylene bridges. Most of the remaining anomalous features present in the molecule of **1** are found also in these molecules. It seems to be highly probable that the molecular geometry of **2** is similar to that of **3**. No thermodynamic study has been reported for this compound.

The present study has been carried out to examine the validity of the suspicion presented by Kao and Allinger[8] on the reported experimental results of **1** and to estimate the strain energy of **2**.[13] For this purpose, standard enthalpies of formation of **1** and **2** in the crystalline and gaseous states have been determined by bomb combustion calorimetry and by the measurement of temperature dependence of vapor pressure.

Experimental

Materials. Compound **1** was prepared by 1,6-Hofmann elimination method according to Winberg *et al.*[14] and purified by successive operations of gel-permeation liquid chromatography, recrystallization from chloroform (twice) and finally sublimation under vacuum (*ca.* 0.1 Pa).

Compound **2** was prepared as previously reported[15] and purified by gel-permeation liquid chromatography and then recrystallization from toluene solution (three times).

Combustion Calorimetry. An isoperibol precision rotating bomb calorimetric system described elsewhere[16] was used in this study without rotating the bomb. The following minor modifications were made on the calorimetric system after the publication of the previous paper: (1) The vacuum tube jacket temperature controller was replaced with a solid state device with proportional, integral and derivative actions. (2) The cooling device of the jacket water using ice was substituted with a refrigerator using semi-conductor Peltier elements which could supply cold water thermostatted within ± 30 mK. (3) The "Teflon" gasket for bomb-sealing was replaced with a rubber "O" ring. (4) The two unified connector-valves on the lid of the bomb using "Swagelok" fittings were replaced with the ones in which rubber "O" rings were used for sealing. (5) For connecting four lead wires to the calorimeter can, pin-connectors were used in place of soldering. (6) The oil-sealing of the calorimeter can were omitted to allow moderate vaporization of calorimeter water.

The calorimeter was calibrated by burning thermochemical standard benzoic acid (N.B.S. SRM-39i) under the standard bomb conditions.[17] The calibration experiments were interspersed between combustion experiments. Energy equivalents for the standard calorimetric system were derived from seven and eight calibration experiments for **1** and **2**, respectively. Mean and standard deviation of the mean were (15162.26 ± 1.08) J K^{-1} and (15164.06 ± 0.48) J K^{-1} for **1** and **2**, respectively.

Compound **1** was pressed into pellets by using a hand-press and an ordinary unevacuable die-set. The pellets exhibited a tendency to explode when partly burnt in the bomb. A deep crucible with a baffle described previously[18] was used for this compound.

Compound **2** was pressed into pellets by using a pellet press and a die-set usually used for making a KBr disk in infrared spectrometry. The pellets were burned in an ordinary platinum crucible. In two of experiments, a pellet of benzoic acid (thermochemical standard) weighing *ca.* 0.2 g was placed upon and under the pellet of the compound, respectively. In any experiments, a pellet of the compound did not explode when burned and significant amount of carbon monoxide was not detected from the bomb gas after combustion. However, the formation of a small amount of soot was observed in the crucible in every experiment.

In order to examine the completeness of combustion and/or the purity of a sample, carbon dioxide recovery was determined by the method developed by Rossini.[19] The absorption tube used in this study is shown in Fig. 1, which is similar in design to Pilcher's.[20] Ascarite (A.H. Thomas & Co., Ltd.) was used as an absorbent of carbon dioxide. In order to capture a small amount of water, which might be removed from the Ascarite layer, a small amount of Anhydrone

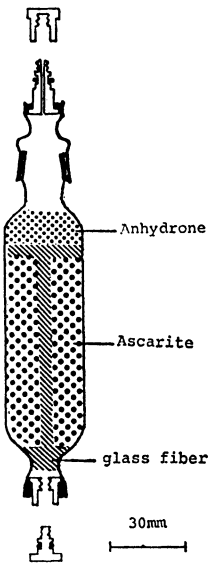

Fig. 1. Absorption tube for carbon dioxide analysis.

(Nakarai, S.P.R.) was placed next to the Ascarite layer. Heart of the absorption tube is the use of a small bundle of glass fiber placed from the inlet through the central portion of the Ascarite layer. The bundle of glass fiber exhibited a significant effect to secure the passage of bomb gas even after more than a half amount of Ascarite had lost its ability to absorb carbon dioxide. The ground glass joint was sealed with picein cement. The use of "O" ring along with metal connectors served to keep the absorption line leak-proof without loss of simplicity of experimental procedures. The flow rate of the gas liberated from the bomb was adjusted to *ca.* 2 $cm^3 s^{-1}$ with a needle valve. The gas was dried thoroughly by passage through the first absorption tube where Anhydrone was packed. The dried gas was then introduced into the second absorption tube, in which Ascarite was packed, and then examined for carbon monoxide by a detector tube (Kitagawa carbon monoxide detector type C, Kōmyo-Rikagaku Co., Ltd.) and finally released to air.

Before the analysis, the absorption train was flushed with oxygen. The carbon dioxide absorption tube was then disconnected, both the inlet and the outlet being closed, and the outer surface was cleaned with a piece of wiping paper wetted with ethyl ether, and then the tube was allowed to stand for 30 minutes. Just before weighing, pressure inside the tube was equalized with outside one by opening the gas inlet instantly. The tube was weighed and connected again to the train to start the absorption of carbon dioxide. After the pressure in the bomb decreased to atmospheric pressure, the bomb was flushed with oxygen (*ca.* 10 dm^3) at the average flow rate of 2 $cm^3 s^{-1}$. This flushing was performed to purge carbon dioxide in the gaseous and liquid phases completely. The absorption tube was then removed from the train and weighed in the same way as before.

From apparent increase in mass of the absorption tube Δm(tube), true mass of carbon dioxide captured, $m(CO_2, \text{obsd})$, was calculated by the following expression given by Rossini:[19]

$$m(CO_2, \text{obsd}) = 1.00045 \times \Delta m(\text{tube}).$$

In order to examine the validity of the results obtained by the procedure described above, combustion products of the calibration experiments were also analyzed. Carbon dioxide recovery defined as ratio of recovered to calculated masses of carbon dioxide $m(CO_2, \text{obsd})/m(CO_2, \text{calcd})$ for successful seven analyses of the calibration experiments is as follows: 1.0000, 0.9997, 1.0002, 0.9999, 0.9999, 1.0001 and 1.0000. Mean and standard deviation of mean were 1.0000 ± 0.0001.

The CO detector is capable of detecting the concentration range of 0 to 3 ppm. Presence of carbon monoxide at the level of 3 ppm gives rise to an error of only 0.0015% in the standard energy of combustion.

Ordinary eight minutes flushing of the bomb prior to charging it with oxygen was sufficient to suppress the amount of nitric acid to a level less than 10^{-5} mol as the substances burned in this study contained no nitrogen. The nitric acid was determined spectrophotometrically using a UV absorption band at 202 nm.[21]

Determination of Sublimation Enthalpy. Enthalpies of sublimation were determined from temperature dependence of vapor pressure. Vapor pressures were measured by using a DuPont model 916 Thermal Evolution Analyzer which was a plug-in module of DuPont 990 Thermal Analysis System. The measurement is based on the gas saturation method in which a flame ionization detector (FID) is used to detect organic vapor present in carrier gas (usually nitrogen).[22]

A small amount (*ca.* 10 mg) of sample was placed in a cylindrical metallic cell with a small hole at the center of the lid together with silver granules used for improving heat conduction. The cell was inserted in a "Vycor" glass tube placed in a temperature-regulated furnace and the carrier gas was allowed to flow at a constant rate only outside the cell. FID current was then recorded. After thermal equilibrium was found to be established in the cell from the recorder trace, a small portion of the carrier gas was allowed to flow through the cell, while the total flow rate was kept constant. Organic vapor ran out through the hole into external carrier gas flow and the FID current increased. After saturation of the internal carrier gas flow with organic vapor was confirmed from the recorder trace, the carrier gas flow pattern was restored. Change in the FID current caused by changing the flow pattern was determined as a function of temperature. The change in the FID current was assumed to be proportional to saturated vapor pressure of the compound at that temperature and logarithm of it was plotted against reciprocal temperature. From the slope of the derived straight line, sublimation enthalpy at a mean temperature was obtained on the basis of the second law method.

The reliability of the method was examined by using naphthalene (Kishida Chemicals, SMA-SP-16) as a test substance in accordance with the recommendation of IUPAC.[23] The naphthalene sample is an organic micro-analytical standard sample certified by the Sub-committee of Organic Microanalysis of the Japan Society for Analytical Chemistry. Enthalpy of sublimation was derived from the vapor pressures in the range 301.8 to 347.2 K (fourteen measurements). The enthalpy of sublimation 70.7 kJ mol^{-1} at 324.5 K was reduced to the value at 298.15 K using heat capacities for gaseous[24] and solid[25] states. Enthalpy of sublimation at 298.15 K obtained in this way was 71.7 kJ mol^{-1}, while the value recommended by IUPAC[23] is 72.5 ± 0.25 kJ mol^{-1}. Accordingly, uncertainty of ± 1.5 kJ mol^{-1} was assigned tentatively to values obtained in this study.

Table 1. Auxiliary quantities

Compound	Formula	ρ / g cm^{-3}	c_p / J K^{-1} g^{-1}	$(\partial E/\partial p)_T$ / J MPa^{-1} g^{-1}
Compd. **1**	$C_{16}H_{16}$	1.229	1.21	−0.15[a]
Compd. **2**	$C_{26}H_{26}$	1.140	1.21[a]	−0.15[a]
Benzoic acid	$C_7H_6O_2$	1.320	1.21	−0.052

a) Estimated value.

Auxiliary Quantities. Experimental results in this paper are based on 1961 atomic weights. Auxiliary data adopted in the calculation of molar standard enthalpies of combustion ΔE_c°, *i.e.* the composition formula and the values (for 298.15 K) of density, ρ, of specific heat capacity, c_p, and of compression energy, $(\partial E/\partial p)_T$, for the combustible substances, are given in Table 1. The values for **1** were taken from Ref. 6. The density **2** was determined from the dimension of a pellet of known mass. Other auxiliary quantities are also collected in the table. Uncertainties are uncertainty intervals defined by Rossini,[26] unless otherwise stated.

Standard energies and enthalpies of combustion given in this paper refer to the following idealized combustion reaction at 298.15 K:

$$C_aH_b(c) + (a+b/4)O_2(g) = aCO_2(g) + (b/2)H_2O(l),$$

where $a=16$, $b=16$ for **1** and $a=26$, $b=26$ for **2**.

Results

Combustion Calorimetry. Results of typical combustion experiments for **1** and **2** are given in Table 2.

Table 2. Typical combustion experiments

	Compd. **1**	Compd. **2**
m^i(compd.)/g	0.65238	0.61825
m^i(fuse)/g	0.00259	0.00250
$m^i(H_2O)$	1.0344	1.0229
p^i(gas)/MPa	3.040	3.040
θ_i/°C	23.139114	23.245857
θ_f/°C	24.971104	24.987338
$\Delta\theta_{corr}$/°C	0.029415	0.028176
$n^f(HNO_3)$/μmol	4	3
ΔE_{ign}/J	7.6	2.7
ε^i(cont.)/JK^{-1}	19.62	16.87
ε^f(cont.)/JK^{-1}	20.98	18.15
ΔE_Σ/J	13.5	13.0
$\Delta E_{I.B.P}$/J	−27359.0	−26007.2
$\frac{\Delta E_c^\circ}{M}$/kJ g^{-1}	−41.8508	−41.9778

Table 3. Summary of combustion calorimetric results for double-layered [2.2]paracyclophane

Exp. No.	$-\Delta E_c^\circ$(c)/kJ mol^{-1}	$\frac{m(CO_2, obsd)^{b)}}{m(CO_2, calcd)}$	$10^6 x$ (CO)	Soot on the bomb wall
3	8715.86	a)	1.5	None
4	8722.28	a)	1.4	None
5	8717.62	0.9994	2.4	None
6	8716.46	0.9993	0.9	None
7	8713.89	0.9985	2.4	Trace
8	8715.31	0.9986	3.0	Trace
11	8714.51	0.9987	0.9	None
13	8710.58	0.9976	0.9	None

a) CO_2 analysis was unsuccessful. b) $m(CO_2, obsd)$ and $m(CO_2, calcd)$ are observed and calculated masses of carbon dioxide for the total of combustible substances in the bomb, respectively.

Of thirteen combustion experiments on **1**, eight gave at least reasonably reliable calorimetric data. In Table 3, results of the successful experiments are summarized together with results of carbon dioxide and monoxide analyses and also with remarks on the presence of soot on the bomb wall after combustion. In no experiments in Table 3, soot was found in the crucible. Numerical values of ΔE_c° given in Table 3 are calculated on the basis of masses of samples.

In the previous letter,[13] the values of ΔE_c° for five experiments (No. 3, 4, 5, 6, and 11), in which no soot formation was observed and carbon dioxide recovery was not less than 99.85% (in the cases where the analysis was successful) have been used to calculate mean and standard deviation of the mean to obtain the following result: $\Delta E_c^\circ = -(8717.13 \pm 1.33)$ kJ mol^{-1} (Procedure I).

Discrepancy between the values of ΔE_c° reported by Boyd[5] and Rodgers *et al.*[6] amounted to only 9.4 kJ mol^{-1} (0.108% of the total) and carbon dioxide recovery higher than 99.90% was experienced only in two (No. 5 and 6) of the experiments given in Table 3. From these viewpoints, re-examination of the results of combustion calorimetry by different procedures seems to be desirable in order to estimate a correct value of ΔE_c° more confidently.

Use of results of experiments No. 5, 6, and 11, where no soot formation was observed and carbon dioxide analysis was successful, instead of the five results used in Procedure I, leads to the following result: $\Delta E_c^\circ = -(8716.20 \pm 0.29)$ kJ mol^{-1} and $m(CO_2, obsd)/m(CO_2, calcd) = 0.9991 \pm 0.0002$, where uncertainties are standard deviation of mean(Procedure I'). This Presult differs little from that of Procedure I. The carbon dioxide recovery is not satisfactorily high enough to allow for the precise estimation of a correct value for ΔE_c°. It appears to be reasonable to assume that the above-mentioned value gives a lower limit of possible ΔE_c° values.

One of possible procedures is to calculate the individual numerical values of ΔE_c° based on carbon dioxide recovery. Mean and standard deviation of the mean calculated in this way from the results of six experiments where the analysis was successful are as follows: $\Delta E_c^\circ = -(8726.21 \pm 1.33)$ kJ mol^{-1} (Procedure II). This procedure would be favorably applicable if a sample contaminated with incombustible impurities, such as water, was completely burnt or incompletely burnt in the sence that part of the sample remained unchanged after a combustion experiment. The same would hold if a pure sample was burnt incompletely in the same sence as described above. However, the present sample is not likely to be contaminated with incombustible impurities in view of the method of purification and possible impurities, if present, would be organic in nature. In addition to this, soot on the bomb wall is the product of the most significant side reaction. The numerical value of the mean given by Procedure II would therefore give an upper limit of possible ΔE_c° values.

Another possible procedure is to apply a least-squares analysis for the results of experiments to which Procedure II has been applied, to get ΔE_c° as a linear function of carbon dioxide recovery, $[m(CO_2, obsd)/m(CO_2, calcd)]$ (Procedure III). Derived linear function is as follows: ΔE_c°/kJ mol^{-1} $= -3669.00\,[m(CO_2, obsd)/m(CO_2, calcd)] - 5050.56$. Extrapolation of the function to $[m(CO_2, obsd)/m(CO_2, calcd)] = 1$ leads to the following result: $\Delta E_c^\circ = -(8719.56 \pm 0.56)$ kJ mol^{-1}, where uncertainty is standard deviation. In this procedure, results of, rigorously speaking, more or less incomplete combustion experiments for a sample of unknown purity are extrapolated practically to complete combustion of a pure sample. This procedure appears to the authors to be more reasonable than the other ones.

Consequently, the numerical value estimated by Procedure III was adopted as a correct ΔE_c° value for **1**.

Six of seven experiments on **2** were successful. The results are summarized in Table 4. The more complete combustion was achieved in general than for **1** possibly because of improvement in the preparation of the pellets, although a small amount of soot was found in the crucible after every experiment. The numerical values of ΔE_c° given in Table 4 are calculated on the basis of the masses of samples and corrected for soot formation by using ICSU-CODATA key value for

Table 4. Summary of combustion calorimetric results for triple-layered [2.2]paracyclophane

Exp. No.	$-\Delta E_c^\circ$(c)[a] / kJ mol^{-1}	$m(CO_2$, obsd)[b] / $m(CO_2$, calcd)	$10^6 x$ (CO)	m(soot) / mg
1	14210.33	1.0005(1.0008)	0.5	0.15
2	14208.94	0.9994(0.9997)	0.2	0.14
3	14217.38	———(———)[e]	0	0.14
4	14212.18	0.9990(0.9993)	0.6	0.17
6	14214.52[d]	0.9986(0.9991)	0.9	0.26
7	14210.88[d]	0.9984(0.9987)	0.1	0.16
mean and sdm[c]	14214.76±1.65	0.9992±0.0004 (0.9995±0.0003)		

a) Corrected for soot formation. b) Numerical values in parenthesis are corrected for soot. c) Standard deviation of mean. d) Benzoic acid was used as an auxiliary substance. e) CO_2 analysis was unsuccessful.

$\Delta H_f^\circ(CO_2, g)$.[27] The correction amounted to −8.52 kJ mol^{-1} (0.085% of the total) for an extreme case and to −5.57 kJ mol^{-1} in average. As an error was found in the calculation of the soot correction given in the previous letter,[13] ΔE_c° values are increased by 4.61 kJ mol^{-1} in comparison with the previous values. Corresponding revisions were made also on the numerical values of ΔH_c°(c) and ΔH_f°(c). As no significant difference was observed between the results of experiments with and without the use of benzoic acid as an auxiliary substance, all the values in Table 4 were used equally to calculate the mean value.

Enthalpy of Sublimation. Plots of log h against reciprocal temperature T^{-1} are given in Figs. 2 and 3 for **1** and **2**, respectively, where h is the increase in FID current caused by changing the flow pattern of the carrier gas so that part of the carrier gas flows through the sample cell while keeping the total flow rate constant. Analyses of the experimental data by means of the second law method gave the following enthalpies of sublimation at mean temperatures: 96.4±1.5 kJ mol^{-1} at 381.4 K and 119.1±1.5 kJ mol^{-1} at 405.7 K for **1** and **2**, respectively. Enthalpies of formation at 298.15 K were derived by use of the Kirchhoff's equation. For **1**, molar heat capacities of the gas calculated by Boyd[7] and those of the solid obtained by extrapolation of experimental heat capacities measured by Andrews and Westrum[28] were used in the calculation. For **2**, molar heat capacities of the gas and the solid were estimated from the corresponding values of **1** by assuming that specific heat capacity is of the same magnitude for both compounds. The corrections to 298.15 K amounted to 3.2±1.0 kJ mol^{-1} and 6.8±2.0 kJ mol^{-1} for **1** and **2**, respectively, where uncertainties were estimated arbitrarily.

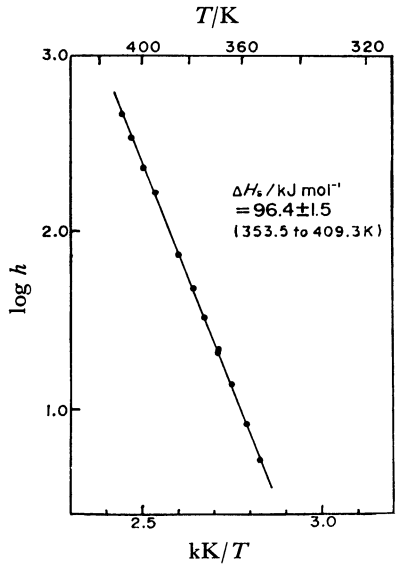

Fig. 2. Temperature dependence of vapor pressure of double-layered [2.2]paracyclophane in the crystalline state. Unit of FID current h, which is proportional to vapor pressure, is arbitrary.

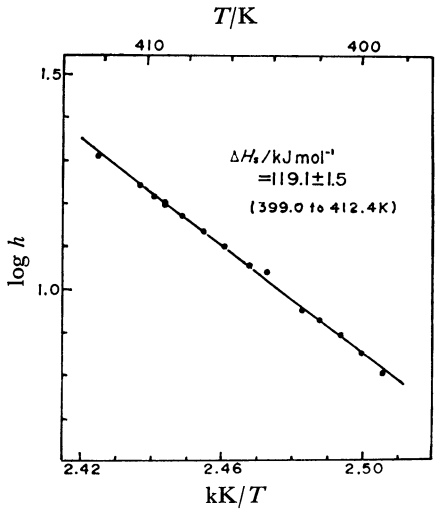

Fig. 3. Temperature dependence of vapor pressure of triple-layered [2.2]paracyclophane in the crystalline state. Unit of FID current h, which is proportional to vapor pressure, is arbitrary.

Thermodynamic Quantities. Standard thermodynamic quantities at 298.15 K were calculated and summarized in Table 5. ICSU-CODATA key values[27] were used in the calculation of standard enthalpies of formation. Uncertainty for ΔE_c° of **2** was calculated as if all the combustion experiments were carried out by use of benzoic acid. So the result will be naturally overestimated.

Discussion

Comparison with Qiterature Values. The selected numerical value of ΔH_c° for **1** given in Table 5 is only by 2.21 kJ mol^{-1} more negative than the previously

Table 5. Thermodynamic quantities

	Double-layered [2.2]paracyclophane	Triple-layered [2.2]paracyclophane
$-\Delta E_c^\circ$(c)/kJ mol^{-1}	8719.56±1.80	14214.76±3.59
$-\Delta H_c^\circ$(c)/kJ mol^{-1}	8729.48±1.80	14230.87±3.59
ΔH_f°(c)/kJ mol^{-1}	146.69±2.77	283.82±4.96
ΔH_s°/kJ mol^{-1}	99.6± 1.8	125.9 ±2.5
ΔH_f°(g)/kJ mol^{-1}	246.3± 3.3	409.7 ±5.6

reported value of the authors[13] and lies between the values reported by Boyd[5] and by Rodgers *et al.*,[6] being closer to the latter. Both of the literature values are barely in the range of possible ΔH_c° values as estimated in the preceding section. It appears to be more reasonable and more consistent to employ the present value for the discussion in later sections, partly because the present value is substantiated by carbon dioxide analysis.

The present value for ΔH_s° at 298.15 K for **1** agrees with the Boyd's value 96.2 ± 4.2 kJ mol^{-1} [5] within the sum of assigned uncertainties. Re-examination of Boyd's experimental values of vapor pressure reveals that in the log p *vs.* T^{-1} plots one (at 373.10 K) deviates significantly from a straight line obtained by a least squares treatment of the remaining four values. Neglect of the deviated point leads to the following result (instead of reported 92.8 kJ mol^{-1}): $\Delta H_s^\circ = 94.2$ kJ mol^{-1} at 363 K. Furthermore, correction from 363 to 298.15 K was recalculated by using the (extrapolated) experimental molar heat capacities of Andrews and Westrum.[28] The correction amounted to $+2.5$ kJ mol^{-1}. Enthalpy of sublimation at 298.15 K thus calculated is (96.7 ± 4.2) kJ mol^{-1}, where uncertainty is unchanged from the original one. This value is close to Boyd's original value. Method and apparatus used in the present determination of ΔH_s° were examined as described in the preceding section, while no description is found in Boyd's papers.[5,29] Hence, the present value has been adopted to calculate the value of ΔH_f°(g).

Standard enthalpy of formation for gaseous **1** derived in this study is 246.3 ± 3.3 kJ mol^{-1}, which is 47.1 kJ mol^{-1} more positive than the value predicted by Kao and Allinger[8] based on the combined molecular orbital-molecular mechanics method. Even if scatter of experimental values of ΔH_c° and ΔH_s° described above and their uncertainties were taken into consideration, the predicted value is definitely away from the range of possible ΔH_f°(g) values. Generally speaking, the method of Kao and Allinger[8] were successful in reproducing precisely experimental enthalpies of formation of a number of gaseous conjugated hydrocarbons, but the above-mentioned fact seems to reveal that the method has been applied, in this case, to a too highly strained molecule beyond the applicability limit. On the other hand, ΔH_f°(g) value deduced from Lindner's[9] calculated enthalpy of atomization† is 257 kJ mol^{-1}, which is rather closer to the present experimental value.

No literature values are available for ΔH_c° and ΔH_s° of **2**.

Estimation of Strain Energy of Triple-Layered [2.2]-Paracyclophane. Strain energy brought about in a molecule of **2** by the formation of two larger ring systems composed of aromatic rings and methylene groups was estimated by the following two different methods.

(i) Group Method. In order to estimate the total strain energy U_s, standard enthalpy of formation in gaseous state for a "strain-free" reference structure ΔH_f°(g, ref.) was calculated by means of the group increments given by Cox and Pilcher,[30] which, together with terms for steric effect from *ortho* alkyl groups, had been proved to account for standard enthalpies of formation in gaseous state of nineteen simple alkyl-substituted benzenes within ±4 kJ mol^{-1}, and it was compared with experimental standard enthalpy of formation in gaseous state ΔH_f°(g, exp.):

$$U_s = \Delta H_f^\circ(\text{g, exp.}) - \Delta H_f^\circ(\text{g, ref.}) - 2RT \qquad (1)$$

The final term in Eq. 1 is the (PV) correction,[31] which is needed in *a priori* estimation of ring strain energy. In this paper, standard enthalpy of formation in gaseous state for the reference structure was calculated without inclusion of steric effect from *ortho* methylene groups. The resultant value of ΔH_f°(g, ref.) is 152.8 kJ mol^{-1} for **2** and substitution of this value in Eq. 1 gives 251.9 ± 5.6 kJ mol^{-1} for the total strain energy. Total strain energy for **1** calculated similarly amounts to 126.0 ± 3.3 kJ mol^{-1}, which is of a half magnitude in comparison with the corresponding value for **2**.

(ii) Chemical Similarity Method. Another approach for estimating the total strain energy is to compare the reaction enthalpy for gas-phase homolytic hydrogenation-cleavage of four dimethylene bridges of **2** with four times the reaction enthalpy for the corresponding cleavage of the central C–C bond of 1,2-diphenylethane. The procedure, together with estimate of the total strain energy, is summarized in Table 6. Standard enthalpy of formation of gaseous toluene and xylene were taken from Ref. 32. The value of ΔH_f°(g) for 1,2-diphenylethane was calculated from standard enthalpy of formation in the crystalline state[32] and enthalpy of sublimation reported by Morawetz.[33] The value of ΔH_f°(g) for 1,2,4,5-tetramethylbenzene was calculated from standard enthalpy of formation for undercooled liquid at 298.15 K[34,35] and hypothetical enthalpy of vaporization at 298.15 K derived from Antoine equation analysis of liquid vapor pressures.[36] Derived strain energy 245.6 ± 9.8 kJ mol^{-1} is almost twice the value for **1**, 122.6 ± 5.4 kJ mol^{-1}, derived similarly. The strain energies calculated by this method agree with the corresponding values derived in the preceding section within the sum of uncertainties.

Analysis of the Total Strain Energy of Triple-Layered [2.2]paracyclophane. For **1**, Gantzel *et al.*[37] made an *a priori* estimation of total strain energy by using Brown's structure[1] and Whiffen's spectroscopic force constants.[38] Boyd[5] also made a similar analysis by using structure determined by Lonsdale[2] and force constants given by Kakiuti and Shimanouchi.[39] Later, Boyd[7] carried out a calculation based on molecular mechanics to determine molecular structure, strain energy and thermodynamic functions, simultaneously. The distribution of the total strain energy amounting to 147 kJ mol^{-1} among six parts thus determined is as follows: (i) out-of-plane deformation of aromatic rings, 43 kJ mol^{-1}; (ii) deformation of *para*-substituents, 35 kJ mol^{-1}; (iii) aliphatic bridge eclipsing, 29 kJ mol^{-1}; (iv) aliphatic bridge angle deformation, 3 kJ mol^{-1}; (v) aliphatic bridge bond stretching, 3 kJ mol^{-1}; and (vi) ring repulsion(non-bonded aromatic C···C), 34 kJ

† The quantity given if Ref. 9 as "Atomisierungenergie" is supposed to mean the enthalpy of atomization from the context of Refs. 9 and 10. The value 152.06 eV/molecule derived by the improved method II was employed in the calculation of the value in the text.

TABLE 6. SCHEME FOR ESTIMATING THE STRAIN ENERGY OF TRIPLE-LAYERED [2.2]PARACYCLOPHANE (2) BY CHEMICAL SIMILARITY METHOD

(i) Compd. **2** (g) + $4H_2$(g) = $2CH_3$-⟨○⟩-CH_3(g) + ⟨○⟩(CH_3)$_4$ (g)

ΔH_f°(g)/kJ mol^{-1}:	409.7±5.6	0	18.0±0.9	−48.1±2.0[a]

ΔH_r°(i) = −421.8±6.2 kJ mol^{-1}

(ii) 4 ⟨○⟩-CH_2CH_2-⟨○⟩ (g) + $4H_2$(g) = 8 CH_3-⟨○⟩ (g)

ΔH_f°(g)/kJ mol^{-1}:	143.0±1.8	0	50.1±0.3

ΔH_r°(ii) = −171.2±7.6 kJ mol^{-1}

Strain energy, $U_S = \Delta H_r^\circ(\text{ii}) - \Delta H_r^\circ(\text{i}) - 2RT$ = 245.6±9.8 kJ mol^{-1}

a) Assigned uncertainty

mol^{-1}. Rodgers *et al.*[6] suggested the necessity of downward revision for the value of item (iii), because two methylene groups eclipse completely in the final conformation determined by Boyd.[7] However, general agreement between the calculated and experimental structures and the calculated and experimental total strain energies is to be noted. Wynberg *et al.*[40] and Iwamura *et al.*[41] studied the stability of a bent benzene ring theoretically by molecular orbital methods.

In this paper, the total strain energy of **2** has been analyzed by dividing it into components in a similar way to that used in Boyd's molecular mechanical calculation.[7] The total strain energy of **2**, U_S, is expressed in a general form as follows:

$$U_S = 2U_1 + U_1^* + 2U_2 + 2U_2^* + 4U_3 + 4U_4 + 4U_5 + 2U_6 + 2U_7, \quad (1)$$

where U_1 is the contribution from the out-of-plane deformation of the outer aromatic ring, U_2, that from the deformation of the *para*-substituent on the outer aromatic ring, U_3, that from a pair of the eclipsing bridge methylenes, U_4, that from the deformation of the aliphatic bridge angle, U_5, that from the stretching of the aliphatic bridge bond, U_6, that from the repulsion between a pair of the aromatic rings, U_7, that from the repulsion between a pair of bridge methylenes bonded *ortho* with each other to the inner aromatic ring, U_1^*, that from the twisting of the inner aromatic ring, and U_2^*, that from the deformation of the substituent on the inner aromatic ring. Similarly, total strain energy of **1**, U_S', is expressed as follows:

$$U_S' = 2U_1' + 2U_2' + 2U_3' + 2U_4' + 2U_5' + 2U_6', \quad (2)$$

where U_i'(i=1∼6) are quantities corresponding to U_i(i=1∼6), respectively.

In Table 7, distances and angles which are relevant to the components of the total strain energies are compared among compounds **1**,[4] **3**[11] and **4**.[12] The symbols for distances and angles in Table 7 are schematically illustrated in Fig. 4. Similarity of the values for the parameters between **3** and **4** indicates that **3** can be a good model compound for **2** with respect to molecular structure. The values of parameters l_1, l_2, l_3, l_4, α, β, δ and ε for **1** are nearly equal to the corresponding values for **3**. This fact leads to an approximation that

$$U_i = U_i' \ (\text{i}=1\sim6) \quad (3)$$

In the preceding section, the following relation has been shown experimentally to hold:

$$U_S = 2U_S'. \quad (4)$$

From equations (1) to (4), the following expression is obtained:

$$U_1^* = 2U_1 + 2(U_2 - U_2^*) - 2U_7. \quad (5)$$

TABLE 7. COMPARISON OF MOLECULAR PARAMETERS RELEVANT TO STRAIN ENERGY COMPONENTS

Strain energy component[a]	Distance or angle[b]	Compound		
		Compd. **1**[4]	Compd. **3**[11]	Compd. **4**[12]
U_6, U_6'	l_1/nm	0.278	0.2744, 0.2753	0.2776, 0.2781
	l_2/nm	0.309	0.3061, 0.3047	0.3130, 0.3043
	l_3/nm	—	0.3184, 0.3192	0.3161, 0.3259
U_5, U_5'	l_4/nm	0.1562 (0.1593)[c]	0.1587, 0.1581	0.1581, 0.1597
U_1, U_1'	α/°	12.6	12.1, 12.3	12.5, 12.9
U_2, U_2'	β/°	11.2	10.9, 11.5	11.8, 10.8
U_2^*	β'/°	—	4.4, 6.7	6.5, 6.9
U_1^*	γ/°	—	13.6	13.4
U_4, U_4'	δ/°	113.7	111.6, 113.1	112.7, 112.0
	δ'/°	—	112.3, 111.8	111.5, 112.1
U_3, U_3'	ε/°	(6.4)[c]	6.8	8

a) For symbols, see the text. b) Symbols were defined as illustrated in Fig. 4. c) Distances and angles in compd. **1** have been determined less definitely due to the presence of molecular disorder in the crystal at room temperatures. Parenthesized values and the remaining values were calculated from parameters of Tables 7 and 1, respectively, of Ref. 4.

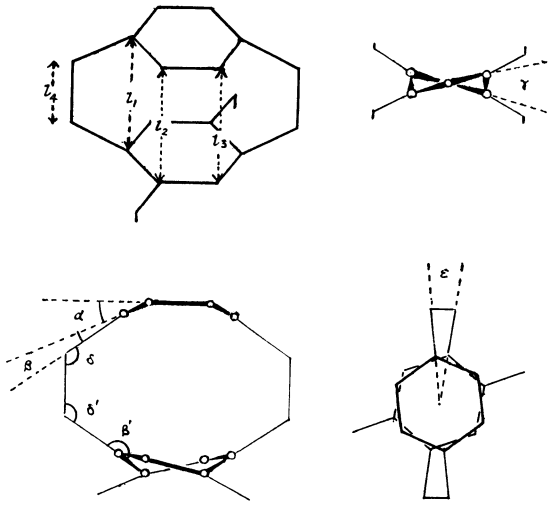

Fig. 4. Schematic illustration of interatomic distances and angles given in Table 7.

U_2* is estimated to be much smaller than U_2 on the basis of Boyd's definition of strain energy,[7] because a methylene carbon atom attached to the inner aromatic ring is significantly more coplanar with the adjacent three carbon atoms on one and the same aromatic ring than the one attached to the outer aromatic ring as shown in Table 7. The magnitude of U_7 is evaluated to be *ca.* 2 kJ mol^{-1} from extra contribution, assigned by Cox and Pilcher,[30] of a pair of *ortho* methyl and/or methylene groups to standard enthalpy of formation in gaseous state. Boyd's calculation[7] gave 21.5 and 17.5 kJ mol^{-1} for U_1' and U_2', respectively. From these considerations, the contribution from the twisted inner aromatic ring is estimated to be of more than two-fold magnitude as compared with that from the bent outer aromatic ring.

In the foregoing discussion, the contribution from transannular π-electron repulsion in **1** and **2** were assumed to be equal in magnitude. While this appears to be a sound approximation from the comparison of the values of l_1, l_2 and l_3 given in Table 7, there are evidences which indicate that the transannular repulsion is more enhanced in **2** than in **1**. Charge transfer bands in tricarbonylchromium,[42] tetracyanoethylene[15a] and 1,3,5-trinitrobenzene[15a] complexes of multilayered[2.2]-paracyclophanes show bathochromic shifts with the increase of the number of layers. Infrared bands for the tricarbonylchromium complexes associated with C=O stretching shift to lower frequencies with the increase of the number of layers. These facts show enhanced Lewis basicity of π-electrons with the increase of the number of layers, which reflects enhancement of the transannular π-electron repulsion. While there is little characteristic in the electronic spectra of multilayered [2.2]metacyclophanes in which transannular π-electron interaction is estimated to be much weaker than in [2.2]paracyclophanes due to small overlap of the aromatic rings, the electronic spectra of multilayered [2.2]paracyclophanes show marked bathochromic and hyperchromic shifts with the increase of the number of layers. This fact also suggests that the transannular π-electron repulsion is enhanced with the increase of the number of layers.

If this effect is taken into account, the contribution from the twisted inner aromatic ring is decreased correspondingly. While the magnitude of U_6' was evaluated to be 36 kJ mol^{-1} by Boyd, that of U_6 is still unknown at present. However, the difference between U_6 and U_6' is supposed to be small from the similarity of relevant nonbonding interatomic distances.

In conclusion, even if various approximations and suppositions made in the foregoing discussions were taken into consideration, it seems to be valid to argue that the twisted inner aromatic ring in triple-layered [2.2]paracyclophane molecule is at least more strained energetically than the bent outer ones, or that the contribution from the former ring to the total strain energy is approximately twice that from the latter ring. In other words, stabilization due to π-electron delocalization in the former ring is deteriorated at least more significantly than in the latter ring or possibly deteriorated by twice the magnitude as compared with that in the latter ring.

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