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Thermochemical Properties of Triphenylalkanes and Tetraphenylmethane. Strain in Phenyl Substituted Alkanes

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The standard ($p° = 0.1$ MPa) molar enthalpies of sublimation $\Delta_{cr}^{g}H_m°$ at the temperature $T = 298.15$ K for 1,1,2-triphenylethane, triphenylmethane, 1,1,1-triphenylethane, 1,1,1-triphenylbutane, and tetraphenylmethane were obtained from the temperature function of the vapor pressure measured in a flow system. Standard molar enthalpy of formation $\Delta_f H_m°$(cr) at the temperature $T = 298.15$ K was measured using combustion calorimetry for 1,1,1-triphenylbutane. Enthalpies of fusion of all compounds were measured by differential scanning calorimetry. These experimental results together with the data available from the literature were used for the estimation of strain enthalpies of phenyl substituted alkanes and for the improvement of group-contribution methodology.

Introduction

Qualitatively, organic chemists usually recognize a strained molecule when they see its structural formula. Quantitative knowledge of strain provides the possibility of predicting the stability or reactivity of a molecule. Investigations of strain in mono- and diphenyl compounds have been made recently (Verevkin, 1997a, 1999). It was found that the geminal diphenyl substituted alkanes are almost strainless (Verevkin, 1999). What is the interaction energy among three or four geminal phenyls placed on the alkane chain? A reason, which stipulated our interest to phenyl substituted alkanes, was logicaly motivated from our experience in improvement of the group-additivity methodology. In recent years we covered a lack of thermochemical information on branched representatives of the homological rows of ethers and esters (Verevkin et al., 1992, 1996; Rakus, 1995a), nitriles (Rakus et al., 1994), imines (Verevkin et al., 1997), ketones (Verevkin, 1998a), amines (Verevkin 1997b, Verevkin et al. 1997, 1998), alcohols (Verevkin, 1998c), nitro compounds (Verevkin, 1997c), and phenols (Verevkin 1998c,d), The experimental investigation of thermochemical properies of the crysalline organic compounds is usually easier than measurements of a liquid one. We have developed a very useful procedure, which has allowed the reliable measurements even in the homological rows of thermolabile compounds, such as fluorocompounds (Schaffer et al., 1997), ketones (Nölke et al., 1995), or ortho esters (Rakus et al., 1995b). If it was synthetically possible, we designed the molecules for our systematic investigation within the aforementioned homological series, which were congested with at least one phenyl ring. The introduction of the phenyl substituents into the compound of interest provided very often the required solid compound. Thus, such a compound was more suitable for the successful purification by recrystallization or sublimation in comparison with the sometimes problematical distillation. Also another advantage of the solid state was the additional possibility of controlling the purity of a compound by study of the melting with differential scanning calorimetry (DSC) (Hemminger and Cammenga, 1989). For the interpretation of thermochemical results for phenyl substituted compounds in terms of group-additivity correlation (we use the like-Benson scheme) arose the necessity to assess the strain enthalpies of the molecules of interest. But only a very few reliable thermochemical quantities of geminal phenyl substituted alkanes are known from the literature (Pedley et al., 1986). The series of polyphenyl substituted alkanes has been studied by Coops et al. (1947, 1953), using combustion calorimetry, but the absence of the systematical investigation on enthalpies of sublimation for these compounds thwarted the interpretation of their thermochemical properties in the gaseous phase. Beckhaus et al. (1990) measured some tetraphenyl substituted compounds. This limited set of thermochemical information fails to provide a reliable concept of strain and the prediction of enthalpies of formation of polyphenylalkanes. We report here a systematic study of the thermochemical properties of a series of triphenyl substituted alkanes 1,1,2-triphenylethane (**A**), triphenylmethane (**B**), 1,1,1-triphenylethane (**C**), 1,1,1-triphenylbutane (**D**), and tetraphenylmethane (**E**) (see Figure 1). The resulting standard enthalpies of formation $\Delta_f H_m°$(g) of these polyphenylalkanes were obtained from enthalpies of sublimation by a transpiration method and calorimetrically measured in this work enthalpy of combustion of **D** and $\Delta_f H_m°$(cr) for **A**, **B**, **C**, and **E**, available from the literature. These experimental results together with the data available from the literature provide a quantitative understanding of the relation between the structure and properties of polyphenylalkanes. The results of the study also could be aimed at improvement of the Benson group-contribution methodology (Benson, 1976).

Experimental Procedure

Materials. Samples of **A**, **B**, and **E** were purchased from Aldrich. **C** and **D** were synthesized by known procedures (Gomberg and Cone, 1906). The structures of compounds **C** and **D** were proved by NMR spectroscopy. The crystalline compounds **A**−**E** were purified by repeated crystallization from ethanol and petroleum ether (boiling range, 303 K to 323 K) and further sublimed in vacuo to remove any traces of solvent. A purity greater than mass fraction 0.9999 was established by DSC studies of the melting process (Hemminger and Cammenga, 1989). The purity of the samples was determined also by GLC. No impurities (≥0.01 mass

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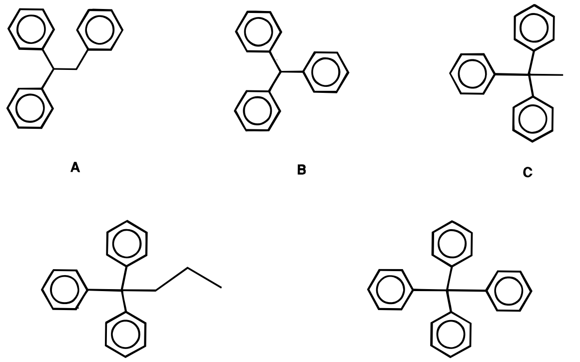

Figure 1. Structures of 1,1,2-triphenylethane (**A**), triphenylmethane (**B**), 1,1,1-triphenylethane (**C**), 1,1,1-triphenylbutane (**D**), and tetraphenylmethane (**E**).

%) could be detected in all samples used for the thermochemical measurements.

All compounds were handled under an inert atmosphere (N_2) using carefully dried solvents. We used the following equipment: GLC, Carlo Erba Fraktometer Vega Series GC 6000; Hewlett-Packard Integrator 3390A; N_2-flow, 0.333 $cm^3{\cdot}s^{-1}$; SE-30 capillary column of length 25 m. The standard temperature program of the GLC was $T = 313$ K for 60 s, followed by a heating rate of 0.167 $K{\cdot}s^{-1}$ to $T = 523$ K. Enthalpies of fusion and specific heat capacities were determined with a Perkin-Elmer DSC-2C.

Combustion Calorimetry. For measurement of the enthalpy of combustion of 1,1,1-triphenylbutane an isoperibol macrocalorimeter fitted with a stirred water bath was used. The samples were pressed into tablets of mass ≈ 300 mg and burned in oxygen at a pressure of 3.04 MPa. The completeness of the combustion of the samples was ensured by the addition of about 50 mg of oil to the tablet. The detailed procedure has been described previously (Beckhaus et al., 1980; Verevkin et al., 1992). The combustion products were examined for carbon monoxide (Dräger tube) and unburnt carbon (visual inspection), but neither was detected. The energy equivalent of the calorimeters ϵ_{calor} were determined ($25\,112.6 \pm 1.9$ $J{\cdot}K^{-1}$) with a standard reference sample of benzoic acid (sample SRM 39i, NIST). For reduction of the data to standard conditions conventional procedures (Hubbard et al., 1956) were used. The atomic weights used were those recommended by the IUPAC Comission (CODATA, 1989). The density of the solid substance **D** was determined by submerging a tablet of the substance in water in a calibrated 10 cm^3 pycnometer. The specific heat capacities and enthalpies of fusion were measured by DSC. The temperature scale of the DSC was calibrated by measuring the melting points of the recommended high-purity standards: benzoic acid, tin, and indium (Hemminger and Cammenga, 1989). The power scale was calibrated using high-purity indium (mass fraction, 0.999 99) as standard material. A summary of auxiliary quantities for the combustion experiments and the information necessary for reducing the apparent mass to mass in vacuo are given in Table 1.

Transpiration Method. The enthalpies of vaporization/sublimation of compounds **A**−**E** were determined using the method of transference in a saturated N_2 stream (Cox and Pilcher, 1970; Beckhaus et al., 1980; Chickos et al., 1995). About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. A nitrogen flow of (0.28−0.56) $cm^3{\cdot}s^{-1}$ was optimal in order to achieve saturation of the transporting gas at each temperature of the investigation. The amount of condensed product was determined by GLC analysis using an internal standard (hydrocarbons n-$C_{11}H_{24}$ or n-$C_{13}H_{28}$). The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period, and the small value of the residual vapor pressure at the temperature of condensation was added. The latter was calculated from a linear correlation between ln p and T^{-1} obtained by iteration. With the assumption that Dalton's law of partial pressures applied to the saturated nitrogen stream, values of p from the ideal gas law were calculated. The molar enthalpies of vaporization or sublimation were calculated from the slope of the following linear correlation: $\Delta_{cr}^{g}H_m° = -R[d(\ln p)/dT^{-1}]$. The observed enthalpies of vaporization or sublimation at temperature T obtained by this procedure are listed in Table 2.

Table 1. Density ρ (293 K), Specific Heat Capacity c_p (298.15 K), and Expansion Coefficients $(dV_m/dT)_p$ of the Materials Used in the Present Study

	ρ(293 K)[a]/ ($g{\cdot}cm^{-3}$)	c_p(298.15 K)[b]/ ($J{\cdot}K^{-1}{\cdot}g^{-1}$)	$10^{-6}(dV_m/dT)_p$ [c]/ ($dm^{-3}{\cdot}K^{-1}$)
1,1,1-triphenylbutane	1.080	1.30	0.1
oil[d]	1.500	1.67	1.0
cotton[e]	0.880	0.84	0.1

[a] Measured with the pycnometer. [b] From DSC measurements. [c] Estimated. [d] $\Delta_c u°(CH_{1.940}) = -(46\,003.6 \pm 4.0)$ $J{\cdot}g^{-1}$, where $\Delta_c u°$ denotes the standard specific energy of combustion. [e] From 10 combustion experiments $\Delta_c u°$ $(CH_{1.774}O_{0.887}) = -(16\,945.2 \pm 4.2)$ $J{\cdot}g^{-1}$.

Results and Discussion

Combustion Calorimetry. Results for a typical combustion experiment on compound **D** are given in Table 3. The individual values of the standard specific energy of combustion ($\Delta_c u°$), enthalpies of combustion (the given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials), and enthalpies of combustion and formation of compound **D** are given in Table 4. To derive $\Delta_f H_m°$(cr) from $\Delta_c H_m°$, the following molar enthalpies of formation were used (CODATA, 1989): for H_2O(l), $-(285.83 \pm 0.04)$ $kJ{\cdot}mol^{-1}$; for CO_2(g), $-(393.51 \pm 0.13)$ $kJ{\cdot}mol^{-1}$. Table 5 lists the derived standard molar enthalpies of formation in the crystalline and the gaseous states.

The standard enthalpies of formation $\Delta_f H_m°$(cr) of compounds **A**−**C** and **E** have been determinated by Coops et al. (1947, 1953) using combustion calorimetry. Two compounds measured by this group have been remeasured by Beckhaus et al. (1990), and their new results were in acceptable agreement with those from Coops. Therefore the values $\Delta_f H_m°$(cr) from Coops et al. (1947, 1953) were taken into account for the calculation of the gaseous standard enthalpies of formation $\Delta_f H_m°$(g) of these compounds (Table 5).

Measurements of thermochemical properties of 1,1,1-triphenylbutane are reported for the first time.

Enthalpies of Vaporization or Sublimation. The resulting enthalpies of vaporization, $\Delta_l^g H_m°$, or sublimation, $\Delta_{cr}^g H_m°$, at $T = 298.15$ K are recorded in Table 2. Because of the deviations from $T = 298.15$ K, the observed values of the enthalpies of vaporization or sublimation of phenylalkanes measured by transpiration had to be adjusted to the reference temperature. The values of corrections were estimated via the "Sidgwick correction":

Table 2. Results from Measurements of the Vapor Pressure *p* with the Transpiration Method

T^a/K	m^b/mg	$V(N_2)^c$/dm^3	p^d/Pa	T^a/K	m^b/mg	$V(N_2)^c$/dm^3	p^d/Pa
1,1,2-Triphenylethane; $\ln(p/\mathrm{Pa}) = (29.99 \pm 0.16) - (10702 \pm 56)\,(T/\mathrm{K})^{-1}$							
335.1	1.47	101.6	0.1391	353.1	1.67	21.65	0.7397
338.5	1.12	54.35	0.1980	358.1	2.71	23.40	1.111
343.0	1.20	38.57	0.2985	362.7	2.59	15.46	1.603
348.0	1.71	35.55	0.4613	367.8	1.29	5.13	2.414
$\Delta_l^g H_m°(351.4\mathrm{K}) = (88.98 \pm 0.47)$ kJ·mol^{-1}; $\Delta_l^g H_m°(298.15\mathrm{K}) = (92.18 \pm 0.47)$ kJ·mol^{-1}							
Triphenylmethane; $\ln(p/\mathrm{Pa}) = (36.39 \pm 0.20) - (12832 \pm 66)\,(T/\mathrm{K})^{-1}$							
323.0	0.796	231.1	0.03490	341.0	4.09	142.9	0.2903
328.4	1.44	218.4	0.06687	344.2	4.48	109.2	0.4160
333.1	2.22	192.3	0.1172	346.5	3.97	78.80	0.5100
338.0	2.72	135.3	0.2037	353.1	4.91	48.42	1.0280
$\Delta_{cr}^g H_m°(338.0\mathrm{K}) = (106.69 \pm 0.55)$ kJ·mol^{-1}; $\Delta_{cr}^g H_m°(298.15\mathrm{K}) = (109.08 \pm 0.55)$ kJ·mol^{-1}							
1,1,1-Triphenylethane; $\ln(p/\mathrm{Pa}) = (35.97 \pm 0.30) - (12678 \pm 103)\,(\mathrm{T/K})^{-1}$							
338.4	1.63	70.56	0.2223	353.3	1.29	11.32	1.093
342.5	2.01	56.46	0.3420	358.6	2.22	11.83	1.803
347.1	1.90	31.36	0.5815	363.2	2.75	9.14	2.889
$\Delta_{cr}^g H_m°(350.8\ \mathrm{K}) = (105.41 \pm 0.86)$ kJ·mol^{-1}; $\Delta_{cr}^g H_m°(298.15\ \mathrm{K}) = (108.57 \pm 0.86)$ kJ·mol^{-1}							
1,1,1-Triphenylbutane; $\ln(p/\mathrm{Pa}) = (37.18 \pm 0.39) - (13479 \pm 130)\cdot(\mathrm{T/K})^{-1}$							
323.3	0.296	231.1	0.01108	341.4	1.65	143.6	0.09921
328.7	0.527	218.4	0.02084	344.6	1.85	110.9	0.1442
333.4	0.825	192.3	0.03711	346.8	1.65	79.20	0.1805
338.3	1.10	135.3	0.06999				
$\Delta_{cr}^g H_m°(335.0\mathrm{K}) = (112.1 \pm 1.1)$ kJ·mol^{-1}; $\Delta_{cr}^g H_m°(298.15\mathrm{K}) = (114.3 \pm 1.1)$kJ·mol^{-1}							
Tetraphenylmethane; $\ln(p/\mathrm{Pa}) = (38.02 \pm 0.42) - (16280 \pm 155)(\mathrm{T/K})^{-1}$							
363.1	0.0584	408.3	0.001106	378.3	0.161	193.8	0.006402
368.2	0.106	409.5	0.001992	383.5	0.213	138.8	0.01187
373.3	0.182	370.4	0.003789	388.5	0.496	184.5	0.02078
$\Delta_{cr}^g H_m°(375.8\mathrm{K}) = (135.4 \pm 1.3)$ kJ·mol^{-1}; $\Delta_{cr}^g H_m°(298.15\mathrm{K}) = (140.0 \pm 1.3)$ kJ·mol^{-1}							

[a] Temperature of saturation, N_2 gas flow (0.26−0.52) cm^3·s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer sample. [d] Vapor pressure at temperature T of experiment; corrections for residual vapor pressure at $T = 243$ K were made.

Table 3. Results for Typical Combustion Experiment at $T = 298.15$ K ($p° = 0.1$ MPa)[a]

	1,1,1-triphenylbutane		1,1,1-triphenylbutane
m(substance)^b/g	0.352 313	$(\epsilon_{cont})(-\Delta T_c)$/J	−8.77
m'(cotton)^b/g	0.000 888	$\Delta U_{corr}{}^d$/J	8.08
m''(oil)^b/g	0.058 065	$-m'\Delta_c u'$/J	15.04
$\Delta T_c{}^c$/K	0.689 25	$-m''\Delta_c u''$/J	2671.22
$(\epsilon_{calor})(-\Delta T_c)$/J	−17 308.86	$\Delta_c u°$(substance)/(J·g^{-1})	−41502.0

[a] For the definition of the symbols see Hubbard et al. (1956): $T_h = 298.15$ K; $V_{bomb} = 0.2664$ dm^3; $p^i{}_{gas} = 3.04$ MPa; $m^i{}_{water} = 0.78$ g; $E_{ignition.} = 1.46$ J; $m_{platin} = 12.181$ g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr.}$; $(\epsilon_{cont})(-\Delta T_c) = (\epsilon^i{}_{cont})(T^i - (298.15\ \mathrm{K})) + (\epsilon^f{}_{cont})(298.15\ \mathrm{K} - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to standard state is the sum of items 81−85, 87−90, 93, and 94 in Hubbard et al. (1956).

Table 4. Summary of Experimental Specific Energies of Combustion and Standard Molar Thermodynamic Functions of 1,1,1-Triphenylbutane at $T = 298.15$ K ($p° = 0.1$ MPa), Where $\langle -\Delta_c u° \rangle$ Denotes the Average Value

$[(\Delta_c u°)\{1,1,1\text{-triphenylbutane, cr, } 298.15\ \mathrm{K}\}]/(\mathrm{J\cdot g^{-1}})$	−41 502.0, −41 526.6, −41 509.7, −41 499.0, −41 511.6
$\langle -\Delta_c u° \rangle/(\mathrm{J\cdot g^{-1}})$	−41509.8 ± 4.8
$\Delta_c H_m°(\mathrm{cr})/(\mathrm{kJ\cdot mol^{-1}})$	−11902.9 ± 1.7
$\Delta_f H_m°(\mathrm{cr})/(\mathrm{kJ\cdot mol^{-1}})$	101.6 ± 1.7

$$\{\Delta_{cr}^g H_m°(\langle T \rangle) - \Delta_{cr}^g H_m°(298.15\mathrm{K})\}/(\mathrm{kJ\cdot mol^{-1}}) = -6 \times 10^{-2}((\langle T \rangle/\mathrm{K}) - 298.15)$$

following the recommendation of Chickos et al. (1992). With these corrections and the measured values of $\Delta_l^g H_m°(T)$ and $\Delta_{cr}^g H_m°(T)$ the standard molar enthalpies of vaporization or sublimation at $T = 298.15$ K were calculated (Table 2).

Determinations of the enthalpies of sublimation and vaporization of triphenylmethane have been made by a number of groups in recent years (see Table 6). The observed values $\Delta_{cr}^g H_m°(T)$ and $\Delta_l^g H_m°(T)$ given in the literature were extrapolated to $T = 298.15$ K in the same manner with our results, using "Sidgwick's correction" (Chickos et al., 1992). The values of $\Delta_{cr}^g H_m°$ from the different techniques are very consistent with this research (excepting the much earlier value from Aihara (1959)) as can be seen by reference to Table 6. The value of $\Delta_l^g H_m° = (88.4 \pm 4.7)$ kJ·mol^{-1} from Sasse et al. (1989) is also in very good agreement with the $\Delta_{cr}^g H_m° = (109.08 \pm 0.55)$ kJ·mol^{-1} from this work (taking into account the enthalpy of fusion $\Delta_{cr}^l H_m° = 20.71$ kJ·mol^{-1} (Table 5): $\Delta_{cr}^g H_m° = 88.4 + 20.71 = 109.1$ kJ·mol^{-1}.

Measured in this work, the value of $\Delta_{cr}^g H_m° = (140.0 \pm 1.3)$ kJ·mol^{-1} (at 298.15 K) for tetraphenylmethane is in aceptable agreement with the value of $\Delta_{cr}^g H_m° = (150.6 \pm 4.2)$ kJ·mol^{-1} from Kana'an (1972) for this compound (taking into account the uncertainties of experiments and the long way of extrapolation to the reference temperatue 298.15 K). Measurements of enthalpies of vaporization of 1,1,2-tripheylethane (**A**) and triphenylalkanes **C** to **D** have been reported for the first time.

Diffrencial Scanning Calorimetry. The enthalpies of fusion $\Delta_{cr}^l H_m°$ (Table 5) and melting points, 328.2 K for **A**, 367.2 K for **B**, 375.9 K for **C**, 351.1 K for **D**, and 554.2 K for **E**, were measured by DSC. The values of $\Delta_{cr}^l H_m°$ reported for triphenylmethane 21.98 kJ·mol^{-1} (Spaght et al., 1932), 20.92 kJ·mol^{-1} (Eibert, 1944), and 18.20 kJ·mol^{-1} (Hildebrand et al., 1917) are in reasonable agreement with our result (20.71 ± 0.21 kJ·mol^{-1}).

Strain Enthalpy H_S of Polyphenylalkanes. The group additivity scheme of the Benson type (Benson, 1976; Cohen

Table 5. Thermochemical Results at $T = 298.15$ K ($p° = 0.1$ MPa)

	$\Delta_{cr}^{g}H_m°$ [a]/(kJ·mol^{-1})	$\Delta_{cr}^{l}H_m°$ [b]/(kJ·mol^{-1})	$\Delta_f H_m°$(cr)/(kJ·mol^{-1})	$\Delta_f H_m°$(g)/(kJ·mol^{-1})
1,1,2-triphenylethane (**A**)	116.57 ± 0.51[c]	24.39 ± 0.21	130.2 ± 2.2[d]	246.8 ± 2.2
triphenylmethane (**B**)	109.08 ± 0.55	20.71 ± 0.21	171.2 ± 1.4[e]	280.3 ± 1.5
1,1,1-triphenylethane (**C**)	108.57 ± 0.86	19.95 ± 0.21	157.2 ± 2.1[d]	265.8 ± 2.3
1,1,1-triphenylbutane (**D**)	114.3 ± 1.1	21.84 ± 0.21	101.6 ± 1.7	215.9 ± 2.0
tetraphenylmethane (**E**)	140.0 ± 1.3	48.28 ± 0.21	247.1 ± 2.6[e]	387.1 ± 2.9

[a] From the measurements of vapor pressures at different temperatures (Table 2) using the Clausius−Clapeyron equation. [b] Measured by DSC. [c] Calculated from the measurement above the melting temperature $\Delta_{l}^{g}H_m° = 92.18 \pm 0.47$ kJ·mol^{-1} (Table 2) and $\Delta_{cr}^{l}H_m°$ from this table. [d] Taken from Coops et al. (1953). [e] Taken from Coops et al. (1947).

Table 6. Comparison with Earlier Values of Enthalpy of Sublimation $\Delta_{cr}^{g}H_m°$ (kJ·mol^{-1}) of Triphenylmethane[a]

technique	T_{av}/K	obsd at T_{av}	extrapolated[a] to $T = 298.15$ K	ref
viscosity gauge	339	100.0 ± 0.4	102.5 ± 0.4	Aihara, 1959
transpiration	330.65	106.8 ± 6.4	108.8 ± 6.4	Hansen and Eckert, 1986
static manometer	353.13	113.9 ± 2.0	117.2 ± 2.0	Sasse et al., 1989
static manometer	402.74	82.1 ± 4.7[b]	88.4 ± 4.7[b]	Sasse et al., 1989
transpiration	338.0	106.69 ± 0.55	109.1 ± 0.6	this work

[a] The observed value at T_{av} was extrapolated to 298.15 K using the "Sidgwick correction" (see text), if it was not done in the reference. [b] Enthalpy of vaporization $\Delta_{l}^{g}H_m°$ measured above the melting point.

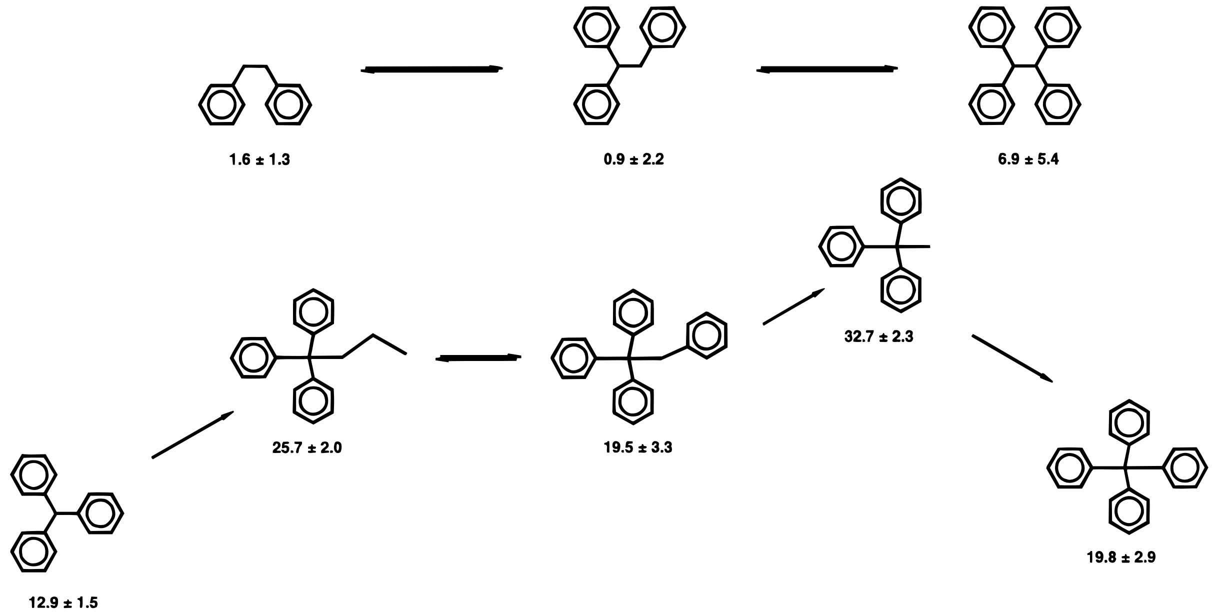

Figure 2. Comparison of the strain energies H_S (kJ·mol^{-1}) of phenyl substituted alkanes.

and Benson, 1993; Cohen, 1996) is widely used for the calculation of standard molar enthalpies of formation at 298 K. The system of strain-free increments (Schleyer et al., 1970) is based on the standard enthalpies of formation $\Delta_f H_m°$(g) of simple homologous ("strainless") molecules. Strain-free group-additivity increments for hydrocarbons (Schleyer et al., 1970) and arenes (Beckhaus, 1983) are well-defined (see Table 7). Their advantage with respect to the classic Benson increments (Benson, 1976) is the possibility of determining the strain enthalpy of a molecule.

We define the strain H_S of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_f H_m°$(g) and the calculated sum of the strain-free Benson type increments (Table 7) for this molecule. The summary of strain enthalpies of polyphenylalkanes is given in Table 7.

Table 7. Strain Enthalpies H_S of Phenyl Substituted Alkanes at $T = 298.15$ K ($p° = 0.1$ MPa)

	$\Delta_f H_m°$(g)/ (kJ·mol^{-1})	Σ (strain-free increments)[a]/ (kJ·mol^{-1})	H_S[b] (kJ·mol^{-1})
1,2-diphenylethane	142.9 ± 1.3[c]	141.3	1.6 ± 1.3
1,1,2-triphenylethane (**A**)	246.8 ± 2.2	245.9	0.9 ± 2.2
1,1,2,2-tetraphenylethane	357.3 ± 5.4[d]	350.4	6.9 ± 5.4
tri-phenylmethane (**B**)	280.3 ± 1.5	267.4	12.9 ± 1.5
1,1,1,2-tetraphenylethane	365.3 ± 3.3[d]	345.8	19.5 ± 3.3
1,1,1-triphenylbutane (**D**)	215.9 ± 2.0	190.2	25.7 ± 2.0
1,1,1-triphenylethane (**C**)	265.8 ± 2.3	233.1	32.7 ± 2.3
tetraphenylmethane (**E**)	387.1 ± 2.9	367.3	19.8 ± 2.9

[a] Estimated as a sum of strain-free increments for alkanes (Schleyer et al., 1970), $CH_3[C] = -42.05$, $CH_2[2C] = -21.46$, $CH[3C] = -9.04$, $C[4C] = -1.26$ kJ·mol^{-1}, and for arenes (Beckhaus, 1983), $C_BH[2C_B] = 13.72$, $C_B[C,2C_B] = 23.51$ kJ·mol^{-1}. [b] Estimated: $H_S = (\Delta_f H_m°(g) - \Sigma(\text{strain-free increments}))$; the uncertainties of the H_S values were suggested to be only equal to those of the experimental $\Delta_f H_m°$(g) of phenylalkanes. [c] Taken from Pedley et al. (1986). [d] Taken from Beckhaus et al. (1990).

Evolution of strain in phenyl substituted alkanes is presented in Figure 2. Starting from strainless 1,2-diphenylethane, $H_S = (1.6 \pm 1.3)$ kJ·mol^{-1}, no significant steric interactions of phenyl substituents can be detected for 1,1,2-triphenylethane, $H_S = (0.9 \pm 2.2)$ kJ·mol^{-1}, and even for 1,1,2,2-tetraphenylethane, $H_S = (6.9 \pm 5.4)$ kJ·mol^{-1}. But a considerable destabilization that arises in triphenylmethane, $H_S = (12.9 \pm 1.5)$ kJ·mol^{-1}, is definitely due to the sterical repulsions of geminal phenyl rings. The introduction of the fourth substituent onto the geminal central C-atom provides further destabilization in 1,1,1,2-tetraphenylethane, $H_S = (19.5 \pm 3.3)$ kJ·mol^{-1}, and in 1,1,1-triphenylbutane, $H_S = (25.7 \pm 2.0)$ kJ·mol^{-1}, due to a decrease of the free space around the geminal center of a molecule. The latter two molecules exibit about the same (within the boundaries of the experimental uncertainties) level of destabilization, because they have the same CH_2 group attached to the central C-atom. The resulting sterical repulsions of the three geminal phenyl rings with the geminal methyl group in 1,1,1-triphenylethane is (32.7 ± 2.3) kJ·mol^{-1}. This value is definitely as large as the interactions of three geminal rings with the CH_2 group in 1,1,1-triphenylbutane and 1,1,1,2-tetraphenylethane, because the CH_3 group is apparently large. The spacious size of the phenyl substituent is more comparable with the CH_2 group than with the CH_3 one. That is why tetraphenylmethane, $H_S = (19.5 \pm 3.3)$ kJ·mol^{-1}, is less strained than 1,1,1-triphenylethane.

Calculation of the Group-Additivity Contributions. The additive terms CH[3C_B] and C[3C_B,C] for a carbon atom attached to the three benzene rings are the significant bricks of the strained molecules. Their values contain the inherent strain from the sterical repulsions of the phenyl substituentes. These increments could be calculated from the experimental results from this work (Table 5) and strain-free group-additivity values for alkanes and arenes (Table 7). The group-additivity value CH[3C_B] $= -3.9$ kJ·mol^{-1} was calculated from the enthalpy of formation of triphenylmethane. The group-additivity increment C[3C_B,C] $= 22.8$ kJ·mol^{-1} was calculated as the mean value from the enthalpy of formation of 1,1,1-triphenylbutane (24.5 kJ·mol^{-1}) and 1,1,1,2-tetraphenylethane (18.2 kJ·mol^{-1}). The uncertainties of $\Delta_f H_m°(g)$ were taken into account as the weight (Oleynik, 1973) by estimation of the mean value of the increment C[3C_B,C].

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