Heats of Hydrogenation. IX. Cyclic Acetylenes and Some Miscellaneous Olefins[1]

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Abstract: The heats of hydrogenation in acetic acid solution at 25° of octyne-4, cyclooctyne, cyclononyne, cyclodecyne, cycloundecyne, cyclododecyne, and cyclotetradecadiyne-1,8 have been determined. Results for 16 miscellaneous olefins are also reported.

In this paper, we report results which extend the data on heats of hydrogenation to cyclic systems containing acetylenic linkages (see Table I). As a reference point for measurements of the heats of hydrogenation of the cyclic acetylenes, we have determined the heat of hydrogenation of octyne-4. The value obtained in acetic acid solution, −62.8 kcal/mol, is, as expected,[4] somewhat lower than the vapor phase result for butyne-2 (−65.6 kcal/mol) reported by Kistiakowsky and his associates.[5] Closer correspondence is achieved between the value calculated for partial hydrogenation of octyne-4 to *cis*-octene-4 in solution (−35.4 kcal/mol) and the value calculated for partial hydrogenation of butyne-2 to *cis*-butene-2 in the vapor phase (−36.9 kcal/mol).

Table I. Heats of Hydrogenation in Acetic Acid Solution at 25°

Compd	$-\Delta H$, kcal/mol
Octyne-4	62.80 ± 0.16
Cyclooctyne	69.0[a]
Cyclononyne	61.93 ± 0.31
Cyclodecyne	56.46 ± 0.23
Cycloundecyne	57.20 ± 0.20
Cyclododecyne	61.75 ± 0.40
Cyclotetradecadiyne-1,8	125.4 ± 0.14
cis-Octene-4	27.39 ± 0.14
Cyclopentene	26.04 ± 0.44[b]
3,3-Dimethylcyclohexene (**1**)	27.66 ± 0.16
4,4-Dimethylcyclohexene (**2**)	26.62 ± 0.12
cis-1,2-Diisopropylethylene (**3**)	28.69 ± 0.02
trans-1,2-Diisopropylethylene (**4**)	26.82 ± 0.05
cis-1,2-Dineopentylethylene (**5**)	26.90 ± 0.06
trans-1,2-Dineopentylethylene (**6**)	26.04 ± 0.15
1,1-Di-*tert*-butylethylene (**8**)	28.02 ± 0.01
9	61.04 ± 0.27
10	26.89 ± 0.11
11	69.18 ± 0.30
12	35.36 ± 0.11
13	31.93 ± 0.21
Bicyclo[3.2.1]octa-2,6-diene (**16**)	57.86 ± 0.27
Bicyclo[3.2.1]oct-2-ene (**17**)	26.83 ± 0.11

[a] Uncertainties in this value are discussed in the text. [b] Whereas the other values in the table are averages of duplicate runs, the spreads between which are given by twice the ± values, the value for cyclopentene (API sample 288–55) is the average of 12 determinations made over a 10-year period (W. D.).

For the purpose of comparing triple bond strain in the various medium-sized rings, the problem which arises from transannular hydrogen–hydrogen repulsion in members of this series can be minimized by using the calculated values for partial hydrogenation of the acetylene to cis olefin derived in Table II.

Table II. Calculated Heats of Hydrogenation of Acetylene to Cis Olefin in Acetic Acid (25°)

Compd	Product	$-\Delta H$, kcal/mol
Octyne-4	*cis*-Octene-4	35.4
Cyclooctyne	*cis*-Cyclooctene[a]	45.5
Cyclononyne	*cis*-Cyclononene[a]	38.3
Cyclodecyne	*cis*-Cyclodecene[a]	35.8
Cyclododecyne	*cis*-Cyclododecene[b]	35.4

[a] Values from ref 6. [b] J. Sicher, M. Svoboda, B. J. Mallon, and R. B. Turner, *J. Chem. Soc. B*, 441 (1968).

It will be noted that the results for octyne-4 (−35.4 kcal/mol), cyclodecyne (−35.8 kcal/mol), and cyclododecyne (−35.4 kcal/mol) show a spread of only 0.4 kcal/mol. It is hence concluded that triple bond strain in the 10- and 12-membered rings is negligible. The differences among the heats of hydrogenation of these three substances recorded in Table I are thus ascribed to strain differences in the saturated hydrogenation products. Although a value for *cis*-cycloundecyne is not available to complete the comparison, there is no reason to suppose that strain on the triple bond in cycloundecyne should be significant (*cf.* Table I).

Comparison of cyclononyne with octyne-4 (Table II) shows a discrepancy of 2.9 kcal/mol, which suggests that accommodation of a triple bond in a nine-membered ring is beginning to encounter difficulty. The most interesting example is, of course, that of cyclooctyne which possesses the smallest ring of the cyclic acetylenes thus far isolated as a pure entity. We therefore regret that the value of −69.0 kcal/mol reported for the heat of hydrogenation of this substance must be regarded as approximate. Despite the fact that the sample employed for hydrogenation was gas-chromatographically homogeneous and was pure as judged by spectroscopic criteria, the material absorbed only 90% of 2 molar equiv of hydrogen. The value recorded in Table I is based upon the amount of hydrogen absorbed. Although the question of this discrepancy has not been resolved, it is not unlikely that some polymerization (or reaction with solvent) may have occurred during hydrogenation. The found

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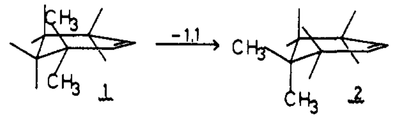
(4) *Cf.* R. B. Williams, *J. Amer. Chem. Soc.*, 64, 1395 (1942).

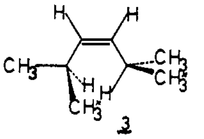
(5) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *ibid.*, 61, 1868 (1939).

heat of hydrogenation probably represents a minimum value. In any event it is clear that strain is now appreciable, since the heat of the change, cyclooctyne → *cis*-cyclooctene, is 10 kcal/mol higher than that of the reference system, octyne-4 → *cis*-octene. Triple-bond strain in cyclooctyne is thus at least as high as double-bond strain in *trans*-cyclooctene, which we have estimated at 9.2 kcal/mol.[6]

The remaining cyclic acetylene derivative which has been examined in connection with the present investigation is cyclotetradecadiyne-1,8, for which a heat of hydrogenation of −125.4 kcal/mol has been obtained. This result is almost exactly twice the octyne-4 figure and seems to preclude any interaction between the two triple bonds.[7,8] The validity of this conclusion is dependent upon the assumption that changes in enthalpy associated with nonbonded interactions in the conversion of octyne-4 to *n*-octane (or whatever other model is selected) and cyclotetradecadiyne to cyclotetradecane are the same. While this is likely to be true as a first approximation, it should be noted that the most recent value for the heat of combustion of cyclotetradecane, −2216.4 kcal/mol (vapor phase),[8] yields a heat of combustion of −158.3 kcal per methylene group as compared with −157.4 kcal per methylene for cyclohexane[9] or for an aliphatic methylene group[10] in the vapor phase. It follows that cyclotetradecane possesses 12.6 kcal (0.9 × 14) of strain relative to cyclohexane. Arguments concerning cyclotetradecadiyne based upon thermochemical deductions are therefore subject to considerable uncertainty.

3,3-Dimethylcyclohexene (**1**) and 4,4-dimethylcyclohexene (**2**) constitute a pair of double bond isomers for which hydrogenation data have now been obtained. The heats of hydrogenation of these substances are respectively −27.7 and −26.6 kcal/mol, and the heat of isomerization of **1** into **2** is −1.1 kcal/mol. A free energy difference of approximately 0.8 kcal/mol in favor of isomer **2** has been obtained in a study of the acid-catalyzed equilibration of these substances.[11] With regard to the conformational properties of these molecules it will be noted that the methyl groups in **1**, but not in **2**, occupy quasi-axial and quasi-equatorial positions.





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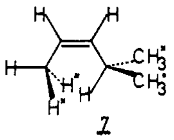

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Two further examples have been added to the list of cis–trans olefin pairs examined previously. These are *cis*- and *trans*-1,2-diisopropylethylene (**3** and **4**) and *cis*- and *trans*-1,2-dineopentylethylene (**5** and **6**). The data, together with that for appropriate reference substances, are given in Table III. Enthalpy differences between cis and trans isomers (*i.e.*, heats of isomerization) are taken as approximate measures of steric interactions between cis substituents on the double bond.

Table III. Heats of Hydrogenation of Acyclic Cis–Trans Olefin Pairs in Acetic Acid Solution at 25°

Compd	$-\Delta H$, kcal/mol Cis	Trans	$-\Delta H$, isomerization Cis→trans
$CH_3CH{=}CHCH_3$[a]	28.6	27.6	1.0
$CH_3CH{=}CHCH(CH_3)_2$[b]	27.3	26.4	0.9
$CH_3CH{=}CHC(CH_3)_3$[b]	30.8	26.5	4.3
$(CH_3)_3CCH{=}CHC(CH_3)_3$[b]	36.2	26.9	9.3
$(CH_3)_2CHCH{=}CHCH(CH_3)_2$	28.7	26.8	1.9
$(CH_3)_3CCH_2CH{=}CHCH_2C(CH_3)_3$	26.9	26.0	0.9

[a] Vapor phase data of G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **57**, 876 (1935). [b] Reference 12.

As noted earlier[12] substitution of one methyl group of butene-2 by isopropyl does not significantly alter the heat of isomerization, an observation which suggests that the isopropyl group can adopt a conformation in which it is sterically equivalent to methyl (*cf.* structure **7**). In this connection it is assumed that nonbonded interactions between starred hydrogen and methyl groups is not significant. For *cis*-1,2-diisopropylethylene the corresponding preferred conformation is presumably that shown in structure **3**. The net change in passing from **7** to **3** is the replacement of one starred hydrogen–methyl interaction by a methyl–methyl repulsion (starred in **3**). Since the distance separating the starred methyl of **3** is identical with that separating the methyl groups of *cis*-butene, it is probably not surprising that the heat of isomerizations of *cis*-1,2-diisopropylethylene (−1.9 kcal/mol) is 1.0 kcal/mol larger than that of the corresponding methyl isopropyl derivative.

Changes in the heat of isomerization of cis to trans isomers accompanying replacement of one or of both methyls by *tert*-butyl groups (*cis*- and *trans*-methyl-*tert*-butylethylene and *cis*- and *trans*-di-*tert*-butylethylene) have been reported previously (Table III).[12] The high degree of strain associated with the opposition of two *tert*-butyl groups in *cis*-1,2-di-*tert*-butylethylene is revealed by the high heat (−9.3 kcal/mol) of isomerization of the cis isomer into the trans.

The effect of the introduction of two *tert*-butyl groups on a single carbon atom has been investigated in the case of 1,1-di-*tert*-butylethylene (**8**), in which the heat of hydrogenation, −28.0 kcal/mol, is only slightly greater than the heats of hydrogenation of 2,4-dimethyl-1-pentene-1 (−26.7 kcal/mol) and 2,4,4-trimethylpentene-1 (−25.5 kcal/mol).[12] Strain, if present, must at least be comparable in olefin and in saturated product.

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(6) R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(7) J. H. Wotiz, R. F. Adams, and C. G. Parsons, *ibid.*, **83**, 373 (1961).

(8) M. A. Frisch, R. G. Bautista, J. L. Margrave, C. G. Parsons, and J. H. Wotiz, *ibid.*, **86**, 335 (1964).

(9) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1952.

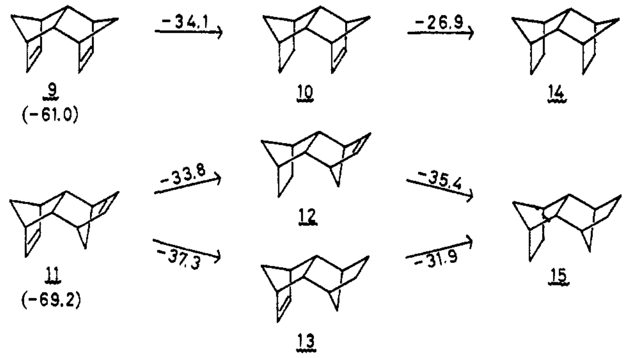
(10) Taken as the difference between the heats of combustion of *n*-heptane (−1,160.01 kcal/mol) and *n*-octane (−1,317.45 kcal/mol); see ref 9.

(11) J. Champagne, H. Favre, D. Vocelle, and I. Zbikowski, *Can. J. Chem.*, **42**, 213 (1964).

(12) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Amer. Chem. Soc.*, **80**, 1430 (1958).

Of interest in connection with the di-*tert*-butyl compounds are the *cis*- and *trans*-1,2-dineopentylethylenes (**5** and **6**) which likewise possess bulky substituent groups. Here, however, appropriate rotation of the substituents in the cis isomer can minimize steric repulsions. Consistently, both the heats of hydrogenation for the cis and trans compounds (Table I) and their heat of isomerization (Table III) are scarcely distinguishable from the values obtained for *cis*- and *trans*-methylisopropylethylene.[12]

Through the kindness of the late Professor Saul Winstein we have had an opportunity to examine the heats of hydrogenation of the five bridged dimethanonaphthalene derivatives, **9–13**, prepared in his laboratory.[13] Interest in these substances is associated with nonbonded repulsions between hydrogen atoms which arise in the reduction products, **14** and **15**. If norbornene with a heat of hydrogenation of −33.1 kcal/mol[14] be taken as a model, it can be seen that the discrepancies between norbornene and compounds **12** and **13** are not only small, but that the difference in the heats of hydrogenation of **12** and **13** (3.4 kcal/mol) is in the direction expected if repulsion between methano and ethano bridges exceeds that between methano and ethyleno bridges. The result for diene **11** is less than 2 kcal/mol higher than the sum of the figures for **12** and **13**. The heat of hydrogenation of the first double bond of diene **9**, −34.1 kcal/mol (obtained by difference), is likewise in the normal range. The heat of hydrogenation of **10** to **14** (−26.9 kcal/mol), however, is 6.2 kcal/mol lower than that of the norbornene model and 7.3 kcal/mol lower than the heat of partial hydrogenation of **9** to **10**. The repulsive interactions between internal hydrogens of the two ethano bridges in **14** are thereby clearly manifested.



The pair of bicyclic olefins, bicyclo[3.2.1]octa-2,6-diene (**16**, −57.9 kcal/mol) and bicyclo[3.2.1]oct-2-ene (**17**, −26.8 kcal/mol), bring further information on the interaction of strain and ring size.[15] Ground state, homoallylic conjugation was concluded to play no major role in bicyclo[2.2.1]hepta-2,5-diene or bicyclo-[2.2.2]octa-2,5-diene[14] and appears not to play a major role in bicyclo[3.2.1]octa-2,6-diene either, despite the remarkable enhancement in acidity of the methylene hydrogen atoms at C_4 discovered by Brown and Occolowitz.[16] The heat of partial hydrogenation of the five-membered double bond (−31.1 kcal/mol) is significantly higher rather than lower than that of cyclopentene (−26.0 kcal/mol) and probably reflects incremental strain associated with the 3,5 closure of the second ring by the three-carbon propylene bridge. In the bicyclo[2.2.1]heptyl system bridging by the two-carbon ethylene group had revealed an even higher (by 3.9 kcal/mol) partial hydrogenation [−35.0 kcal/mol, the difference between bicyclo[2.2.1]hepta-2,5-diene (−68.1 kcal/mol) and bicyclo[2.2.1]hept-2-ene (−33.1 kcal/mol)]. The normal heat of hydrogenation of the monoolefin **17** (−26.8 kcal/mol against −27.1 kcal/mol for cyclohexene) indicates little difference in difficulty of 3,5 bridging by the two-carbon ethano bridge in cyclohexene and cyclohexane.

Experimental Section

Materials. Cyclooctyne was prepared by the method of Wittig and Krebs.[17] The sample of cyclononyne, generously supplied by G. B. Carter and M. Anderson of the Shell Chemical Co., had been purified on a 10-ft silicone oil column and bulb-to-bulb distillation. Cyclodecyne, $n^{20}{}_{\mathrm{D}}$ 1.4902, had an ir spectrum identical with that reported by Blomquist, Burge, and Sucsy.[18] We wish to thank Dr. J. Sicher of the Czechoslovak Academy of Science for the sample of cyclododecyne, Dr. J. H. Wotiz of the Diamond Alkali Co. for the cyclotetradecadiyne, Professor M. S. Newman for the sample of 1,1-di-*tert*-butylethylene[19] and the samples of *cis*- and *trans*-1,2-dineopentylethylene,[20] and the late Professor Saul Winstein for the samples of compounds **9** through **13** which had been prepared by Dr. K. C. Pande. Compounds **16** and **17** were furnished through the kindness of Dr. M. Rosenblum and Dr. L. Schiff, Brandeis University, Waltham, Mass. Cyclopentene and *trans*-1,2-diisopropylethylene were obtained from the American Petroleum Institute.

Calorimetric Measurements. Heats of hydrogenation were measured in the apparatus, and by the general procedure, previously described.[14] Samples of olefins sufficient to provide for an uptake of approximately 3 mmol of hydrogen were introduced in evacuated, sealed ampoules, and the hydrogenation reaction was initiated by breaking an ampoule containing approximately 100 mg of previously calibrated PtO_2 catalyst.

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(13) For references, see J. K. Stille and D. R. Witherell, *J. Amer. Chem. Soc.*, **86**, 2188 (1964).

(14) R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

(15) These data and remarks from the thesis of Dr. Barbara J. Mallon [*Diss. Abstr.*, **27**, 1095-B (1966)] were not included in Professor Turner's drafts for this paper (W. D.).

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(17) G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3260 (1961).

(18) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952).

(19) M. S. Newman, A. Arkell, and T. Fukunaga, *ibid.*, **82**, 2498 (1960).

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