with the hydrogen bonds of the base pairs enclosed in a domain of the stacked unsaturated rings. Recent experiments on countercurrent distribution of DNA from bacteria show that newly replicated DNA is more soluble in a nonaqueous phase than in an aqueous phase.[25] This also suggests that these experiments in nonaqueous solvents may have more relevance to behavior in biological systems than would be anticipated otherwise.

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Iodine-Catalyzed Isomerization of *n*-Heptenes. Thermodynamic Data for the Positional and Geometrical Isomerization and the *cis* Effect in the Entropy Difference of Geometrical Isomer Pairs

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Abstract: The equilibrium compositions of the iodine atom catalyzed isomerization of 1-, 2-, and 3-heptenes have been studied in the gas phase over a temperature range from 148.5 to 333.5°. The equilibrium constants for the positional and geometrical isomerization obtained from gas-chromatographic analysis show straight lines in a van't Hoff plot of log K against $1/T$(°K). Least-squares fits of the data yield (with standard errors) differences in heats of formation and entropies between the geometrical and positional isomers for a mean temperature of 510°K. In addition, the measured equilibrium constants have been fitted to quadratic equations of the form $\log K = (a/T^2) + (b/T) + c$. The results show that the experimental data are best represented with linear equations, and that for both geometrical isomer pairs ΔC_p° (400–600°) equals 0 ± 0.5 cal/deg mole. Refined values for partial group contributions (increments) to the heat of formation and entropy of olefins as well as isomer corrections thereof are given. These data confirm previous estimates and they demonstrate the anticipated *cis* effect in the entropy differences of various geometrical isomer pairs. This effect can be attributed to differences in barriers to free rotation of the end groups in the *cis* configurations of the isomers.

The value of the method of the iodine-catalyzed, gas-phase isomerization of olefins in obtaining kinetic parameters as well as accurate thermodynamic data through the measurement of equilibrium constants has been demonstrated by Benson and co-workers on a large number of olefins.[1]

The same method and a new experimental setup was used to obtain the equilibrium constants in the *n*-heptene series. Direct experimental literature data on heats of formation, entropies, and specific heats are available only for 1-heptene[2,3] whose heat of hydrogenation[4] and heat of combustion[5] have been measured. API values,[2] calculated from experimental data on the lower olefins, and comparative estimates are available through the hexenes and for 1-heptene only. A value of 16.8 kcal/mole[6] for $\Delta H_f^\circ(299^\circ)$ of *cis*-2-heptene has been reported from calculations in the homologous series of hydrocarbons.

This study is primarily concerned with the differences in heats of formation ($\Delta\Delta H_f^\circ$) and entropies (ΔS°) between the geometrical isomer pairs of 2-heptene and 3-heptene. From previous equilibrium studies on 2-butene,[1a,b] 2-pentene,[1f] and 1,3-pentadiene,[1e] it was to be expected that the differences in enthalpies for the 2- and the 3-heptenes be the same, while the entropy differences between the geometrical isomer pairs should reflect differences in barriers to internal rotation of the end groups in the *cis* configuration of the molecule. Based on the reported variation between 2-butene[1b] and 2-pentene,[1f] the difference in entropy of the *cis–trans* pair of 3-heptene is estimated to be 1.2 cal/deg mole larger than that of the 2-heptenes.

In addition this work gives $\Delta\Delta H_f^\circ$ and ΔS° between the *trans* configurations of 2-heptene and 3-heptene. It is reasonable to expect that *trans* forms of various positional isomers should not only have the same enthalpy but very nearly the same entropy content as well, considering that any differences in entropy would have to arise mainly from variations in barriers to internal rotation of the end groups in the molecules.

Finally, accurate data for the differences in enthalpies and entropies of the *n*-heptene isomers, when combined with earlier work reported in the literature, will result

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Table I.[a] Example of Gas Chromatographic Analysis of Equilibrated Isomer Mixture

BMEA[b]			AgNO$_3$/ethylene glycol	
(*trans*-3) + (1)	105.7			
(*cis*-3)	30.3			
(*trans*-2)	83.9 = 32.4% of ϵ_1		(*trans*-3) + (*trans*-2)	62.48
(*cis*-2)	38.8 = 15.0% of ϵ_1		(*cis*-3) + (*cis*-2) + (1)	28.13
Total C_7 olefins	258.7 (ϵ_1)		Total C_7 olefins	90.61 (ϵ_1')
n-Heptane	12.4 = 4.8% of ϵ_1		*n*-Heptane = 5.0% of $\epsilon_{1'}$	4.96
			(*trans*-3) + (*trans*-2)	62.48
(*trans*-3) + (1)	105.7		(*trans*-2) = 32.4% of $\epsilon_{1'}$	29.37
(*trans*-3)	94.5 = 36.5% of ϵ_1	←	(*trans*-3) = 36.5% of $\epsilon_{1'}$	33.11
(1)	11.2 = 4.3% of ϵ_1	→	(1) = 4.3% of $\epsilon_{1'}$	3.91
			(*cis*-3) + (*cis*-2) + (1)	28.13
			(*cis*-3) + (*cis*-2)	24.22
			(*cis*-2) = 15.0% of $\epsilon_{1'}$	13.59
			(*cis*-3)	10.63
(*trans*-3)/(*cis*-3)	3.12		(*trans*-3)/(*cis*-3)	3.12
(*trans*-2)/(*cis*-2)	2.16			
(*trans*-3)/(*trans*-2)	1.13			
(*trans*-3)/(1)	8.43			

[a] Numbers represent deflection units of the integrator pen. [b] BMEA stands for bis(2-methoxyethyl) adipate.

in more precise and experimentally well-founded group contributions[7] to the enthalpies and entropies of olefins in general.

Experimental Section

A. **Procedure and Apparatus.** The principal features of the method and the experimental setup have been reported earlier.[1a] A "thermal" reaction system has been built, similar to the one described in detail in the literature.[1b] Measurements were carried out in cylindrical glass vessels placed in a very well-insulated stainless steel block furnace which can be operated at temperatures up to 1000°. The reaction temperature is maintained with an integral-proportional controller (platinum resistance probe) acting upon 10% of the total load only. The maximum temperature difference across the reaction vessel as measured by five fixed thermocouples at extreme positions never exceeded 0.2°. The effective dead space amounting to 0.2% of the total reaction volume of 1000 ml was always kept at ~130°.

Pressure differences were measured with a PACE pressure transducer and Model CD 25 indicator unit, connected on the null side to mercury and silicone oil manometers. Pressure differences as low as 0.02 torr are measurable. Iodine concentrations were measured by light absorption. For this purpose the reaction cells have been equipped with parallel windows. The intensity of the collimated light beam from a stabilized light source was measured after passing through the reaction vessel (CdS cell in connection with a microammeter).

The reaction cell is connected through stopcocks (silicone grease) to a vacuum system, a gas-storage system, a handling system, a gas-collection system, and an iodine reservoir. To avoid precipitation of the iodine or the reaction products, parts of the glass tubing connections as well as some stopcocks and the pressure measuring device were kept at temperatures between 100 and 120°.

Iodine was admitted to the evacuated (10^{-5} torr) reaction cell and measured both by direct pressure measurement and by the change in light absorption. An experiment was started by adding the gaseous hydrocarbon from a reservoir. Changes in pressure and light intensity were followed during the reaction. An experiment was stopped by expanding the reaction mixture into the gas collection system and quenching the reaction products in a fractionating manner in a series of five U traps kept at different temperatures. The first three traps, filled with NaOH pellets, removed all traces of HI that were formed in the course of the reaction. Iodine was condensed when the gaseous reaction mixture passed through the first trap which was kept at 10–15°. In this trap all higher boiling hydrocarbons formed in side reactions (dimerization of heptadienes and heptatrienes) were condensed together with the iodine. This was seen in a liquid phase precipitated along with iodine crystals. The C_7 fraction of the hydrocarbons, condensed in the last trap over liquid nitrogen, was subsequently withdrawn from the system for gas chromatographic analysis. Where large amounts of heptenes had been used, the reaction mixture was carefully and gradually expanded into the collection system to avoid premature condensation of the heptenes in the first traps of the sampling system. This precaution was made necessary by the relatively low vapor pressure (~50 torr) of the *n*-heptenes at room temperature.

In addition to the gas chromatographic analysis, the mass balance of the isomers was checked in a few experiments by pressure measurements in calibrated volumes. It was found that the losses in *n*-heptenes were especially large with high initial iodine and small hydrocarbon pressures. This is in agreement with the measured very fast initial losses of iodine and the finding that with increasing ratio of initial iodine to hydrocarbon pressures, increasing amounts of *n*-heptane were formed in the system. These side reactions had been expected from the analogous work with 2-butene[1a] and 2-pentene[1f] and are discussed later in the text.

B. **Analysis.** The C_7 fractions of the reaction products have been analysed by gas–liquid chromatography. A Model 810 F&M research gas chromatograph equipped with TC detectors was used. The quantitative analysis of the samples was carried out by measuring peak areas with a Model 201 B Disc chart integrator connected to a modified Honeywell recorder and automatic attenuator designed for fully automated operation.

The quantitative separation of all the *n*-heptene isomers proved to be considerably more difficult than was anticipated. The best results have been obtained by combining the data from two separate analysis using different column materials. A 50-ft × 0.5-in. column of 20% BMEA[1b] on Chromosorb W (60–80 mesh) was operated at 40° with a He flow of 60 ml/min. It separated the *n*-heptene isomers to 98% or better, except for *trans*-3-heptene from 1-heptene. Overlap corrections have been applied where necessary. The following retention times have been measured (in minutes after the air peak): *n*-heptane, 43.1; 1-heptene, 60.3; *trans*-3-heptene, 60.5; *cis*-3-heptene, 64.0; *trans*-2-heptene, 69.4; *cis*-2-heptene, 74.7; heptadienes, >120.

A second analysis was carried out on a 6-ft column of 17% ethylene glycol, saturated with silver nitrate and coated onto Chromosorb W (60–80 mesh). This column, operated at 40° and 100 ml of He/min, separated the *trans*-2- and 3-heptene from the *cis*-2- and 3-heptene quantitatively. 1-Heptene was only partly separated from the *cis*-olefins.

Attempts to separate 1-heptene from the remaining isomers in a quantitative utilizable manner failed, even though a large number of column materials has been tested. An example of the anlysis of the *n*-heptene isomers is given in Table I.

Completely independent sets of analyses yielded maximum deviations of ±2% for the ratio of the geometrical isomer pairs of 2- and 3-heptene. For more than half of the experiments the deviation was less than 1%. Larger uncertainties necessarily accompany the indirect method of measuring 1-heptene. In addition, the amount of 1-heptene in the equilibrium mixture never exceeded 7% of the total of the *n*-heptene isomers. It was therefore not surprising that up to ±6% (maximum deviations) in the

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[7] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 662.

Table II. Composition of Equilibrated Mixtures of *n*-Heptene Isomers

	Starting compound n-C_7H_{14}[a]			Iodine pressure,[b] torr				Final equilibrium ratios[a,b]			
Temp, °C	Pressure, torr	Isomer	$[t/c]_0$	$[I_2]_0$	$[I_2]_f$	Time, min	n-Heptane[c] in % of total n-C_7H_{14}	$K_{1,2}$ 3t/3c	$K_{3,4}$ 2t/2c	$K_{5,6}$ 3t/2t	$K_{7,8}$ 3t/1
148.5	75.9	2	0.26	29.6	27.7	3754	2.70	3.74[d]	2.45[d]	0.86[d]	15.4
	100.8	3	0.54	29.5	...	4213	2.26	3.87	2.67	1.11	16.2
149.5	88.2	Equil mixt[e]		29.9	...	1379	4.80	4.22	2.89	1.11	14.8
177.7	85.9	2	0.26	28.2	24.5	2700	1.97	3.53	2.56	>0.99[d]	
	39.4	3	*cis*	9.4	4.6	2553	1.06	3.47	2.39	<1.78[d]	
	62.9	3	0.54	17.0	15.1	420	<0.1	1.86[d]	2.39		
	171.5	3	0.54	32.7	...	396	0.38	2.54[d]	2.40		
	100.5	3	0.54	30.9	...	440	0.15	2.71[d]	2.46		
	106.4	3	0.54	29.7	22.7	603	0.56	3.23[d]	2.48		
	45.4	3	*cis*	27.6	27.6	530	0.30	1.93[d]	2.43		
200.2	61.4	3	3.6	13.0	10.8	116	...	3.32[d]	2.53		
	58.2	3	3.6	32.1	25.3	297	0.97	3.51	2.57	<1.49[d]	14.0[d]
	98.2	3	0.54	32.5	32.0	344	0.76	3.55	2.42	<1.42[d]	13.9[d]
	65.0	3	0.54	13.3	9.2	933	0.85	3.59	2.42	<1.30[d]	18.7[d]
	46.3	3	*cis*	29.7	29.1	281	...	3.56	2.56	<1.70[d]	10.9[d]
233.3	146.4	2	0.26	29.2	...	98	1.63	3.42	2.38	1.09	16.4[d]
	115.6	3	0.54	25.1	...	165	2.01	3.37	2.32	1.15	12.6[d]
233.6	110.9	1	...	4.6	...	937	5.36	3.35	2.20	1.09	>4.85[d]
	105.2	3	0.54	12.5	...	204	3.60	3.18	2.22	1.18	11.0[d]
272.7	128.8	1	...	21.6	5.7	60	4.29	3.14	2.05	1.09	>4.45[d]
	99.8	1	...	11.7	...	889	32.33	3.06	2.15	1.11	8.79
	71.2	2	0.26	4.5	~0	107	2.00	3.13	2.11	1.09	9.02
	61.9	2	0.26	19.7	~2.9	60	6.29	3.04	2.15	1.11	7.69
	50.3	3	0.54	3.9	~0	67	0.74	3.08	2.16	<1.33[d]	8.72
	110.3	3	0.54	26.7	9.1	45	4.57	3.14	2.16	1.13	8.48
332.0	77.6	3	0.54	12.5	...	10	1.19	2.72	2.02	1.16	5.59
332.3	162.9	1	...	13.6	...	30	3.81	2.96	2.03	1.14	5.73
	92.0	2	0.26	4.2	...	15	1.05	2.87	1.89	>0.89[d]	5.52
332.4	25.3	2	0.26	5.8	...	14	1.51	2.94	1.96	>1.03[d]	6.26
332.8	77.1	2	0.26	19.5	...	25	4.45	2.82	2.10	>1.08	5.10
333.5	212.4	3	0.54	7.6	...	106	2.76	2.89	2.01	1.14	6.30

[a] 1, 2, 3 and t, c stand for 1-heptene, 2-heptene, 3-heptene and for *trans* and *cis* isomers, respectively. [b] Subscript 0 and f stand for initial and final concentrations, respectively. [c] Results are based on gas-chromatographic analysis and have not been corrected for losses in high-boiling dimeric products from diolefin formation. [d] Did not reach equilibrium, the conversion being too small. [e] Starting material is equilibrated product from experiment above.

(*trans*-3)/(1) ratio have been found. The response factor for all the *n*-heptene isomers as well as for *n*-heptane was measured to be 1.00 within 1%.

C. Materials. All materials used in the equilibrium study were supplied by the Phillips Petroleum Co., Bartlesville, Okla., and were further purified by distillation under reduced pressure and, in the case of the geometrical isomers, by preparative-scale gas chromatography (12 ft × 0.5-in. column of 17% ethylene glycol saturated with $AgNO_3$, coated onto Chromosorb W). Samples of higher purity for calibration purposes were supplied by Chemical Samples Co., Columbus, Ohio: 1-heptene, 99.4%; *trans*-2-heptene and *trans*-3-heptene, 99.8%; *cis*-2- and *cis*-3-heptene, 95%. Reagent grade resublimed iodine was used.

Results and Discussion

The detailed reaction mechanism of the iodine atom catalyzed positional and geometrical isomerizations of olefins has been reported in the literature.[1c-g] It may be recalled that equilibrium between the geometrical isomers is established much faster than between positional isomers. This can be seen from Table II. In several experiments the geometrical isomers of 2-heptene and 3-heptene are present in the reaction mixture in their equilibrium compositions, while equilibrium between the positional isomers has not yet been established. As mentioned in the Experimental Section, *n*-heptane was the only major side product present in the final C_7 fraction of the reaction products (compare Table II). In most experiments small amounts of heptadienes and heptatriene were also detectable in the gas chromatograms. No attempt was made to measure these side products quantitatively because of unreasonably long retention times of more than 2 hr. Furthermore most of these products escaped analysis anyway, owing to subsequent dimerization reactions in the reaction mixture. The formation of dimeric materials was apparent from the liquid condensate formed in the iodine trap upon fractionated quenching of the reaction products and from the material balance which showed up to 30% losses in C_7 hydrocarbons.

The over-all reaction scheme for the formation of these side products (starting with *n*-heptene and iodine) can be rationalized by

$$n\text{-C}_7\text{H}_{16} \underset{\text{slow}}{\overset{\text{I}_2}{\underset{\text{HI}}{\rightleftarrows}}} n\text{-C}_7\text{H}_{14} \underset{\text{fast}}{\overset{\text{I}_2}{\underset{\text{HI}}{\rightleftarrows}}} \begin{matrix}1,3\text{-C}_7\text{H}_{12}\\ 2,4\text{-C}_7\text{H}_{12}\end{matrix} \underset{\text{fast}}{\overset{\text{I}_2}{\underset{\text{HI}}{\rightleftarrows}}} n\text{-C}_7\text{H}_{10} \tag{1}$$

The same side reactions have been shown to occur in the *n*-butene[1c] and *n*-pentene[1f] systems as well. Eventually equilibrium composition according to eq 1 would be established, if it were not for the instability of the heptadienes and heptatriene under the reaction conditions used.

The small concentration of heptadienes and heptatriene in the final reaction mixtures were obviously significantly lower than required by the equilibrium constants estimated from API[2] and group additivity[7] values, which is in accord with the results from *n*-butene[1c] and *n*-pentene.[1f] It has been reported pre-

Table III. Thermodynamic Data from Least-Squares Fits of the Measured Equilibrium Constants to Linear and Quadratic Equations for a Mean Temperature of 510°K

Equilibrium constant	Fit	MC[a]	$\Delta H°(510°)$, kcal/mole	$\Delta S°(510°)$, cal/deg mole	$\Delta C_p°(510°)$,[b] cal/deg mole
$K_{1,2}$	Linear	0.961	−0.884 ± 0.054	0.63 ± 0.11	...
	Quadr	0.961	−0.880	0.63	0.52
$K_{3,4}$	Linear	0.935	−0.822 ± 0.060	0.01 ± 0.12	...
	Quadr	0.935	−0.817	0.00	0.70
$K_{5,6}$	Linear	0.291	0.052 ± 0.051	0.31 ± 0.10	
$K_{7,8}$	Linear	0.970	−2.678 ± 0.200	−0.83 ± 0.37	

[a] MC stands for multiple correlation coefficient, which would equal 1.000 for an ideal fit. [b] Calculated from the coefficients of the quadratic equation.

viously[1e,f] that the 1,3-pentadiene undergoes rapid radical-catalyzed dimerization and possibly cyclization reactions under similar conditions to those used in this study. This then explains the measured fast initial losses of iodine forming HI.

Most of the dienes and triene formed in this fast initial reaction are at first consumed presumably *via* the iodine atom catalyzed dimerization route. The dimerization rate decreases as the concentration of the diolefins decreases and the back-reaction, the dissociation of the dimer,[8] increases. With longer reaction times an increasing proportion of the heptatriene and heptadiene molecules react with HI to give back *n*-heptenes.[9]

The large amount of HI built up during the initial stages of the reaction enhances the formation of *n*-heptane and thus the regeneration of iodine. This causes an increase in isomerization rate. The amount of *n*-heptane formed during the reaction constitutes a rough measure of the conversion that has been reached in the isomerization system (compare Table II). Eventually the over-all reaction system including the dimerization products would reach an equilibrium state.

No evidence for monomeric products from cyclization reactions of radical intermediates could be found by gas-chromatographic analysis. The results from this work (summarized in Table II) show that, despite these side reactions, equilibrium between the *n*-heptene isomers is established starting with any one of the geometrical or positional isomers. Consistent equilibrium constants were obtained over a temperature range of 190° whether only a few per cent or more than 90% of the initial iodine concentration was consumed.

(a) Equilibrium and Thermodynamic Data of the Geometrical Isomers of 2-Heptene and 3-Heptene. The equilibrium constants for the geometrical isomerizations

$$\text{3-heptene-}cis \underset{2}{\overset{1}{\rightleftharpoons}} \text{3-heptene-}trans \tag{2}$$

and

$$\text{2-heptene-}cis \underset{4}{\overset{3}{\rightleftharpoons}} \text{2-heptene-}trans \tag{3}$$

are given by

$$K_{1,2} = k_1/k_2 = (trans\text{-}3)/(cis\text{-}3)$$

$$K_{3,4} = k_3/k_4 = (trans\text{-}2)/(cis\text{-}2)$$

The results of the equilibrium measurements are listed in Table II and Figure 1 shows plots of log K against $1/T$(°K) for the same data. As can be seen from Table II both equilibrium constants $K_{1,2}$ and $K_{3,4}$ are, at any given temperature, within a maximum spread of 9%. They are independent of the composition of the starting material. Up to eightfold variations in the ratio of initial hydrocarbon to iodine pressures have been used. Starting with any one of the geometrical or positional isomers of *n*-heptene, equilibrium compositions were established.

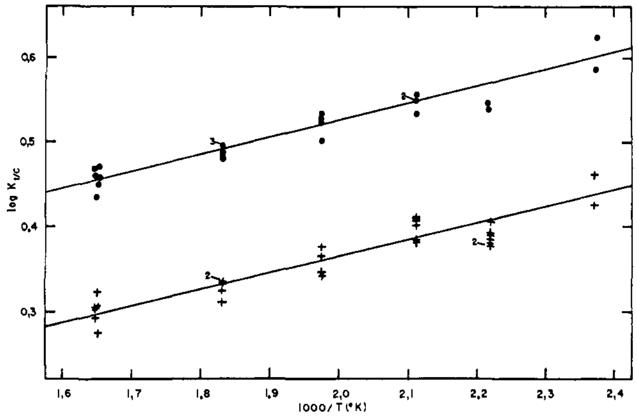

Figure 1. van't Hoff plot of the equilibrium constants for the geometrical isomerization of *n*-heptanes. The equilibrium constants $K_{1,2}$ for 3-heptene are indicated with ●, and $K_{3,4}$ for 2-heptene are shown with +. Numbers indicate overlapping points.

The data have been fitted to both a linear (van't Hoff) and a quadratic equation of the form $\log K = (a/T^2) + (b/T) + c$, using a regular least-squares regression program. The thermodynamic data, calculated from the computed coefficients and their standard errors, are shown in Table III for an average temperature of 510°K. As a measure of the accuracy of the fit of the measured log K data to either the linear or the quadratic equation, the computer program yields multiple correlation coefficients which would equal 1.0000 in the case of an ideal fit.

As can be seen from Table III, our data are equally well represented by a linear and a quadratic equation, indicating that $(\Delta C_p°)_{1,2}$ and $(\Delta C_p°)_{3,4}$ are nearly equal to zero for the temperature range studied. This conclusion is supported by the values of $(\Delta C_p°)_{1,2} \sim 0.5$ and $(\Delta C_p°)_{3,4} \sim 0.7$ cal/deg mole, calculated from the coefficients of the quadratic equation.

The values for the differences in heats of formation and entropies of the geometrical isomers of 2-heptene

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(8) Some measurements of the equilibrium position and thermal rate of the similar 1,3-pentadiene dimerization will be reported later. The dissociation equilibrium constant $K_{2,1} = (D)/(M)^2$ for dimer $\underset{1}{\overset{2}{\rightleftharpoons}}$ 2(monomer) was found to be about 15 torr at 600°K and 70 torr at 640°K.

(9) K. W. Egger and S. W. Benson, *J. Phys. Chem.*, submitted.

Table IV. Differences in Heats of Formation and Entropies for Various Positional and Geometrical Isomer Pairs at 298°K[a]

Isomer pair	$\Delta\Delta H°_f$, kcal/mole	$\Delta S°$, cal/deg mole
(2-Butene-*trans*)–(1-butene)	-2.8 ± 0.2	$-3.1 \pm 0.4\,(+0.5)^b$
(2-Pentene-*trans*)–(1-pentene)	-2.6 ± 0.1	$-1.4 \pm 0.1\,(+0.9)^b$
(2-Heptene-*trans*)–(1-heptene)	-2.7 ± 0.2	$-1.2 \pm 0.4\,(+1.1)^b$
(3-Heptene-*trans*)–(1-heptene)	-2.7 ± 0.2	$-0.9 \pm 0.4\,(+1.4)^b$
(2-Butene-*trans*)–(2-butene-*cis*)	-1.2 ± 0.2	-1.3 ± 0.2
(2-Pentene-*trans*)–(2-pentene-*cis*)	-0.75 ± 0.1	0.0 ± 0.4
(2-Heptene-*trans*)–(2-heptene-*cis*)	-0.85 ± 0.1	0.0 ± 0.1
(3-Heptene-*trans*)–(3-heptene-*cis*)	-0.90 ± 0.1	$+0.6 \pm 0.1$
(1,3-Pentadiene-*trans*)–(1,3-pentadiene-*cis*)	-1.00 ± 0.2	-0.1 ± 0.4
(3-Heptene-*trans*)–(2-heptene-*trans*)	0.05 ± 0.1	$+0.3 \pm 0.1$

[a] Results from this work and ref 1a–f. [b] Symmetry-corrected intrinsic values.

and 3-heptene at room temperature have slightly larger errors attached. The data are compared in Table IV with the results previously reported for 2-butene,[1a,b] 2-pentene,[1f] and 1,3-pentadiene.[1e]

Within experimental errors all the geometrical isomer pairs listed in Table IV have the same differences in enthalpies. This is in perfect agreement with previous estimates. The difference in heats of formation of geometrical isomers of linear olefins in general can be given for gas phase and 1 atm as

$$\Delta\Delta H_f°(298°)(trans) - (cis) = -0.9 \pm 0.1$$

In contrast to the enthalpy differences, a significant variation in entropies between the geometrical isomer pairs was to be expected and has previously been reported for 2-butene and 2-pentene. These differences can be attributed essentially to differences in the barriers to internal rotation in the *cis* forms of the olefins. The various *trans* forms of the olefins should have very nearly the same hindrance to free rotation, independent of the chain length of the rotating end groups. This is confirmed by the measured insignificant entropy difference of 0.3 ± 0.1 cal/deg mole between *trans*-2-heptene and *trans*-3-heptene.

It is evident that a much larger restriction to internal rotation is exercised when the end groups are in the *cis* configuration. Significant variations in entropy differences should therefore result between geometrical isomer pairs with methyl–methyl, methyl–ethyl, and ethyl–ethyl end groups. It may be assumed that there is no difference in the hindrance to internal rotation between ethyl and bulkier end groups.

On this basis, *cis*-2-butene should have more motion and thus more entropy than *cis*-2-pentene or *cis*-2-heptene, and *cis*-3-heptene should show approximately this same entropy difference when compared with its 2 isomer. This concept is basically confirmed by the measured entropy differences between the geometrical isomer pairs, listed in Table IV. If we write the difference as $\Delta S°(trans–cis)$, the values should be increasingly more positive going from 2-butene to 2-pentene (equal to 2-heptene) to 3-heptene. This is indeed the case. If we take 2-pentene as 0 ∓ 0.4,[10] we get a difference between the methyl–methyl (butene) and the methyl–ethyl (pentene) barrier of 1.2 ± 0.3 eu and between methyl–ethyl and ethyl–propyl (3-heptene) of 0.6 ∓ 0.3. Disregarding the disputed pentene values and comparing the results from this work only with the value of $\Delta S° = -1.2 \mp 0.2$ for 2-butene, one obtains the same results.

This then means that the *cis* effect in the entropy differences between various geometrical isomer pairs has qualitatively been verified by the general trend of the measured data and the obvious difference between 2-heptene and 3-heptene given here. Quantitatively the results are not quite so conclusive. It appears that the exchange of one methyl group in the dimethyl rotor increases the restrictions to internal rotation about twice as much as does the introduction of the second ethyl or bulkier group. This finding could be taken as an indication that the ethyl–ethyl barrier is lower than expected (as compared to ethyl–methyl barrier), possibly owing to a more coordinated rotation of the two groups against each other instead of a strictly random movement.

(b) Equilibrium and Thermodynamic Data of the Positional Isomers of *n*-Heptene. In addition to the results on the geometrical isomers, this work yields the equilibrium constants for the positional isomers as well, even though the study of the composition of equilibrated mixtures of the positional isomers was not the prime object of this work. In Table II the measured positional equilibrium ratios are given with the equilibrium constants from eq 4 and 5, $K_{5,6}$ = (3-*trans*)/(2-*trans*) and $K_{7,8}$ = (3-*trans*)/(1).

$$\text{2-heptene-}trans \underset{6}{\overset{5}{\rightleftharpoons}} \text{3-heptene-}trans \qquad (4)$$

$$\text{1-heptene} \underset{8}{\overset{7}{\rightleftharpoons}} \text{3-heptene-}trans \qquad (5)$$

The same statistical treatment discussed for the geometrical isomers was also used to compute the differences in heats of formation and entropies of the positional isomers. At any given temperature the $K_{5,6}$ data show about the same spread as the $K_{1,2}$ and $K_{3,4}$ values. The corresponding $\Delta H_{5,6}$ and $\Delta S_{5,6}$ are listed with their standard errors in Table III. The very low value for the multiple correlation coefficient is a consequence of the small number of experiments (13) and the very low values of both $\Delta H_{5,6}$ and $\Delta S_{5,6}$. This is the first direct experimental evidence substantiating the previous prediction that there are no significant differences (in enthalpies or in entropies) between the *trans* configurations of two isomeric linear olefins. No attempt is made to attach any significance to the small entropy difference of 0.3 ± 0.1 cal/deg mole.

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(10) There seems to be some question as to the accurate value for the entropy difference.[11] The quoted value satisfies the results from both ref 1f and 11 and is in very good agreement with the data on 2-heptene and 1,3-pentadiene.[1e]

(11) P. I. Abell, *J. Am. Chem. Soc.*, 88, 1346 (1966).

As was to be expected from the specific analytical problems discussed in the Experimental Section, the $K_{7,8}$ values have larger uncertainties attached to them. At any given temperature the variation in $K_{7,8}$ is as much as $\mp$ 9%, or about twice as much as for all the other equilibrium constants. In addition the equilibrium of the positional isomers was only established in 14 of the 31 experiments and they represent only three different temperatures. The high value of the multiple correlation coefficient listed in Table III indicates that the data are best represented with a straight line in a plot of $\log K_{7,8}$ *vs.* $1/T$(°K).

The extrapolation of the thermodynamic values listed in Table III for a mean temperature of 510°K to values at room temperature (listed in Table IV) necessarily introduces larger uncertainties. The error limits quoted in Table IV for the positional isomers represent about twice the limits calculated from the statistical treatment.

Measured differences in heats of formation and entropies between internal and terminal olefins are listed in Table IV for *n*-heptenes (this work), *n*-butenes,[1a] and *n*-pentenes.[1f] Within experimental errors the differences in heats of formation are equal.

The enthalpy difference written as

$$\Delta\Delta H_f°(trans) - (1)$$

for linear isomeric olefins in general can be given as -2.7 ∓ 0.2 kcal/mole. As expected, the intrinsic entropy differences between the positional isomers for all the olefins listed in Table IV agree within experimental errors. The symmetry corrected intrinsic ΔS values are given in parentheses in Table IV.

(c) Group Values for the Estimation of Thermodynamic Properties of Olefins in the Gas Phase (25° and 1 Atm). From the compiled data listed in Table III we can now extract values for refined group contribution (increments), using the symbolism defined by Benson.[7] If C_d represents a double-bonded carbon atom and C a single-bonded one, we can generate different increment contributions for the *trans* and the *cis* configuration of the group $[C_d(C_d)(C)(H)]$.[7] It is reasonable to base all group contributions on the *trans* form of butene-2 and apply *cis* corrections for the higher olefins. On this basis we obtain the results shown in Table V.

Table V

		$S°$, eu	$\Delta H_f°$, kcal
$[C_d(C_d)(C)(H) + C(C_d)(H_3)]_{trans}$	2-Butene	37.6	−1.43
	2-Pentene	38.3	−1.30
	2-Heptene	38.4	−1.38
	3-Heptene	37.8	−1.40
Average		+38.0 (37.9)	−1.38 (−1.37)
Corrections for *cis* isomer			
2-Butene		+1.2 (1.2)	0.9 (1.0)
2-Olefins (C_5 and higher)		0	0.9 (1.0)
3-Olefins		−0.6 (−1.2)	0.9 (1.0)

Except for the discussed differences in the *cis* correction of the 3-olefins, the data are in excellent agreement with previous estimates[1f] shown in parentheses. They confirm the corresponding differences in the *n*-hexene series estimated by Prosen and Rossini[2b] from purely thermochemical data.

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