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The Thermal Intramolecular Rearrangement of Methyl-1,3,5-cycloheptatrienes in the Gas Phase. II. Thermodynamic Data from Equilibrium Studies of the Positional Isomers

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Abstract: The equilibrium concentrations of the positional isomers of methyl-1,3,5-cycloheptatriene (MCHT) have been measured in the gas phase over a temperature range from 146 to 414°. Equilibrium in the reaction system

$$\text{7-MCHT} \underset{2}{\overset{1}{\rightleftharpoons}} \text{3-MCHT} \underset{4}{\overset{3}{\rightleftharpoons}} \text{1-MCHT} \underset{6}{\overset{5}{\rightleftharpoons}} \text{2-MCHT}$$

is attained in a stepwise manner *via* consecutive 1,5-hydrogen-transfer reactions. van't Hoff plots of the data give straight lines. The computed least-squares analyses of the equilibrium constants yield (with standard errors and for a mean temperature of 550°K) the following heats of isomerization (in kcal/mole) expressed for steps 1, 3, and 5 respectively: (1) -1.06 ± 0.07, (3) -0.83 ± 0.01, and (5) 1.10 ± 0.01. The corresponding entropy changes (in cal/deg mole) are (1) 1.9 ± 0.2, (3) -0.22 ± 0.02, and (5) 0.19 ± 0.02. The observed values for $K_{3,4} = k_3/k_4$ and $K_{5,6} = k_5/k_6$ have also been fitted to an equation of the form $\log K_{eq} = a'/T^2 + b'/T + c$. The statistical analyses show that these data are equally well represented with linear and quadratic equations, implying $[\overline{\Delta C_p^\circ}]_{500} = [\overline{\Delta C_p^\circ}]_{550} = 0 \pm 0.2$ cal/deg mole. Within the appropriate error limits the differences in heats of formation and entropies between the MCHT isomers at 298°K and 1 atm equal the values calculated for a mean temperature of 550°K. When compared with estimates, based on the concept of additivity of thermodynamic increment properties, the observed data suggest that a methyl substituent in the 1 position stabilizes the conjugated olefinic system by ~0.6 kcal, and in the 3 position to the extent of ~0.3 kcal.

A previous publication reported the kinetics of the thermal rearrangement of 7-methyl-1,3,5-cycloheptatriene into the 3 isomer. It was shown[1,2] that the thermal isomerization of methyl-1,3,5-cycloheptatrienes (MCHT) proceeds in a stepwise manner *via* consecutive intramolecular 1,5-hydrogen-transfer reactions (I). In the range 150–300° (subsequently denoted as "lower" temperature range), the positional isomers are the only products of the thermal rearrangement of MCHT. At higher temperatures and longer reaction times, the methylcycloheptatriene isomers rearrange into xylenes and ethylbenzene *via* methylbicyclo[4.1.0]hepta-2,4-diene intermediates.[3]

Equilibrium between the positional isomers is established long before any conversion into benzene derivatives can be detected. Results from kinetic measurements of this intramolecular skeletal isomerization of MCHT are reported separately.[3] However, that part of these studies pertaining to the equilibrium constants $K_{1,2}$, $K_{3,4}$, and $K_{5,6}$ has been incorporated into this paper, together with data obtained from independent equilibrium studies in the "lower" temperature range.

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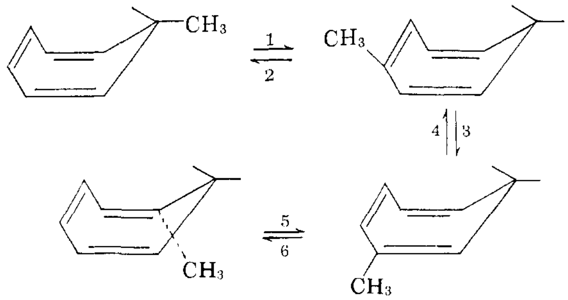
[1] K. W. Egger, *J. Am. Chem. Soc.*, **89**, 3688 (1967).

[2] A. P. Ter Borg, E. Razenberg, and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1230 (1965).

[3] K. W. Egger, *J. Am. Chem. Soc.*, **90**, 6 (1968).



(I).

Very little is known about differences in heats of formation or entropies between positional or geometrical isomers of substituted linear or cyclic conjugated polyolefins. Differences in $\Delta H_f{}^\circ$ and S° between *cis* and *trans* isomers of linear monolefins[4a–c] and 1,3-pentadiene[4d] have been previously reported. Evidence exists that in 2-methyl-1,3-pentadiene[5] and in other substituted linear conjugated polyolefins[6] the thermodynamic differences between the geometrical isomers are much larger because of repulsions of the methyl substituents. Studies of the equilibrium position between the MCHT isomers yield differences in thermodynamic properties, which should be characteristic for positional isomers of monosubstituted, cisoid-conjugated polyolefins.

Experimental Section

A. **Apparatus and Procedures.** The static method and reaction system used in these gas-phase studies have been described in detail earlier.[1,4a,c] The Pyrex glass vessels (one of them packed with glass tubing) and a quartz reaction cell have been coated and conditioned.[1] The pressure transducer was calibrated to measure pressure differences as low as 0.05 torr. For several of the experiments the over-all mass balance of the reaction system was checked. The sum of the products always agreed, within a few per cent, with the initial amount of the hydrocarbon mixture used.

B. **Materials.** 7-Methyl-1,3,5-cycloheptatriene and a mixture of 1-, 2-, and 3-methyl-1,3,5-cycloheptatriene were prepared as before.[1] Isomer mixtures were prepared by heating liquid, degassed samples of 7-MCHT or mixtures of 1-, 2-, and 3-MCHT, in sealed ampoules. Table I lists the mixtures of MCHT isomers used in this study.

C. **Analyses. Gas Chromatography.** The product mixtures were analyzed by gas–liquid partition chromatography (glpc). Apparatus, procedures, and column materials used in this study have been reported earlier.[1,3] Product mixtures which consisted of MCHT isomers only ("lower" temperature range) have been analyzed using a 20 ft × 0.25 in. column containing Chromosorb P (60–80) coated with 10% 3-methyl-3-nitropimellonitrile (MNPN).[1] Except for a few per cent overlap between the 3 and 1 isomers, the methylcycloheptatrienes were completely resolved. Toluene and ocassionally benzene were the only detectable side products obtained from experiments in the "lower" temperature range. They accounted for less than 2% of the total reaction product. The 7-MCHT peak was partially obscured by the considerable tailing of the toluene, which resulted in larger error limits for the small amounts of the 7-MCHT present in equilibrated isomer mixtures.

For the majority of the product mixtures, two or three independent glpc analyses have been carried out. The observed equilibrium constants $K_{1,2}$ were reproducible within ±2% (standard error), $K_{5,6}$ within ±0.7%, and $K_{3,4}$ to ±0.3%.

Product mixtures obtained from experiments carried out in the "higher" temperature range (295 to 414°) consisted of (besides the MCHT isomers) up to 46% xylenes, ethylbenzene, and styrene. Analyses of the individual C_8H_{10} isomers were achieved by combining the results obtained from the MNPN column with those observed, using a 30 ft × 0.25 in. column containing Chromosorb P (60–80) coated with 10% Bentone 34 and 10% silicone gum rubber SE-52 (phenyl–methyl). This procedure gives concentrations of 2- and 1-MCHT to within ±0.5% (standard deviation) and 3-MCHT to within ±1.0%. The amount of the 7 isomer was reproducible within ±1.7%. Details of this analysis are reported together with the results of the kinetic studies of the skeletal rearrangement of the methylcycloheptatrienes.[3]

Table I. Mixtures of Methyl-1,3,5-cycloheptatriene Isomers Used as Starting Materials

	Percentage composition[a]				
Mixture	1-MCHT	2-MCHT	3-MCHT	7-MCHT	Toluene
I	29.1	34.4	34.8	0.0	1.7
II[c]	41.1	10.7	41.7	5.3	1.2
III[b]	6.0	0.3	48.3	44.7	0.7
IV[c]	52.0	18.8	25.7	3.2	0.3
V	30.0	28.8	39.5	0.0	1.7
VI[b]	1.9	0.0	19.3	77.5	1.3

[a] Based on glpc analyses. [b] Prepared from 7-MCHT. [c] Prepared from mixtures I or V.

Proton magnetic resonance studies served to assign the proper structure to the individual isomers.[7]

Infrared Spectra. A Grubb–Parsons "Spectromaster" instrument was used to determine the infrared spectra of the individual MCHT isomers, which agreed with those reported in the literature.[8]

Results

Starting with 7-MCHT or any of the isomer mixtures listed in Table I, equilibrium was established *via* consecutive intramolecular 1,5-hydrogen-transfer reactions. The equilibrium constants for the positional isomerizations can be written as

$$\text{7-MCHT} \underset{2}{\overset{1}{\rightleftarrows}} \text{3-MCHT} \quad K_{1,2} = k_1/k_2 = \frac{[\text{3-MCHT}]}{[\text{7-MCHT}]}$$

$$\text{3-MCHT} \underset{4}{\overset{3}{\rightleftarrows}} \text{1-MCHT} \quad K_{3,4} = k_3/k_4 = \frac{[\text{1-MCHT}]}{[\text{3-MCHT}]}$$

$$\text{1-MCHT} \underset{6}{\overset{5}{\rightleftarrows}} \text{2-MCHT} \quad K_{5,6} = k_5/k_6 = \frac{[\text{2-MCHT}]}{[\text{1-MCHT}]}$$

The results from the thermal equilibration of MCHT isomers over the "lower" temperature range are listed in Table II. Initial hydrocarbon pressures ranged between 13 and 175 torr and varied by as much as tenfold at a given temperature. Pressure changes of a few per cent of the initial hydrocarbon pressure were observed but did not appear to depend on any of the reaction parameters.

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(4) (a) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 504 (1967); (b) K. W. Egger and S. W. Benson, *ibid.*, **88**, 236 (1966); (c) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964); (d) K. W. Egger and S. W. Benson, *ibid.*, **87**, 3311 (1965).

(5) H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 4770 (1965).

(6) T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).

(7) K. W. Egger and W. R. Moser, *J. Phys. Chem.*, **71**, 3699 (1967).

(8) E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, *Ann.*, **675**, 63 (1964).

Additional data of $K_{1,2}$, $K_{3,4}$, and $K_{5,6}$ for the "higher" temperature range have been obtained as a supplement to the kinetic studies of the thermally induced skeletal rearrangement of MCHT into xylenes and ethylbenzene.[3] The equilibrium data resulting from these studies have been incorporated into Table II. The relative amounts of MCHT isomers were found to be independent of the conversion reached for the skeletal rearrangement of these isomers, even though up to 46% of the total of the products consisted of benzene derivatives. The same equilibrium constants were obtained, regardless of the initial isomer ratios.

Regular least-squares regression programs served to compute the best fit of the data to either a linear ($\log K_{eq} = a/T + b$) or a quadratic equation ($\log K_{eq} = a'/T^2 + b'/T + c$). Statistical analyses were carried out using two different sets of data, giving equal weight to all the measured values. A *reduced set* of data did not take into account the equilibrium constants obtained from studies in the "higher" temperature range. This analysis yields differences in thermodynamic properties of the isomers for a mean temperature of 506°K. The *complete set* of the observed equilibrium constants results in thermodynamic data for a mean temperature of 553°K. The differences in enthalpy [$\Delta(\Delta H_f°)$] and entropy [$(\Delta S°)$], calculated from the computed coefficients and their standard errors, are listed in Table III. The accuracy of the fits is reflected in the multiple correlation coefficients, which would equal 1.0000 in case of an ideal fit.

As can be seen from Tables II and III, the data of $K_{1,2}$ show much larger scatter than either $K_{3,4}$ or $K_{5,6}$. This is primarily due to the small equilibrium concentrations of the 7 isomer (~2.4% of the total of the MCHT isomers at 146° and ~4.7% at 414°). For the data of $K_{1,2}$ the maximum deviations from the average value, at any given temperature, range from ±(2.8 to 12.6)% compared to ±(0.2 to 2.4)% for $K_{3,4}$ and ±(0.6 to 2.0)% for $K_{5,6}$. The deviations in $K_{1,2}$ decrease at higher temperatures, *i.e.*, at higher concentrations of 7-MCHT. The large scatter in the $K_{1,2}$ data precludes a comparison of the accuracy of the fits to both a linear and a quadratic equation, and therefore these data have been fitted to a linear equation only. The deviations in the values for the equilibrium constants at a given temperature are about twice as large as the observed reproducibility of the individual glpc analyses.

Discussion

Equilibrium constants for the positional isomerization of MCHT have been reported in the literature for the liquid phase and a temperature of 413°K only.[2] Within experimental error limits, these data agree with the values calculated from this work. For the methylcycloheptatrienes, no heat or entropy data are available in the literature. The only pertinent value is an estimated heat of formation of 37.2 kcal/mole[9] for 7-MCHT (based on a value of 43.5 kcal/mole for $\Delta H_f°$ of cycloheptatriene).[10] This value compares well with 37.8 kcal/mole, calculated on the basis of the concept of additivity of increment properties.[11]

For large variations of the reaction parameters over an unusually large temperature range of 270° consistent values for the equilibrium constants $K_{1,2}$, $K_{3,4}$, and $K_{5,6}$ have been observed. The statistical analyses yield (within the computed error limits) conforming values for the coefficients of the linear and quadratic equations for both the complete and the reduced sets of equilibrium data. This results in equal differences in heats of formation and entropies between the MCHT isomers for mean temperatures of 506 and 553°K (Table III). The computed multiple correlation coefficients, listed in Table III, demonstrate, that both the $K_{3,4}$ and $K_{5,6}$ data are equally well fitted by a linear or a quadratic equation. These findings imply that the specific heats of the 1, 2, and 3 isomers are within experimental error limits the same for the mean temperatures of 506 and 553°K.

Based on the values of $(\Delta C_p°)_T$ (Table III) calculated from the coefficient of the T^2 term of the quadratic equation, the limitations in this conclusion can be estimated to $(\Delta C_p°)_{500} = (\Delta C_p°)_{550} = 0 \pm 0.2$ cal/deg mole. Considering the large temperature range covered, this result is capable of extrapolation to room temperature. $(\Delta C_p°)_{298}$ is estimated at 0 ± 0.4 cal/deg mole.

The larger scatter of the $K_{1,2}$ data is reflected in lower values for the multiple correlation coefficient. The differences in heats of formation and entropies between the MCHT isomers (at room temperature and 1 atm) are listed in Table IV together with corresponding estimates, generated on the basis of the concept of additivity of thermodynamic increment properties.[11,12] For the MCHT isomers the predicted relative stabilities are in general agreement with the experimental data. There is, however, a noteworthy trend in the differences between the estimated and observed values for $\Delta(\Delta H_f°)$. The nonbonded interactions in the 2- and 3-MCHT are expected to be the same and slightly larger than for 1-MCHT. The concept of additivity of increment properties then predicts the same stabilities for the 2 and 3 isomers.[13]

While the observed entropy contents of the two isomers are equal, the measured difference of 0.27 ∓ 0.02 kcal/mole for $\Delta(\Delta H_f°)$ (2-MCHT–3-MCHT) is outside the experimental error limits (providing no systematic error has been introduced). This difference indicates small differences in the properties of the bonding involved. The fact that 1-MCHT is 1 kcal more stable than the 2 or 3 isomers, when only 0.4 kcal has been predicted, could also be attributed to a larger stabilizing effect of a methyl substituent in the 1 position as compared to the 2 or 3 position, Such effects might be expected, if we attribute some polar character to the π-bond system.[14] As a simple first approximation it is suggested that *n*-alkyl substituents in the 1 position

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[9] A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

[10] H. L. Finke, D. W. Scott, M. E. Gross, J. E. Messerly, and G. Waddington, *ibid.*, **78**, 5469 (1956).

[11] (a) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958); (b) D. M. Golden, H. E. O'Neal, and S. W. Benson, *J. Phys. Chem.*, in press.

[12] Estimates of $S°$ and $\Delta H_f°$ for MCHT isomers can be expected to agree with the experimental data within the usually observed[11b] tolerance of ±0.5 cal/deg mole and ±0.5 kcal, respectively. Estimated *differences* in these thermodynamic properties between various isomers are likely to be even more accurate.

[13] Only nearest neighbor interactions are taken into account.

[14] S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

Table II. Composition of Thermally Equilibrated Mixtures of Methyl-1,3,5-cycloheptatriene Isomers

	Starting compound[b,c]					Final equilibrium ratios[b]		
Temp,[a,c] °C	Pressure, torr	[3]/[7][d]	[1]/[3]	[2]/[1]	Time, min	$K_{1,2}$ = [3]/[7]	$K_{3,4}$ = [1]/[3]	$K_{5,6}$ = [2]/[1]
146.2 p	52.4	4.39	1.70	0.29	4609	9.65	2.40	0.288
p	54.9	∞	0.76	0.96	9586	10.12	2.41	0.293
146.5	35.5	6.00	3.92	0.32	5722	11.05	2.40	0.297
151.5 p	175.0	0.25	0.10	...	3977	10.20	2.42	0.301
152.2 p	27.0	6.59	2.14	0.35	5325	10.11	2.42	0.302
169.2 p	85.6	∞	0.76	0.96	5279	8.88	2.33	0.315
169.5 p	48.4				4926	9.11	2.34	0.312
	44.0	[7]	...	...	971	7.44	2.22	0.333
187.8	21.0	5.91	1.28	0.27	1455	7.88	2.27	0.330
	54.4	2.57	0.22	...	3910	8.16	2.23	0.339
188.8	43.0	[7]	...	...	1330	8.27	2.18	0.330
205.8	75.3	[7]	...	...	490	...	2.15	0.357
	26.9	[7]	...	...	1065	8.33	2.15	0.353
206.7	21.4	0.19	0.12	0.28	926	7.72	2.15	0.352
	62.5	[7]	...	...	1000	6.67	2.14	0.353
226.0	36.6	<2.0	<0.25	...	30	6.27	2.01	0.362
	34.3	1.56	0.16	...	60	7.91	2.03	0.364
	67.4	0.72	...	...	279	7.11	2.02	0.373
	65.7	1.56	0.16	...	1022	6.78	2.03	0.365
249.0 p	60.8	∞	0.76	0.96	20	7.69	2.01	0.378
p	31.9				40	6.35	2.02	0.378
p	74.1				60	7.46	2.02	0.384
p	41.2				83	7.52	2.01	0.381
p	55.3				112	6.56	2.03	0.387
287.4 p	24.8	0.25	0.10	...	19	6.11	1.91	0.407
p	47.1			...	82	6.90	1.97	0.399
288.5 p	13.4	[7]	...	...	21	6.65	1.90	0.406
p	25.7	[7]	...	...	28	...	1.93	0.404
p	112.5	0.25	0.10	...	40	6.01	1.90	0.412
p	120.0	[7]	...	...	61	6.33	1.91	0.410
295.5 q	115.5	1.08	0.12	0.05	960	6.83	1.88	0.424
296.3 q	26.7	8.03	2.02	0.36	1025	7.94	1.86	0.417
296.9 q	88.3				1851	6.76	1.88	0.421
297.0 q	68.2				1440	6.89	1.86	0.424
302.6 p	109.4	7.90	0.99	0.26	1440	7.18	1.86	0.423
p	49.2				3780	7.12	1.85	0.428
306.3 q	50.3	8.03	2.02	0.36	435	6.85	1.84	0.428
q	60.7				960	8.18	1.83	0.413
313.0 p	89.3	7.90	0.99	0.26	456	6.50	1.81	0.435
313.2 p	50.5				1440	6.70	1.88	0.426
313.9 p	21.2				963	7.08	1.83	0.433
317.7 p	24.5	∞	0.76	0.96	1.5	6.84	1.82	0.428
p	26.1				2.0	6.75	1.81	0.433
p	52.7				2.5	6.26	1.84	0.432
p	44.5				2.5	6.81	1.83	0.423
p	158.0				3.0	6.90	1.83	0.427
p	42.3				30.0	6.55	1.86	0.421
320.2 p	101.7	0.25	0.10	...	2.5	5.84	1.80	0.434
p	31.2	[7]	...	...	5.0	6.03	1.84	0.426
p	57.0		...	...	10.0	6.36	1.82	0.430
p	16.0	0.25	0.10	...	21.5	6.06	1.84	0.418
322.6 p	17.8	[7]	...	...	120	5.73	1.81	0.440
p	135.5	7.80	0.99	0.26	251	6.66	1.80	0.436
324.8 p	51.7				180	6.64	1.78	0.439
p	72.4				360	6.69	1.75	0.451
337.3 p	78.1	[7]	...	...	105	5.04	1.75	0.453
p	103.6	∞	0.84	1.18	257	6.16	1.76	0.458
354.4	31.5				26	6.15	1.73	0.471
	79.3				50	7.03	1.69	0.473
	57.9	[7]	...	...	106	6.38	1.73	0.466
	92.6	∞	0.84	1.18	143	6.00	1.77	0.458
369.1 p	20.4				91	6.61	1.68	0.470
369.9 p	89.6	7.80	0.99	0.26	15	5.93	1.69	0.469
p	122.9				30	5.94	1.69	0.470
p	46.2				45	6.00	1.76	0.452
395.9 q	33.3	8.03	2.02	0.36	1.5	5.85	1.68	0.487
q	34.0				2.0	5.84	1.65	0.492
q	19.8				2.5	6.09	1.68	0.488
q	32.4				3.5	5.76	1.68	0.489
407.8 q	15.2	8.03	2.02	0.36	1.0	5.71	1.66	0.491
q	20.0				1.0	5.66	1.67	0.487
q	27.5				1.5	5.90	1.65	0.488
q	8.1				2.0	5.57	1.69	0.489
q	13.7				3.0	6.14	1.67	0.498

Table II (*Continued*)

Temp,[a,c] °C	Pressure, torr	Starting compound[b,c] [3]/[7][d]	[1]/[3]	[2]/[1]	Time, min	Final equilibrium ratios $K_{1,2}$ = [3]/[7]	$K_{3,4}$ = [1]/[3]	$K_{5,6}$ = [2]/[1]
414.0 p	23.0				0.8	5.61	1.67	0.487
p	37.0				1.0	5.24	1.61	0.486
p	18.0				2.0	5.50	1.66	0.487
p	62.0				3.0	5.80	1.66	0.480

[a] p stands for the packed; no marks are used for the nonpacked Pyrex reaction vessel; q is used for the quartz vessel. [b] [1], [2], [3], and [7] stand for 1-, 2-, 3-, and 7-methyl-1,3,5-cycloheptatriene, respectively. [c] Unless otherwise stated, the data are the same as the immediately preceding entries. [d] Experiments started with 7-MCHT are marked [7].

Table III. Differences[a] in Heats of Formation $\Delta(\Delta H_f°)$, Entropies ($\Delta S°$), and Specific Heats ($\Delta C_p°$) between the Positional Isomers of Methyl-1,3,5-cycloheptatriene

Isomer pair	Least-squares analyses Fit	MC[b]	$\Delta(\Delta H_f°)$, kcal/mole 506°K	553°K	$\Delta S°$, cal/deg mole 506°K	553°K	$\Delta C_p°$,[c] cal/deg mole 506°K	553°K
3-MCHT–7-MCHT	Linear[d]	0.7319	−1.24 ± 0.13		1.50 ± 0.25			
	Linear	0.7473		−1.06 ± 0.07		1.92 ± 0.13		
1-MCHT–3-MCHT	Linear[d]	0.9833	−0.80 ± 0.02		−0.14 ± 0.03			
	Linear	0.9843		−0.83 ± 0.01		−0.22 ± 0.02		
	Quadr[d]	0.9834	−0.79		−0.14		−0.4	
	Quadr	0.9843		−0.83		−0.21		−0.15
2-MCHT–1-MCHT	Linear[d]	0.9886	1.05 ± 0.02		0.10 ± 0.04			
	Linear	0.9887		1.10 ± 0.01		0.19 ± 0.02		
	Quadr[d]	0.9914	1.03		0.06		−2.1	
	Quadr	0.9887		1.10		0.19		−0.12

[a] Written as shown in the column "Isomer pair." Error limits represent standard deviations. [b] MC stands for multiple correlation coefficient, which would equal 1.0000 for an ideal fit. [c] Calculated from the coefficient of the T^2 term in the quadratic equation. [d] Reduced set of data used for statistical analysis.

Table IV. Comparison of the Observed Thermodynamic Differences between the MCHT Isomers with Estimated Values[a]

Reaction	$\Delta(\Delta H_f°)$, kcal/mole Obsd	Calcd	$\Delta S°$, cal/deg mole Obsd	Calcd
7-MCHT → 3-MCHT	−1.06 ± 0.15	−1.0[b,c]	1.9 + 0.2	1.9[b,d]
3-MCHT → 1-MCHT	−0.83 ± 0.02	−0.4 (−0.7)[e]	−0.22 ± 0.04	0.3[d]
1-MCHT → 2-MCHT	1.10 ± 0.02	0.4 (1.0)[e]	0.19 ± 0.04	−0.3[d]

[a] Based on the principle of additivity of thermodynamic increment properties. Increment values taken from ref 11b. [b] The increment values for $C(C_d)(C)(H)^c$ are estimated to −1.15 kcal ($\Delta H_f°$) and −11.30 cal/deg mole ($S°$). [c] For nomenclature compare ref 11. [d] Corrected for entropy of mixing ($R \ln 2$) in the 1-, 2-, and 3-MCHT. [e] Corrected for the proposed stabilizing effect of the methyl substituent onto the olefinic system.

stabilize conjugated triene systems over three bonds (0.6 kcal), and in the 3 position over two bonds (0.3 kcal); in the 2 position only one bond would be affected. Estimates, including these corrections, are shown in parentheses in Table IV. They are in good agreement with the observed values. More experimental data are needed, to substantiate the suggested stabilizing effect of *n*-alkyl substituents.