using standard deviations in rate constants and the accuracy of ±0.01° in temperature measurements. Deviations in the values of $\Delta\Delta H^{\ddagger}$ represent the estimated error. The error, here, was determined by a complete treatment of all primary errors.

Activation entropies, $\Delta S^{\ddagger}$, were determined from $k = (eKT/h) \exp(-E_a/RT) \exp(\Delta S^{\ddagger}/R)$, and at a given temperature, the free energy of activation, $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

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Enthalpies of Formation of Nortricyclene, Norbornene, Norbornadiene, and Quadricyclane

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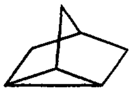
Abstract: Heats of formation of the following gaseous substances at 25° were determined by combustion calorimetry: nortricyclene (**1**), +14.82 ± 0.54 kcal mol^{-1}; norbornene (**2**), +15.12 ± 0.42 kcal mol^{-1}; norbornadiene (**3**), +50.59 ± 0.26 kcal mol^{-1}; and quadricyclane (**4**), +60.54 ± 0.26 kcal mol^{-1}. Discrepancies between these and literature values are discussed.

Because of their manifold and fascinating reactions, nortricyclene (**1**), norbornene (**2**), norbornadiene (**3**), and quadricyclane (**4**) have been the subject of numerous chemical investigations in the past two decades. The reactivity displayed by these compounds suggests that they are highly strained, and estimates of their strain energies and heats of formation obtained in various ways have been published. In this paper we present a brief study of the heats of formation, obtained by combustion calorimetry, of these compounds.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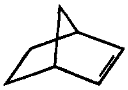
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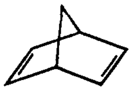
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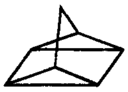
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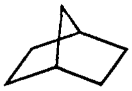
Results

Compounds **1–4**, purified by distillation and preparative gas chromatography, were subjected to combustion in a rotating bomb calorimeter, and the enthalpies of combustion and of formation were calculated by standard procedures. Vapor pressures were measured over a range of temperatures and from these data the enthalpies of vaporization were calculated. With the aid of these values, the enthalpies of formation for the materials in their condensed phases were corrected to the vapor state at 25°. The details of the experiments are given in Tables I–V and are summarized in Table VII, along with those of previous investigators.

Comparison with the Results of Previous Investigators. Norbornane. The enthalpies of formation of the various bicyclic hydrocarbons, which are the subject of this report, have been studied by Turner and his colleagues.[2] Their experimental approach consisted of the determination of the enthalpies of hydrogenation (or hydrogenolysis) of the hydrocarbons in acetic acid solution. By combination of these data with a value for the enthalpy of formation of norbornane (**5**), enthalpies of formation of the other hydrocarbons could readily be deduced.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Turner and coworkers took −8.4 kcal mol^{-1} as the enthalpy of formation of gaseous norbornane. This value was obtained by combining an experimental enthalpy of combustion for solid norbornane[3] with an estimated enthalpy of vaporization. Recently, however, Boyd and his coworkers[4] directly determined the enthalpy of vaporization, obtaining a value of 9.59 kcal mol^{-1}. Our independent determination (Table V) agrees well with this value, 9.40 kcal mol^{-1}. This causes the enthalpy of formation of gaseous bicycloheptane to become −12.4 kcal, and leads to a downward revision of the values deduced by Turner and his coworkers. These revised values are also listed in Table VII.

The earlier workers calculated strain energies of the various hydrocarbons by comparing their values of the enthalpies of formation with hypothetical "strainless" values calculated by the method of Franklin.[5] Recently, however, Schleyer, Williams, and Blanchard[6] showed that this type of calculation is not appropriate for bicyclic hydrocarbons, and that the "single conformation increment" method of Benson and Buss[7,8]

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Table I. Nortricyclene

C_7H_{10} Mol wt 94.158 C_p 1.17 cal deg^{-1} g^{-1} $d^{20}{}_4$ 0.7 g ml^{-1} (est)

Expt	Mass sample	Δt, °K	Q_i, J	Q_f, J	Q_n, J	Q_m, J	Q_w, J	E_c, J deg^{-1}	$\Delta E_c{}^\circ$, kcal mol^{-1}
1	0.516762	1.950646	2.76	79.2	21.3	9610	8.70	0.60	−1004.72
2	0.444724	1.915867	2.89	75.0	18.7	12300	7.32	0.62	−1003.68

Temp, °C	29.5	36.0	41.5	44.5	48.6	54.4	60.0	64.0
Vapor pressure, mm	49.0	68.0	89.0	101.0	121.0	157.0	199.0	230.0

Results, kcal mol^{-1}

$\Delta E_c{}^\circ$	Δn	$\Delta H_c{}^\circ{}_l$	$\Delta H_f{}^\circ{}_l$	$\Delta H_v{}^\circ$	$\Delta H_f{}^\circ{}_g$
−1004.20	−2.50	−1005.68	5.74	9.08	14.82
±0.52		±0.52	±0.52	±0.02	±0.54

Table II. Norbornene

C_7H_{10} Mol wt 94.158 C_p 1.38 J deg^{-1} g^{-1} $d^{20}{}_4$ 0.7 g ml^{-1} (est)

Expt	Mass sample	Δt, °K	Q_i, J	Q_f, J	Q_n, J	Q_m, J	Q_w, J	E_c, J deg^{-1}	$\Delta E_c{}^\circ$, kcal mol^{-1}
1	0.725179	2.512753	13.4	75.4	22.0	9700	13.1	2.52	−1005.96
2	0.617369	2.218038		81.0	20.5	9600	10.8	1.89	−1005.15

Temp, °C	28.0	29.0	33.3	38.3	42.0	47.0	55.0	64.0	67.5	69.5	74.0	77.0
Vapor pressure, mm	68.0	70.0	85.0	108.0	125.0	154.0	209.0	287.0	324.0	346.0	403.0	443.0

Results, kcal mol^{-1}

$\Delta E_c{}^\circ$	Δn	$\Delta H_c{}^\circ{}_l$	$\Delta H_f{}^\circ{}_l$	$\Delta H_v{}^\circ$	$\Delta H_f{}^\circ{}_g$
−1005.56	−2.50	−1007.04	7.09	8.03	15.12
±0.40		±0.40	±0.40	±0.02	±0.42

Table III. Norbornadiene

C_7H_8 Mol wt 92.142 C_p 1.26 J deg^{-1} g^{-1} $d^{20}{}_4$ 0.7 g ml^{-1} (est)

Expt	Mass sample	Δt, °K	Q_i, J	Q_f, J	Q_n, J	Q_m, J	Q_w, J	E_c, J deg^{-1}	$\Delta E_c{}^\circ$, kcal mol^{-1}
1	0.519582	2.190462	2.89	79.2	21.3	13800	9.96	0.66	−972.86
2	0.504676	2.284437	1.92	80.9	32.2	16000	9.50	0.63	−973.54
3	0.626266	2.503413	2.76	74.1	30.2	14300	12.3	0.79	−973.10

Temp, °C	27.0	32.0	37.0	42.0	46.0	54.0	55.0	62.0	66.5	69.0	71.2	78.5	79.5
Vapor pressure, mm	74.0	92.0	114.0	142.0	165.0	225.0	230.0	306.0	345.0	390.0	403.0	526.0	529.0

Results, kcal mol^{-1}

$\Delta E_c{}^\circ$	Δn	$\Delta H_c{}^\circ{}_l$	$\Delta H_f{}^\circ{}_l$	$\Delta H_v{}^\circ$	$\Delta H_f{}^\circ{}_g$
−973.17	−2.00	−974.35	42.72	7.87	50.59
±0.24		±0.24	±0.24	±0.02	±0.26

Table IV. Quadricyclane

C_7H_8 Mol wt 92.142 C_p 1.51 J deg^{-1} g^{-1} $d^{20}{}_4$ 0.7 g ml^{-1} (est)

Expt	Mass sample	Δt, °K	Q_i, J	Q_f, J	Q_n, J	Q_m, J	Q_w, J	E_c, J deg^{-1}	$\Delta E_c{}^\circ$, kcal mol^{-1}
1	0.469006	2.046053	2.13	68.8	28.3	13400	8.76	0.70	−982.39
2	0.273364	1.601332	2.13	77.0	11.5	14600	4.90	0.41	−981.92

Temp, °C	29.5	37.4	44.0	50.5	58.0	71.2	81.3	90.3	99.0
Vapor pressure, mm	34.0	51.0	69.5	91.0	124.0	208.0	297.0	408.0	540.0

Results, kcal mol^{-1}

$\Delta E_c{}^\circ$	Δn	$\Delta H_c{}^\circ{}_l$	$\Delta H_f{}^\circ{}_l$	$\Delta H_v{}^\circ$	$\Delta H_f{}^\circ{}_g$
−982.15	−2.00	−983.34	51.70	8.84	60.54
±0.26		±0.26	±0.26	±0.004	±0.26

should be used. Schleyer and coworkers calculated the "strainless" enthalpies of formation for the hydrocarbons studied in the present paper; those values are quoted in Table VI.

According to these calculations the strain energy of norbornane is 17.6 kcal mol^{-1}.

Norbornene. Our value for the enthalpy of formation of gaseous norbornene is 15.14 kcal mol^{-1}. This is not in good agreement with the revised value of Turner and coworkers, 20.7 kcal mol^{-1}. Possibly the difference in media is responsible. The present data refer to the gas phase at 25°, whereas the hydrogenations were done in acetic acid solution. The discrepancy seems very large to be attributed solely to a medium effect, however.

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Table V. Norbornane

Temp, °C	27.0	42.6	52.7	58.2	70.0	79.6	90.5
Vapor pressure, mm	31.0	68.7	109.5	137.7	228.2	328.6	485.0

$\Delta H_v° = 9.40 \pm 0.03$ kcal mol^{-1}

Table VI. Strain Energies of the Bicycloheptane Hydrocarbons

	"Strainless" $\Delta H_f°_g$, kcal mol^{-1} [a]	Strain energy, kcal mol^{-1}
Nortricyclene (**1**)	−24.0	38.8
Norbornene (**2**)	−2.5	17.6
Norbornadiene (**3**)	25.0	25.6
Quadricyclane (**4**)	−18.1	78.7
Norbornane (**5**)	−30.0	17.6

[a] Calculated values from ref 6.

The strain energy of this molecule is 17.6 kcal mol^{-1}, which, coincidentally, is identical with that of the saturated hydrocarbon.

Norbornadiene. Skuratov[9] gives 48.0 kcal mol^{-1} as the enthalpy of formation of liquid norbornadiene. In order to facilitate comparisons, we combine this with our enthalpy of vaporization to give a value of +55.9 kcal mol^{-1} as the enthalpy of formation of gaseous norbornadiene. This is in excellent agreement with Turner's value, revised as noted above, of +55.7 kcal mol^{-1}. However, our value is significantly lower, +50.59 kcal mol^{-1}.

The strain energy of norbornadiene is 25.6 kcal mol^{-1}, appreciably higher than the value for the monoolefin.

Nortricyclene. The enthalpy of formation for this compound is 14.8 kcal mol^{-1}, and differs from that of norbornene (15.5 kcal mol^{-1}) by only 0.7 kcal mol^{-1}. This small difference between two large numbers is in gratifying agreement with the results of Schleyer,[10] who obtained a value of 0.9 kcal mol^{-1} for the difference in free energies by directly equilibrating the two hydrocarbons over a silica–alumina catalyst. No medium effect is to be expected in such conditions.

The strain energy for this molecule is 38.8 kcal mol^{-1}.

Quadricyclane. The biggest discrepancy between our results and those of preceding investigators comes in the case of quadricyclane. Combination of the enthalpy of hydrogenation with the revised enthalpy of formation of norbornane, in the style of Turner, *et al.*,[2a] gives a calculated value of 79.4 kcal mol^{-1} for the enthalpy of formation of quadricyclane. Our value is 60.6 kcal mol^{-1}. We can offer no explanation for such a large discrepancy.

The strain energy for this compound is 78.7 kcal mol^{-1}.

Conclusions

The enthalpies of formation of hydrocarbons **1** and **4** have been determined and their strain energies have been calculated. Our results give somewhat lower values for the strain energies of **1–4** than those given in the literature, a matter for which no very convincing explanation can be offered. Nevertheless the strain energies are still ample to be responsible for the high reactivities and rearrangement reactions undergone by this remarkable series of compounds.

Table VII. Enthalpies of Formation and Vaporization for Five Bicyclic Hydrocarbons[a]

		Norbornane (s)			Nortricyclene (s)			Norbornene (s)			Norbornadiene (l)			Quadricyclene (l)		
Ref	Method[b]	$\Delta H_f°_c$[c]	ΔH_v	$\Delta H_f°_g$	$\Delta H_f°_c$	ΔH_v	$\Delta H_f°_g$	$\Delta H_f°_c$	ΔH_v	$\Delta H_f°_g$	$\Delta H_f°_c$	ΔH_v	$\Delta H_f°_g$	$\Delta H_f°_c$	ΔH_v	$\Delta H_f°_g$
Present work	A	(−22.01)	+9.40	−12.60	+5.74	+9.08	+14.82	+7.09	+8.03	+15.12	+42.72	+7.87	+50.59	+51.70	+8.84	+60.54
2	B			8.4			+23.8			+24.7			+59.7			+83.6
2	B	(using revised value of $\Delta H_f°_g$ for norbornane)		(−12.42)			+19.8			+20.7			+55.7			+79.6
3	A	−22.01														
d	A										+48.0	(+7.87)	+55.9			
4	A	(−22.01)	+9.59	−12.42												

[a] All values kcal mol^{-1}. [b] Methods: A, from enthalpy of combustion; B, from enthalpy of hydrogenation. [c] $\Delta H_f°_c$ refers to the standard heat of formation for the condensed phase at 25°; $\Delta H_f°_g$ is the corresponding quantity for the gas phase at 25°. [d] S. M. Skuratov, cited in ref 2a.

(9) S. M. Skuratov, cited in ref 2a.

(10) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

Table VIII. Determination of Energy Equivalent of Calorimeter, E_s, by Combustion of Benzoic Acid

Expt	Mass of benzoic acid *in vacuo*, g	ΔR_c, ohm	Δt, °K	q_i, J	q_f, J	q_n, J	E_c, J deg^{-1}	E_s, J deg^{-1}
1	1.100724	0.175781	1.736748	2.88	94.93	15.52	2.31	16,816.7
2	1.180437	0.207506	2.051271	2.13	83.60	16.73	2.93	16,812.5
3	1.248468	0.199454	1.971697	3.60	90.96	15.06	2.98	16,794.8
4	1.169664	0.186735	1.846029	2.13	92.87	20.88	2.61	16,808.9
5	1.153119	0.184128	1.820259	2.76	95.98	17.53	2.54	16,806.9
6	0.966579	0.154428	1.526695	2.76	90.33	14.48	1.78	16,804.4
7	0.965609	0.154273	1.525159	2.34	93.26	13.89	1.78	16,805.8
								Av 16,807.1 ± 4.9

Experimental Section

Materials. Norbornene was a Union Carbide Corp. sample, which was purified by precision fractional distillation. Hydrogenation of norbornene was followed by preparative gas chromatography. Nortricyclene was synthesized by acid-catalyzed treatment of norbornene.[7] Pure material could not be obtained by fractional distillation, so preparative gas chromatography was employed. Norbornadiene, an Eastman Kodak Co. sample, was purified by preparative gc. Quadricyclane was synthesized by irradiation of norbornadiene and purified by preparative gc.[11] All samples were >99.9% pure as shown by gc and by nmr spectroscopy.

As an example of gc purification procedure, nortricyclene was purified on a 2-m (New Prep) column of 25% silicone gum nitrile on Gas Chrom R at 50° with a flow rate of 300 ml of helium/min. The sample size was 0.5 ml. Material with retention time of 61.8 min was collected as nortricyclene (norbornene was taken at 49.1 min). The products from 68 such runs were combined and subjected to bulb-to-bulb distillation under nitrogen. The nmr spectrum of the final product showed no vinyl absorption, and agreed perfectly with the spectrum expected for nortricyclene.

Calorimetry Equipment.[12] The calorimeter was constructed according to the U. S. Bureau of Mines drawings 63-01 through 63-31. The bomb was Parr Model 1004-C which is interchangeable with the U. S. Bureau of Mines bomb. The bomb had an internal volume of 342 ml and its internal fittings and linings were of platinum. The specimen to be burned was placed in a platinum crucible which was supported by gimbols in the bob. The bucket was chrome plates and its shape was exactly the same as the cavity in the isothermal jacket except that it was $^3/_8$ in. smaller in overall dimensions. A hollow cover fitted over the cavity.

The jacket temperature of the circulating water was controlled by a Hallikainen "Thermotrol" unit at 25 ± 0.001°. The complete system was housed in a room kept at 23.0 ± 0.03°. The temperature of the water in the calorimeter and the bucket was measured by Leeds and Northup platinum resistance thermometers of the totally enclosed, necked sheathed type (Model 8160) in conjunction with a Leeds and Northup "Mueller" bridge, Model 9835-B, a guarded Nanovolt detector, Type 9838, and an Azar Type H recorder. This equipment enabled a change in resistance of 0.000007273 ohm (7.86×10^{-5} °) to be recorded as 0.01 of full scale on the Azar recorder paper.

Oxygen from a cylinder was passed through a purifier of four columns, the first packed with wire-form CuO at 550°, the second with Ascarite, the third with $Mg(ClO_4)_2$, and the fourth with P_2O_5.

Procedure for Calibration of the Calorimeter. The energy equivalent of the calorimeter, E_s, was determined *via* the combustion of benzoic acid, National Bureau of Standards Sample No. 39-i, under the standard conditions recommended by Coops, Jessup, and van Nes.[13] The benzoic acid was pelleted and mercerized cotton served as fuse. The only difference from the usual procedure was to fire the bomb at ~23° so that the projected final temperature was 25.000000°. This method was preferred because it led to linear before and after portions of the resistance–time plot and made the determination of ΔR_c easy. The gaseous contents of the bomb after combustion were sampled and analyzed mass spectrometrically; no significant amount of CO, NO, or NO_2 was ever found. The liquid contents were titrated potentiometrically with 0.1 *N* NaOH to determine the amount of nitric acid formed. No soot was ever observed in the combustions.

Calibration Calculations. The calculation followed those described by Prosen,[14] but for 25°. The quantity ΔU_B (25°) for a

$$Q_{\text{total}} = 26{,}433.38 \text{ J g}^{-1} (m_B + q_i + q_n + q_f)$$

$$Q_{\text{total}} = (E_s + C_p m_B)\Delta t_c$$

benzoic acid sample was specified by the National Bureau of Standards as 26.4338 ± 0.0026 absolute kJ g^{-1}. The quantity m_B is the mass of benzoic acid corrected *in vacuo*. The quantity q_i was the heat evolved from ignition of the primary platinum fuse. The quantity q_n, the heat evolved from formation of 0.1 *N* nitric acid, was calculated from the value of 57.8 kJ mol^{-1}. The quantity q_f, the heat of combustion for mercerized cotton, was taken as 17.02 kJ g^{-1}. The value of C_p for benzoic acid, 1.21 J g^{-1}, was that given by Prosen.[14] The thermochemical calorie is taken equal to 4.1840 absolute J. All calculations were done in Fortran V on a Univac 1108 computer. The E_s values refer to the calorimeter plus all contents except the substances to be burned (Table VIII).

Heat of Combustion of Polyethylene Film. Liquid samples for combustion were sealed in three bags of medium density (0.92 g cc^{-1}), medium slip polyethylene. We preferred this to polyester film because it was much easier to seal. It was necessary to determine the heat of combustion of this particular sample (Table IX). The value of C_p at 25° was taken as 2.33 J g^{-1} deg^{-1}.[15] The quantity m_a is the mass of film corrected *in vacuo*.

Preparation of Samples. As mentioned above, the samples were enclosed in polyethylene film. Particular care was taken to avoid loss of material through the film bags. If the specimen plus bag did not come to constant weight immediately, then the specimen plus bag was placed into a second bag; if it still did not come to constant weight, a third bag was employed. Detection of the penetrating odor of these substances was a good preliminary indication of incomplete sealing, and correlated with failure to achieve constant weight. In no case was the specimen odor detectable when three bags were employed. The procedures used follow the table below.

Film weight used	No. of bags used
0.07–0.12 g	1
0.12–0.19	2
0.19–0.25 or 0.30	3

Calculation of Heat of Combustion. We calculated $-\Delta E_{c,l}$ in kcal mol^{-1} as follows:[14,16] $-\Delta E_c{}^\circ{}_l = (E_s + C_p 24^\circ m_s)\Delta t_c - q_i - q_f - q_n - q_a + q_w(M/m_s)10^{-3}/4.1840)$. The term $C_p 24^\circ m_s$ is listed as E_c. The heat capacities C_p at 24° were determined for each sample using a Du Pont scanning calorimeter. The Washburn correction q_w was calculated as described by Prosen[14] but for 25°, by interpolation in the constants. The value m_s is the mass of sample corrected *in vacuo*. M is the molecular weight of the compound. The atomic weights were the 1961 values: C, 12.0115; H, 1.00797; N, 14.0067; O, 15.9994. The enthalpy of combustion was calculated as: $\Delta H_c{}^\circ = \Delta E_c{}^\circ - \Delta nRT$. The values of $\Delta H_f{}^\circ{}_g$ for CO_2 and H_2O were taken from Klotz[17] leading to $\Delta H_f{}^\circ{}_{298}$.

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[12] H. K. Hall, Jr., and J. H. Baldt, *J. Amer. Chem. Soc.*, **93**, 140 (1971).

[13] J. Coops, R. S. Jessup, and K. van Nes in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience, New York, N. Y., 1965, p 27.

[14] E. J. Prosen in ref 13, p 129.

[15] F. S. Dainton, D. M. Evans, F. E. Hoare, and T. P. Melia, *Polymer*, 3, 277 (1962).

[16] A. F. Bedford, J. G. Carey, I. T. Miller, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3895 (1962).

[17] I. M. Klotz, "Chemical Thermodynamics," 2nd ed, W. A. Benjamin, New York, N. Y., 1964, p 64.

Table IX

Expt	Mass film *in vacuo*, g	ΔR_0, ohm	Δt, °K	q_i, J	q_f, J	q_n, J	E_0, J deg^{-1}	$-\Delta E_{B/m}$,^{a} J g^{-1}
1	0.616070	0.172328	1.703355	3.01	94.52	4.02	3.96	46,310
2	0.527113	0.148468	1.466834	3.31	90.29	3.97	3.43	46,660
3	0.557100	0.156014	1.542409	3.56	96.61	5.15	3.59	46,350
								Av 46,440 ± 110

The several values were averaged and the standard deviation was calculated. Densities were taken from Beilstein or estimated. As the heat contributed by the film was only ~10% of the total, we did not make a separate correction for the heat capacity of the film.

Enthalpies of Vaporization. Vapor pressures were measured by use of a sickle cell, a differential pressure measuring device (glass Bourdon gauge).[18,19] The sickle cell pressure indicator pointer is displaced from its null point when a pressure difference exists between the open and closed parts of the cell to bring the measuring pointer to its null position, thus equalizing the pressure in both parts of the system. The pressure in the open part is then read by a McLeod gauge or mercury manometer and is taken as the pressure of the closed part of the system.

Measurements were made by attaching the 225-ml cell to a vacuum system and bringing both parts of the cell to a pressure of 10^{-5} mm. The cell was then brought to atmosphereic pressure by adding dry nitrogen to both parts. The specimen was introduced into the cell and frozen by immersing in a mixture of Dry Ice–acetone. While the specimen remained frozen, both sections of the cell were evacuated to a pressure of 10^{-5} mm and the sample entrance port was sealed off. The cell was then allowed to reach room temperature and was placed into a controlled bath of Dow-Corning 550 silicone oil. The temperature of the bath was then brought to a constant temperature of 30 ± 0.05° and allowed to stand for 20–25 min. The pressure of the open part of the system was adjusted to match the pressure of the closed part of the system by admitting dry air. This brought the measuring pointer of the sickle cell to its null point and the pressure of the open part of the system was read. Additional pressures were read in increments of 15–20° up to the boiling point of the specimen under investigation.

Enthalpies of vaporization were calculated from

$$\Delta H_v = \left[\frac{\log P_2 - \log P_1}{1/T_2 - 1/T_1}\right]2.303R$$

There were no discontinuities in the vapor pressure plots for the solid hydrocarbons at the melting points. Plots were linear over the range studied. The vapor pressure data are collected in Tables I–V.

A variety of compounds for which we obtained satisfactory agreement with literature values is given in ref 12.

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[2.2.2](1,3,5)Cyclophane and Its Derivatives. An Extreme Example of Face-to-Face Crowding of Aromatic Rings[1]

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Abstract: The reaction of 1,3,5-tris(bromomethyl)benzene with sodium sulfide yields 2,11,20-trithia[3.3.3](1,3,5)-cyclophane (**6**) which, on subjection to a Stevens rearrangement followed by a Hofmann elimination, leads to [2.2.2](1,3,5)cyclophane-1,9,17-triene (**11**). The average distance between the two aromatic rings of **11** is only 2.80 Å and represents the most extreme example of face to face crowding of two aromatic rings presently known. The physical and chemical properties of **11** and its derivatives are discussed. The chemical effects of this interfacial crowding are especially evident in the facile conversion of **15** to the novel cage structure **24**.

Recently, we have described a procedure for the transformation of a sulfide linkage to a carbon–carbon double bond.[3] This involved a Stevens rearrangement followed by a Hofmann elimination and has been utilized for syntheses of *cis*- and *trans*-15,16-dimethyldihydropyrene,[3,4] *trans*-15,16-dihydropyrene,[5] [2.2]metaparacyclophane-1,9-diene,[6] and [2.2](2,6)pyridinophane-1,9-diene.[7] As a further test of the generality of this synthetic method, we have now investigated its application for the synthesis of [2.2.2](1,3,5)-cyclophanes.[8]

In an interesting approach to cyclophane chemistry Hubert has previously shown that trimerization of diacetylenes, such as **1**, using a Ziegler catalyst yields tris-bridged (1,3,5)cyclophanes of the general formula

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