Thermochemical and X-ray Crystallographic Investigations of Some $(CH)_{10}$ Hydrocarbons: Basketene, Nenitzescu's Hydrocarbon, and Snoutene

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The enthalpies of formation [ΔH_f^0 (g)] of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene (**9**, basketene) and pentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]dec-9-ene (**14**, snoutene) have been determined by measurement of their heats of combustion in a microcalorimeter as 110.2 ± 0.5 kcal·mol^{-1} and 78.4 ± 0.3 kcal·mol^{-1}, respectively. These values and the strain energies (*SE*s) [*SE*(**9**) = 110.3 kcal·mol^{-1}, *SE*(**14**) = 78.4 kcal·mol^{-1}] derived from them were compared with values obtained from MM2/MM3 calculations. The enthalpy of isomerization of **9** to tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**8**, Nenitzescu's hydrocarbon) was measured by differential scanning calorimetry (DSC) as –20.7 ± 0.3 kcal·mol^{-1} (384.1 K), corresponding to a strain energy *SE*(**8**) of 44.6 kcal·mol^{-1}. The enthalpy of activation for this rearrangement was also determined from the DSC measurements to be 28.6 ± 0.1 kcal·mol^{-1}. The obtained strain energies and the derived heats of isomerization to 9,10-dihydronaphthalene (**7**) did not correlate in any way either with the activation energies of the thermal isomerizations of these $(CH)_{10}$ hydrocarbons or with the structural features determined experimentally for basketene (**9**) and computationally (DFT at the B3LYP/6-311+G* level) for snoutene (**14**). Compounds **8**, **9**, **10**, and **14** exhibited solid-state phase transitions in a narrow temperature range (–55 to –70 °C), whereas the melting points or rearrangement temperatures varied to a much greater extent (in the 0–126 °C range). Compound **9** formed intermediate plastic phases, **8** had a plastic and a disordered phase, while **10** and **14** both formed phases intermediate between plastic and disordered. Crystal structure determinations based on disordered models could be carried out for **10** and **14**. Basketene **9** could be crystallized from solution directly into the ordered phase at low temperatures (–178 °C). The obtained molecular geometry contrasted with results from an older gas-phase diffraction study, but agreed very well with DFT calculations.
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Families of $(CH)_n$ hydrocarbons are characterized by the multiple rearrangements into one another that their members can undergo.[1] These rearrangements can be initiated thermally, photochemically, or under metal catalysis conditions.[2] The thermodynamic sink of all interconversions of $(CH)_{10}$ hydrocarbons is apparently *cis*-9,10-dihydronaphthalene (**7**), which is formed by thermal rearrangement from bullvalene (**1**), lumibullvalene (**2**), isobullvalene (**3**), and isolumibullvalene (**4**), from bicyclo[4.2.2]decatetraene (**5**) and its intramolecular Diels−Alder adduct **6**, from pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene (**9**, basketene) and tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**8**, Nenitzescu's hydrocarbon), from hexacyclo[4.4.0.$0^{2,4}$.$0^{3,9}$.$0^{5,7}$.$0^{8,10}$]decane (**10**, diademane) and triquinacene (**11**), from the *syn*- and *anti*-tricyclo[4.4.0.$0^{2,5}$]decatrienes (**12**), from *all-cis*-cyclodecapentaene (**13**), and from pentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]dec-9-ene (**14**, snoutene) (Scheme 1).[1,2]

Many of these interconversions do not afford **7** directly. Basketene (**9**), for example, is known to rearrange to Nenitzescu's hydrocarbon **8** upon heating[3] and under rhodium(I)[4a] and $LiCB_{11}Me_{12}$ catalysis conditions,[4b] while un-

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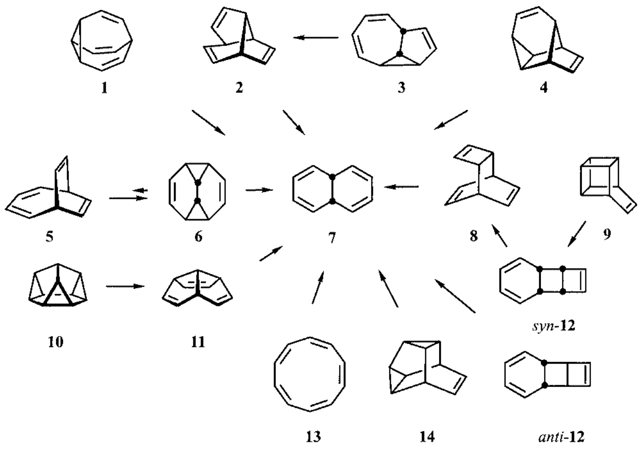
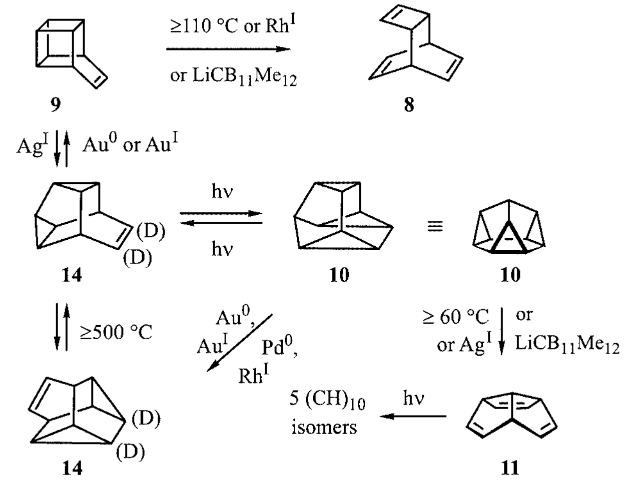


Scheme 1. Interconversions of $(CH)_{10}$ hydrocarbons

der silver(I) catalysis conditions it rearranges to snoutene (**14**).[4a,5] In the presence of gold (Au^0 or Au^I), however, snoutene (**14**) rearranges to basketene (**9**),[6] a fact that apparently has to do with the relative stabilities of the intermediate metal complexes. Upon heating to 500 °C, snoutene (**14**) undergoes an interesting automerization, detectable by appropriate labelling, which interchanges the two vinylic and the cyclopropyl methyne positions.[7] When irradiated with UV light, snoutene (**14**) reversibly rearranges to diademane (**10**).[8] Thermally,[9] and under silver(I),[10] copper(I)[10] or $LiCB_{11}Me_{12}$ [4b] catalysis conditions, diademane (**10**) rapidly rearranges to triquinacene (**11**), and this in turn undergoes photochemical isomerization to a number of other $(CH)_{10}$ hydrocarbons (Scheme 2).[11] Diademane (**10**) also underwent isomerization to snoutene (**14**) under Au^0, Au^I, Pd^0, or Rh^I catalysis conditions.[10]



Scheme 2. Thermally, photochemically, and catalytically induced isomerizations of basketene (**9**), diademane (**10**), and snoutene (**14**)

As work on $(CH)_{10}$ hydrocarbons has drastically slowed down during the last two decades, the goal as formulated in 1981 – "The heats of formation of all these compounds, as well as activation parameters, must be determined in order to construct a meaningful energy surface"[1a] – is still far away. Although 24 isomers of the 93 theoretically possible $(CH)_{10}$ valence isomers[2] are known, the enthalpies of formation [ΔH_f^0(g)] only of bullvalene (**1**) (79.7 kcal·mol^{-1})[12] and snoutene (**14**) (72.4 ± 0.9 kcal·mol^{-1})[13] have been reported, both some time ago, although the purity of the sample in the latter case was only 97.5%. Values of 83.7 and 73.6 kcal·mol^{-1} have been calculated for isobullvalene (**3**) and lumibullvalene (**2**), respectively, by the force-field (MMP2) method.[14] In order to understand better to what extent thermodynamics plays a role in these isomerizations, we have initiated a program to determine the heats of formation of several of these polycyclic $(CH)_{10}$ hydrocarbons by precise measurements of their heats of combustion. We have previously discussed our experimental findings for the energetics of diademane (**10**) and triquinacene (**11**),[15] and here we report new determinations of the enthalpies of formation [ΔH_f^0(g)] of basketene (**9**), snoutene (**14**), and Nenitzescu's hydrocarbon **8**.

The hydrocarbons basketene (**9**)[8a,16] and snoutene (**14**)[8a] were prepared by established procedures; Nenitzescu's hydrocarbon **8** was obtained by thermal reorganization of **9**. All three hydrocarbons were purified thoroughly (see Exp. Sect.) for the thermochemical measurements. The heat of combustion measurements, performed as described previously,[17] gave ΔH_f^0(g) = 110.2 ± 0.5 kcal·mol^{-1} for basketene (**9**) and 78.4 ± 0.3 kcal·mol^{-1} for snoutene (**14**). The latter value was 5.95 kcal·mol^{-1} higher than that reported for a less pure sample.[13] The enthalpy of isomerization of **9** to **8** was experimentally determined by differential scanning calorimetry (DSC) to be −20.7 ± 0.3 kcal·mol^{-1} (measured at 384.1 K), and from this, the ΔH_f^0(g) value for Nenitzescu's hydrocarbon **8** was derived as 89.6 ± 0.6 kcal·mol^{-1} (see Exp. Sect., Table 7 and 8). These values for **8**, **9**, and **14** were in fairly good agreement with those computed by the older MM2 method[18a] (91.6, 109.7 and 78.4 kcal·mol^{-1}, respectively), while the newer MM3 parametrization[18b] surprisingly produced an over- and an underestimation (98.2, 120.4 and 71.6 kcal·mol^{-1}, respectively). Recently performed DFT computations at the B3LYP/6-311+G* level of theory gave heats of reaction values of $\Delta\Delta H_f^0$(g) = −11.0 for **8** → **14**, −33.5 for **9** → **14**, and 22.5 kcal·mol^{-1} for **8** → **9**, thus exceeding the experimentally obtained data by only 0.2–1.8 kcal·mol^{-1}.[19] Surprisingly, the quality of the agreement with the experimental values [$\Delta\Delta H_f^0$(g) = −11.2, −31.9, and 20.7 kcal·mol^{-1}, respectively] was only slightly better than for that obtained by the simple MM2 method [$\Delta\Delta H_f^0$(g) = −13.2, −31.3, and 18.1 kcal·mol^{-1}, respectively]. The strain energies for **8**, **9**, and **14** were derived from the ΔH_f^0 values by use of Benson-type increments[20] for a strain-free model as proposed by Schleyer et al.[21] For comparison, relevant data from the literature are compiled along with those for **8**, **9**, and **14** in Table 1.

Since experimental data for the rather labile key hydrocarbon *cis*-9,10-dihydronaphthalene (**7**) would not be available, the heat of formation of **7** was calculated by DFT methods (at the B3LYP/6-311+G* level), in order to be able

Table 1. Experimentally determined and calculated enthalpies of formation [ΔH_f^0(g)], strain energies (*SE*), and strain release (ΔSE) for some $(CH)_{10}$ hydrocarbons and their isomerizations (all values in kcal·mol^{-1}).

	Starting Material			Product		
	ΔH_f^0(g)	*SE*		ΔH_f^0(g)	*SE*	ΔSE
1	79.74[a]	37.0	**7**	61.34[b]	−3.1	40.1
3[c]	83.70	40.7	2	73.63	30.7	10.0
10	86.90[d]	108.6	**11**	57.51	14.5	94.1
11	57.51[e]	14.5	**7**	61.34[b]	−3.1	17.6
9[f]	110.24	110.3	**8**	89.55	44.6	65.7
8[f]	89.55	44.6	**7**	61.34[b]	−3.1	47.7
14[f]	78.35	78.4	**7**	61.34[b]	−3.1	81.5

[a] Ref.[12,22]. [b] Derived from the experimentally obtained $\Delta H^0{}_f$(g) values for **8**, **9**, and **14** and relative energies for **7**, **8**, **9**, and **14** computed in this work (DFT at the B3LYP/6-311+G* level of theory). [c] ref.[14] (calculated value). [d] ref.[15] [e] ref.[1a,15] [f] Experimentally determined in this work.

to make a reasonable comparison and to draw a conclusion. It is obvious that all known thermal isomerizations of $(CH)_{10}$ hydrocarbons proceed from higher to lower ΔH_f^0(g); that is, with considerable strain release.

As the concept of strain[23] and strain energies provides a basis that may help to correlate the structures, stabilities, and reactivities of compounds in general[24,25] and the $(CH)_{10}$ hydrocarbons in particular, some experimentally determined activation barriers of $(CH)_{10}$ hydrocarbon isomerizations are summarized in Table 2. For basketene (**9**) and a series of homobasketenes, a direct linear correlation between strain energy (*SE*) release and free energy of activation $\Delta G^‡$ [$\Delta G^‡ = 49.9 - 0.39 \times \Delta SE$ (kcal·mol^{-1})] has been reported;[26] the values of ΔH_f^0(g) and *SE* in these calculations were derived from the energetic parameters for the saturated hydrocarbons with the same skeleton as calculated by the MM2 method.[27]

Table 2. Activation enthalpies for some $(CH)_{10}$ hydrocarbon isomerizations

Isomerization	*T* [K]	$\Delta H^‡$ [kcal·mol^{-1}]	Ref.
1 → **7**	569.7	45	[28]
3 → **2**	243.2	19.5	[22]
5 → **7**	518.2	34	[28]
6 → **5**	258.2	21	[28,29]
9 → *syn*-**12**	383.2	29	[30]
9 → *syn*-**12**	384.1	28.6 ± 0.1	this work
syn-**12** → **8**	338.2	23.5 ± 1.0	[31]
8 → **7**	553.2	45.1	[32]
10 → **11**	298.2	28.4 ± 0.2	[15]
10 → **11**	363.2	28.3 ± 1.0	[9b]

Comparison of all the values in Table 1 and 2 does not, however, reveal any general direct correlation between the values for strain energy release (ΔSE) and the enthalpies of activation $\Delta H^‡$ for the corresponding rearrangement. Thus, $\Delta H^‡$ for the transformation **3** → **2** is almost twice as large as ΔSE, but for **9** → **8** and **10** → **11** it amounts to only 44 and 30% of the ΔSE, respectively. The obtained strain energies do not in any way correlate with the activation energies for the thermal isomerizations of these $(CH)_{10}$ hydrocarbons.

X-ray Structure Investigations

a) Powder Diffraction Experiments and DSC Thermograms

In order to find out whether any unusual structural features might be attributable to strain and putative strain release, X-ray crystal structure analyses of the $(CH)_{10}$ hydrocarbons **8**, **9**, **14**, and diademane **10** were attempted. However, all these compounds only formed intermediate phases between their respective melting points and the low temperature, ordered phases, as indicated by endothermic peaks in the DSC heating curves. Nenitzescu's hydrocarbon **8** showed two transitions at −63 and −60 °C and a strong one at −46.4 °C, indicating a plastic phase in the range up to the melting point at 2 °C. The X-ray powder pattern (Cu-K_α) directly below the melting point gave only two signals, at $2\,\theta = 16.8$ and 19°, while at −53 and −163 °C, many peaks were found only in the range between $2\,\theta = 16$ and 20°. Any indexing for these peaks failed, as did many attempts to grow a single crystal from a saturated solution below −70 °C. Basketene **9** has a melting point at 59.6 °C and endothermic phase transitions at −50.2 and −54.6 °C (ref.[33a] 58.5−59 and −52 °C[33b]). X-ray powder diffractograms taken at 24 and −158 °C showed the characteristics of the high-temperature (HT) and low-temperature (LT) phases. While cubic lattice symmetry was found for the HT phase [a = 9.1975(19) Å, V = 778.1(1) Å^3], the LT phase could be indexed for a monoclinic cell [a = 5.502(3), V = 662.8(9) Å^3]. The calculated densities for the HT and LT phases were 1.111 and 1.305 g·cm^{-3}, respectively, in agreement with the expected properties for plastic phases. Diademane **10** showed a weak endothermic phase transition at −62.4 °C, it rearranged at 126 °C, and the formed triquinacene **11** displayed a melting point at 22.1 °C. X-ray powder diffraction at room temperature gave a rhombohedral cell with a = 6.027(8) Å, α = 109.47(2)°, V = 168.5(2) Å^3, ρ = 1.283 g·cm^{-3} (could also be hexagonal or cubic or tetragonal) and a tetragonal cell at low temperature (−168 °C) with a = 9.5686(12), c = 13.513(5) Å, V = 1237.2(7) Å^3, ρ = 1.398 g·cm^{-3}. Attempts to solve the structure from the powder data of the tetragonal LT phase failed. For snoutene **14**, a melting point at 65.6 °C and a weak endothermic phase transition at −70.6 °C were detected, the powder diffraction pattern at 20 °C was not typical for a plastic phase, although the cell could be indexed on cubic symmetry with a = 7.052(3) Å, V = 350.7(7) Å^3, ρ = 1.233 g·cm^{-3}, the LT phase at −168 °C was orthorhombic a = 19.303(13), b = 9.707(6), c = 7.261(5) Å, V = 1360(3) Å^3, ρ = 1.271 g·cm^{-3}.[34] Again, structure solutions for the LT phase failed, although a detailed diffraction pattern was available.

b) Single-Crystal X-ray Investigations

A technique recently elaborated for compounds that form plastic phases[35] was employed, and gave good results for basketene (**9**) (Figure 1 and Table 3).

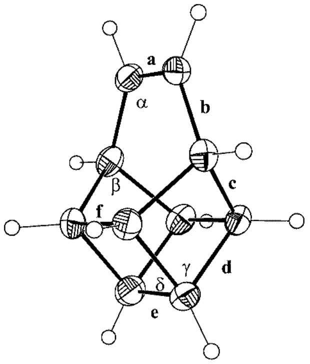


Figure 1. Structure of basketene (**9**) in the crystal[36]

The structural parameters of basketene (**9**) obtained in the crystal structure analysis were apparently more accurate than those from gas-phase electron diffraction,[37] and the agreement between the X-ray parameters and the calculated values (especially those obtained by the DFT method at the B3LYP/6-311+G* level of theory[39]) was thus far better than that between the GED values and the calculated ones. While the length of the double bond corresponds to the standard value, the adjacent single bonds (bonds **b**) are shorter than usual for $C_{sp^2}-C_{sp^3}$ bonds.[40] All the other single bonds (bonds **c**, **d**, **e**, **f**) are within cyclobutane rings and are lengthened, as typical for cyclobutyl C−C bonds (Table 3). The high strain energy (*SE*) of **9** (110.3 kcal·mol^{-1}) is adequately reflected in its structure and thus must be mainly due to angle strain. However, even though the angle α is 4.5° smaller than the normal value, the total *SE* is only slightly larger than the sum of the *SE*s of four cyclobutane units ($26.90 \times 4 = 107.6$ kcal·mol^{-1}).

By means of the in situ crystallization technique, a single crystal of diademane **10** was grown by careful heating with the IR laser to only about 60 °C, in order to avoid rearrangement to **11**. The structure solution resulted in a model of a truncated tetrahedron with four tetrahedrally oriented three-membered rings, a significant residual electron density being found in each of the four ring centers. The real model is therefore apparently a tetrahedrally disordered structure in which the apical C atom of the diademane structure is in each three-membered ring.[34,41]

Single-crystal data for snoutene **14** were obtained at −55 °C by the in situ crystallization method, but according to the DSC thermogram, a disordered structure was obtained. The refined model on the basis of a cubic cell contains four overlapping snoutene molecules of different orientations, incidentally resulting in the same truncated tetrahedron as for diademane **10**, and did not allow structural details of the molecule to be derived.[34,42]

In order to make sure that the structures of **10** and **14** were not identical, each polyhedron refinement model was applied to the other structure. The two sets of data turned out to be essentially different, which confirmed the respective models. Ab initio calculations performed for snoutene (**14**) did not reveal any drastic deviations from the normal values of bond lengths and angles, except for a slight lengthening of four cyclopropane bonds (1.517 Å). However, the total *SE* of **14** (78.4 kcal·mol^{-1}) exceeded the sum of the *SE*s of two cyclopropane units ($28.13 \times 2 = 56.26$ kcal·mol^{-1}) by ca. 22 kcal mol^{-1}.

Experimental Section

Preparation and Purification of Compounds: The hydrocarbons **9**[8a,16] and **14**[8a] were prepared by the previously published procedures. Compound **8** was obtained by heating basketene (**9**, 5.0 g, 38.4 mmol) in hexane solution (5 mL) in a sealed tube at 180 °C for 15 min. The solution was carefully concentrated by use of a 30 cm rectification column to afford 4.76 g (95%) of **8**, containing about 2% of naphthalene. For the thermochemical measurements the triene **8** was purified by a sequence of column chromatography on silica gel, repeated preparative gas chromatography (20% SE 30 on Chromosorb W-AW-DMCS, 1000 mm × 8.2 mm column, 70 °C), and finally distillation under reduced pressure (0.1 Torr) over

Table 3. Comparison of experimental and calculated bond lengths and angles for basketene (**9**): mean values according to C_{2v} symmetry (standard deviations are given in parentheses)

Bond length [Å] or angle [°]	X-ray[a]	GED[b]	Calculated at the level of	
			IMOA[c]	B3LYP/6-311+G* [a]
a	1.340(1)	1.360(9)	1.336	1.339
b	1.485(1)	1.511(13)	1.521	1.490
c	1.564(1)	1.517(9)	1.542	1.571
d	1.569(1)	1.563(6)	1.563	1.568
e	1.554(1)	1.609(14)	1.551	1.554
f	1.560(1)	1.609(14)	1.536	1.568
α	115.5(1)	113.0	113.9	115.6
β	86.44(8)	91.9	94.5	86.0
γ	86.18(5)	88.5(1.0)	85.6	90.3
δ	90.11(4)	90.0	89.9	90.2

[a] This work. [b] Gas electron diffraction: ref.[37]. [c] Iterative Maximum Overlap Approximation: ref.[38].

4 Å molecular sieves. Snoutene (**14**) and basketene (**9**) were purified by column chromatography on silica gel (which, in the case of **14**, contained 5% of absorbed silver nitrate), followed by repeated (twice) sublimation under reduced pressure (0.01 Torr) at 40 °C. Analysis by gas chromatography established their purities to be ≥99.99%. For Nenitzescu's hydrocarbon (**8**) and basketene (**9**), purities of ≥99.95% were also established by differential scanning calorimetry (DSC) measurement of the melting process.[43] The purity of snoutene (**14**) was established by this method to be only 99.88%.

Combustion Calorimetry: For the measurements of the enthalpies of combustion of the $(CH)_{10}$ hydrocarbons, an isoperibolic aneroid microcalorimeter with a stirred water bath was used. The substances were placed in MYLAR bags, which were burned in an oxygen atmosphere at a pressure of 3.04 Mpa as has been described in detail previously.[44] Preliminary combustion experiments with basketene (**9**) and snoutene (**14**) showed traces of soot. In order to ensure complete combustion, auxiliary substances (benzoic acid and mineral oil) were employed. The energy equivalent of the calorimeter ε_{calor} (see Table 4) was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). The summary of auxiliary quantities for the combustion experiments and information necessary for the reduction of apparent mass (measured in air) to mass, conversion of the energy of the actual bomb process to that of the isothermal process, and reduction to standard states[45] is given in Table 5. Typical combustion experiments are described in Table 4. The densities of $\rho_{(293)} = 1.07\ g\cdot cm^{-3}$ for basketene (**9**) and of $\rho_{(293)} = 1.10\ g\cdot cm^{-3}$ for snoutene (**14**) were determined by floatation of crystals in aqueous KCl solutions. The specific heat capacities $c_p = 1.41\ J\cdot K^{-1}$ for **9** and $c_p = 1.42\ J\cdot K^{-1}$ for **14** were measured by DSC. The expansion coefficient was estimated to be $(\delta v/\delta T)_p = 0.1\cdot10^{-6}\ dm^3\cdot K^{-1}$ for both compounds. The energies of combustion of the auxiliary compounds used have been published previously.[15]

Table 4. Results for typical combustion experiments at T = 298.15 K (p^0 = 0.1 MPa)[a]

[a]	Basketene (**9**)	Snoutene (**14**)
m (substance)/g[b]	0.017506	0.031287
m' (cotton)/g[b]	0.000817	0.000735
m'' (mylar)/g[b]	0.012551	0.009710
m''' (auxiliary)	0.019050[c]	0.006745[d]
ΔT_c /K[e]	1.06349	1.27619
$(\varepsilon_{calor})\cdot(-\Delta T_c)$/cal	−377.25	−454.07
$(\varepsilon_{cont})\cdot(-\Delta T_c)$/cal	−0.70	−0.82
$\Delta U_{corr.}$/cal	0.24	0.23
$-m'\cdot\Delta_c u'$ /cal[f]	3.31	2.98
$-m''\cdot\Delta_c u''$/cal	68.51	53.00
$m'''\cdot\Delta_c u'''$/cal	120.35	74.17
$\Delta_c u^0$ (sub)/(cal·g^{-1})	−10578.2	−10331.1

[a] For definitions of the symbols see reference:[45] T_h = 298.15 K; V(bomb) = 0.0460 l; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 0.23 g; ΔU(ign) = 1.46 J; m(Pt) = 2.883 g; ε_{calor} = (354.73 ± 0.05) cal·K^{-1} for basketene (**9**); ε_{calor} = (335.80 ± 0.05) cal·K^{-1} for snoutene (**14**). [b] Masses obtained from apparent masses. [c] Combustion with addition of benzoic acid. [d] Combustion with addition of mineral oil. [e] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont})\cdot(-\Delta T_c) = (\varepsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\varepsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T_{corr.})$. [f] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference[45].

The individual values of the energies of combustion, together with the mean values and their standard deviations, are given in Table 5. The given standard deviations of the means include the uncertainties from calibration and the combustion energies of the auxiliary materials.

Table 5. Values of specific energies of combustion $\Delta_c u^0$ at T = 298.15 K (p^0 = 0.1 MPa); $<\nu\Delta_c u^0>$ denotes mean value

Basketene (**9**)	Snoutene (**14**)
$\Delta_c u^0$/(cal·g^{-1})	
−10578.2	−10323.7
−10591.4	−10323.5
−10586.1	−10332.5
−10573.3	−10.333.1
−10584.9	−10331.1
	−10330.7
$<\nu\Delta_c u^0>$ /(cal·g^{-1})	
−10582.8 ± 3.2	−10329.1 ± 1.8

Transpiration Method: The enthalpies of sublimation of basketene (**9**) and snoutene (**14**) and the enthalpy of vaporization of Nenitzescu's hydrocarbon (**8**) were determined by the transfer method in a saturated N_2 stream[46] by use of the Clausius−Clapeyron equation. About 0.2 g of the sample was mixed with glass beads and placed in a thermostatted U-tube of length 20 cm and diameter 0.5 cm. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cooled trap. A flow of 0.28 to 0.56 cm^3·s^{-1} of nitrogen was optimal to reach the equilibrium of saturation of transporting gas at each temperature investigated. The amount of condensed substance was determined by GC analysis with an internal standard. The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period with the help of the ideal gas equation $p = m\cdot R\cdot T/V(N_2)\cdot M$, in which $R = 8.31451\ J\cdot K^{-1}\cdot mol^{-1}$, m = mass of transported compound, $V(N_2)$ = volume of transporting gas, M = molar mass of compound, and T = saturation temperature. The vapor pressure p was corrected for the residual vapor pressure at the condensation temperature. The latter was calculated from a linear correlation between ln p and T^{-1} obtained by iteration. The molar enthalpy of vaporization or of sublimation was calculated from the slope of the linear Clausius−Clapeyron correlation: $\Delta H^0_{sub} = -R(d\ln p/dT^{-1})$. The observed enthalpies of vaporization $\Delta H^0_{vap}(T)$ or sublimation $\Delta H^0_{sub}(T)$ at the temperature T obtained by this procedure are given in Table 6. Because of the deviations of the average temperature of measurement by the transpiration method from T = 298.15 K, the observed values of the sublimation/vaporization enthalpies were adjusted to this reference temperature by use of the corrections recommended by Chickos et al.[47]

DSC Measurements:[48] DSC measurements were carried out as follows. Samples of 2−4 mg of basketene (**9**), together with a solvent (see Table 8), were placed in small, screwable high-pressure steel pans. The sample and the reference pan with solvent (10 µL) were heated in a differential scanning calorimeter (Perkin−Elmer DSC-2, calibrated with indium) at a constant heating rate of 5 K·min^{-1} from 300 K to 480 K. In all experiments, an exothermic peak at 384.1 K showed up as a result of the interconversion of basketene (**9**) into Nenitzescu's hydrocarbon (**8**). The areas of the signals, which are proportional to the enthalpy of reaction, were determined as previously published in detail.[48] The results of these DSC measurements are summarized in Table 8. The activation parameters of the thermal interconversion of **9** to **8** were obtained by simulation of the signals.[48] No significant difference was found for the values of the enthalpy of reaction (ΔH^0_r) obtained in the rather

Table 6. Results from measurements of the vapor pressure p by the transpiration method

T/K[a]	m/mg[b]	$V(N_2)$/dm^3[c]	p/Pa[d]	T/K[a]	m/mg[b]	$V(N_2)$/dm^3 [c]	p/Pa[d]
Basketene (**9**), $\ln(p/\text{Pa}) = (27.14 \pm 0.21) - (6668 \pm 61)\cdot(T/\text{K})^{-1}$							
274.1	1.12	1.37	16.32	298.4	4.23	0.641	126.4
278.5	1.45	1.17	24.40	303.4	3.96	0.426	177.9
283.5	1.96	1.04	36.71	308.4	3.45	0.274	240.7
288.7	2.92	0.961	58.59	313.3	2.63	0.146	343.8
293.4	3.19	0.747	81.96				
$\Delta H^0_{\text{sub}}(293.7\ \text{K}) = (13.25 \pm 0.12)$ kcal·mol^{-1}; $\Delta H^0_{\text{sub}}(298.15\ \text{K}) = (13.22 \pm 0.12)$ kcal·mol^{-1}							
Snoutene (**14**), $\ln(p/\text{Pa}) = (28.04 \pm 0.20) - (7084 \pm 58)\cdot(T/\text{K})^{-1}$							
274.1	0.695	1.50	9.131	298.4	2.70	0.686	75.34
278.5	0.876	1.26	13.55	303.4	2.62	0.457	109.3
283.5	1.18	1.11	20.62	308.4	2.53	0.294	164.1
288.7	1.62	0.956	32.58	313.3	1.99	0.170	222.9
293.4	1.97	0.800	47.19				
$\Delta H^0_{\text{sub}}(293.7\ \text{K}) = (14.08 \pm 0.11)$ kcal·mol^{-1}; $\Delta H^0_{\text{sub}}(298.15\ \text{K}) = (14.04 \pm 0.11)$ kcal·mol^{-1}							
Nenitzescu's hydrocarbon (**8**) $\ln(p/\text{Pa}) = (24.47 \pm 0.17) - (5676 \pm 53)\cdot(T/\text{K})^{-1}$							
296.4	3.36	0.335	193.6	316.4	4.23	0.121	668.6
301.5	3.52	0.243	278.4	321.5	4.23	0.092	878.4
306.5	3.58	0.183	374.8	326.5	5.54	0.092	1150.0
311.4	4.00	0.152	503.6				
$\Delta H^0_{\text{vap}}(311.4\ \text{K}) = (11.28 \pm 0.10)$ kcal·mol^{-1}; $\Delta H^0_{\text{vap}}(298.15\ \text{K}) = (11.45 \pm 0.10)$ kcal·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 mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K.

Table 7. Thermochemical results at $T = 298.15$ K in kcal·mol^{-1}

	ΔH^0_c [a]	ΔH^0_f(g) (cr or l)	ΔH^0_{sub} [b]	ΔH^0_{fus} [c]	ΔH^0_f(g) (exp.)	ΔH^0_f(g)[d] (strain-free, calcd.)	SE[e]	ΔH^0_f(g) (MM2)	ΔH^0_f(g) (MM3)
Basketene (**9**) (cr)	−1379.25 (± 0.45)	97.18 (± 0.45)	13.22 (± 0.12)	0.65 (at 331.8 K)	110.40 (± 0.47)	−0.07	110.47	109.9	120.6
Snoutene (**14**) (cr)	−1346.24 (± 0.31)	64.43 (± 0.31)	14.04 (± 0.11)	1.88 (at 334.0 K)	78.47 (± 0.33)	−0.07	78.54	77.2	71.7
Nenitzescu's hydrocarbon (**8**) (l)		78.23 (± 0.55)	11.45[f] (± 0.10)	0.35 (at 293.7 K)	89.68[g] (± 0.56)	42.97	46.71	91.7	93.8

[a] Calculated from the specific energies of combustion in Table 5. [b] From the measurements of vapor pressures at different temperatures from Table 6 by the Clausius−Clapeyron equation. [c] From DSC measurements with the usual uncertainty of ± 0.05 kcal·mol^{-1}. [d] Calculated as the sum of the strain-free increments:[20,21] [CH] = −2.16; [=CH] = 8.60 kcal·mol^{-1}. [e] Strain energy $SE = \Delta H^0{}_f(\text{g, exp.}) - \Delta H^0{}_f(\text{g, strain-free, calcd.})$ [f] Enthalpy of vaporization. [g] Derived from the enthalpy of interconversion of basketene (**9**) into Nenitzescu's hydrocarbon (**8**) by DSC measurements (see text).

polar solvent *N*-methylacetamide and in the nonpolar solvent tetradecane. This may be taken to indicate that the enthalpy of interconversion of **9** to **8** would also be the same in the gaseous phase. The average of the values measured in solution was therefore used as an equivalent for the gas phase value. The temperature dependence of the enthalpy of reaction was expected to be negligible within the limits of the experimental uncertainties. Therefore, the enthalpy of reaction $\Delta H^0_r = -(20.7 \pm 0.3$ kcal·mol$^{-1})$ measured at 384.1 K was ascribed to the reference temperature 298.15 K without extrapolation. With this reaction enthalpy and the enthalpy of formation of basketene (**9**) as measured by combustion calorimetry (see Table 7), the standard molar enthalpy of formation of Nenitzescu's hydrocarbon (**8**) $\Delta H^0_f(\text{g}) = (89.55 \pm 0.55$ kcal·mol$^{-1})$ was derived (Table 7). Moreover, by taking into account the vaporization enthalpy as measured by transpiration, the enthalpy of formation of **8** in the liquid state $\Delta H^0_f(\text{l}) = (78.11 \pm 0.55$ kcal·mol$^{-1})$ was obtained (Table 7).

Enthalpies of fusion and specific heats for **8**, **9**, and **14** were measured by DSC. The temperature scale of the DSC apparatus (Perkin−Elmer DSC-2C) was calibrated by measurement of the melting temperatures of the recommended high-purity standards benzoic acid, tin, and indium. The power scale was calibrated with sapphire as a standard material. Samples were studied from 293 to 480 K at a rate of 5 K·min^{-1}.

Calculation of Strain Energies: The strain of a molecule in general is defined as the difference between the experimental standard enthalpy of formation ΔH^0_f(g) and the calculated sum of the Benson type increments[20] for a strain-free model.[21] The system of strain-free increments is based on the standard enthalpies of formation

Table 8. Results from the measurements of the enthalpy of reaction ΔH_r^0, Eyring parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the isomerization basketene (**9**) ↔ Nenitzescu's hydrocarbon (**8**) at $T = 384.1$ K in liquid phase by DSC[48]

Medium	Mass of sample mg	$-\Delta H_r^0$ kcal·mol^{-1}	$\Delta H^\ddagger$ kcal·mol^{-1}	$\Delta S^\ddagger$ cal·mol^{-1}·K^{-1}
Tetradecane	4.057	20.00	29.02	1.00
Tetradecane	3.695	20.60	28.80	0.05
Tetradecane	2.395	21.30	28.42	−0.76
N-Methylacetamide	2.448	21.00	28.51	−0.84
Mean values		20.72 ± 0.29	28.68 ± 0.14	−0.14 ± 0.43

ΔH_f^0(g) of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons[21] are well defined. Their advantage with respect to the classic Benson increments is the potential to determine strain enthalpies. All other increments used in this work are listed in Table 7. By using the group-additivity parameters given in Table 7 and the values of ΔH_f^0(g) of the $(CH)_{10}$ hydrocarbons (Table 7) derived in this research, values for the strain enthalpies [$SE = \Delta H_f^0$(g) $-\ \Sigma$ increments] for these compounds were estimated (Table 7).

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