The total olefin obtained in this way, after recrystallization from acetone and from ether-methanol, melted at 85.8–87°, $[\alpha]_D$ +6°. The infrared spectrum indicated contamination by small amounts of cholest-6-ene, which could not be removed by repeated crystallization.[38] The product was finally rechromatographed on alkaline alumina and, after several passes, a sample, m.p. 86–87°, $[\alpha]_D$ +11.7°, free of cholest-6-ene was obtained.

Cholest-8:14-ene, m.p. 53.5–55°, $[\alpha]_D$ +20° (*c* 1.0, chloroform) was prepared from cholest-7-ene by isomerization over palladium (hydrogenation conditions) as described by Eck and Hollingsworth.[25]

The 3α-hydroxy-Δ^{11}-cholenic acid employed in this investigation was a purified sample, m.p. 165–166°, of material prepared some years ago at the laboratories of Merck and Co., Rahway, N. J.

Acid Isomerization at 85°.—A solution of the olefin and an equal weight of *p*-toluenesulfonic acid in a mixture of acetic acid and cyclohexane (4:1, 6 ml. of solvent for 30 mg. of olefin) was heated to reflux temperature in an electrically heated oil-bath in a flask fitted with a thermometer extending below the surface of the solution. At the end of the selected heating period, the solution was poured into dilute sodium hydroxide, and the aqueous layer was extracted three times with petroleum ether. The combined organic fractions were then washed with dilute alkali, water, saturated sodium chloride and filtered through anhydrous magnesium sulfate. After evaporation of the solvent, the product was twice dissolved in carbon disulfide and taken to dryness in order to ensure removal of the last traces of hydrocarbon solvent prior to infrared analysis.

Acid Isomerization at 120°.—The procedure employed for isomerizations at the higher temperature resembled that described above, except that after the reflux temperature had been reached, about 30% of the solvent was distilled off. The cyclohexane and water passed over as an azeotrope, and the temperature of the solution rose to about 120°. When reactions were carried out in acetic acid alone, without removal of small amounts of water that are present under these conditions, the results obtained were erratic. At the end of the reaction period, the products were isolated as before, and the acetate esters were removed by chromatography on alumina before infrared analysis of the hydrocarbon fractions.

Hydrogenation of Product XI.—A sample of product XI was dissolved in 40 ml. of acetic acid–cyclohexane (4:1) and stirred in a hydrogen atmosphere with pre-reduced platinum oxide catalyst. No hydrogen was absorbed, and the recovered material proved to be unsaturated in the tetranitromethane test. The experiment was then repeated with 200 mg. of XI in 35 ml. of acetic acid–cyclohexane (4:1), to which 4 drops of 12 *N* hydrochloric acid was added. After 42 hr. at 60°, 110% of the calculated amount of hydrogen had been absorbed, and the product gave no reaction with tetranitromethane. The infrared absorption spectra of the reduced material showed no detectable amounts of cholestane or of coprostane.

Hydrogenation of Product XIV.—Hydrogenation was carried out at 60° with added hydrochloric acid as described in the preceding experiment. The reaction product showed a negative tetranitromethane test for unsaturation, and the infrared spectrum gave evidence of the presence of small amounts of cholestane.

HOUSTON, TEXAS

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[38] Cremlyn and Shoppee obtained pure cholest-7-ene directly from the alumina column.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE RICE INSTITUTE AND OF YALE UNIVERSITY AND FROM THE HICKRILL CHEMICAL RESEARCH FOUNDATION]

Heats of Hydrogenation. III. Hydrogenation of Cycloöctatetraene and of Some Seven-membered Non-benzenoid Aromatic Compounds[1]

BY RICHARD B. TURNER, W. R. MEADOR, W. VON E. DOERING, L. H. KNOX, J. R. MAYER AND D. W. WILEY

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The heats of hydrogenation of several potentially aromatic substances have been measured in solution, and resonance energies have been estimated by comparison of the heats of hydrogenation of these compounds with heats calculated for reasonable models. The compounds that have been examined together with the ΔH values and calculated resonance energies are as follows: cycloöctatetraene ($-\Delta H$ 97.96 ± 0.05 kcal./mole, R.E. 2.4 kcal./mole), 1,3,5-cycloöctatriene ($-\Delta H$ 72.36 ± 0.26 kcal./mole, R.E. 0.9 kcal./mole), azulene ($-\Delta H$ 98.98 ± 0.13 kcal./mole, R.E. 28 kcal./mole), heptafulvene ($-\Delta H$ 92.63 ± 0.41 kcal./mole, R.E. 13 kcal./mole), heptafulvalene ($-\Delta H$ 130.77 ± 0.31 kcal./mole for six molar equivalents of hydrogen, R.E. 28 kcal./mole), dihydroheptafulvalene ($-\Delta H$ 138.81 ± 0.20 kcal./mole) and tropone ($-\Delta H$ 67.58 ± 0.30 kcal./mole to cycloheptanone).

Since the heats of hydrogenation of benzene, and of various related substances including styrene, hydrindene and furan, were measured by Kistiakowsky and his associates[2] some twenty years ago, no further studies of heats of hydrogenation in the aromatic series have been reported. In the meantime several potentially aromatic compounds of considerable theoretical interest have been prepared in sufficiently pure condition for hydrogenation studies. Of these substances cycloöctatetraene, azulene, methylenecycloheptatriene (heptafulvene), cycloheptatrienylidenecycloheptatriene (heptafulvalene), 7-(7′-cycloheptatrienyl)-cycloheptatriene (dihydroheptafulvalene) and cycloheptatrienylium oxide (tropone) have now been examined in the hydrogenation calorimeter.

Experimental

The technique for measurement of heats of hydrogenation in solution described in Paper I[3] was employed in the present investigation with the following modifications. In the cases of heptafulvene and heptafulvalene, Diethylcarbitol was used as the solvent, since these substances are subject to rapid polymerization in acetic acid. Despite extensive purification of the Diethylcarbitol, reduction of the platinum oxide catalyst gave higher heat values in this solvent (−32.94 ± 0.21 cal./100.0 mg.) than in acetic acid (−30.95 ± 0.13 cal./100.0 mg.) and consumed one cc. more hydrogen (*e.g.*, 16.25 cc./100.0 mg. in 275 cc. of Diethylcarbitol *vs.* 15.12 cc./100.0 mg. in 225 cc. of acetic acid). The results were nevertheless consistent, and no discrepancies traceable to the solvent have been noted. All reductions in

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[1] This work was supported by the Eli Lilly Co., Indianapolis, and by the Office of Ordnance Research, Contract DA-19-059-ORD-1562 with Yale University.

[2] (a) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **58**, 146 (1936); (b) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *ibid.*, **59**, 831 (1937); (c) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, *ibid.*, **60**, 440 (1938).

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

Diethylcarbitol were carried out in volumes of 275 ml.; hydrogenations in acetic acid were conducted in 225 ml. of solvent.

The hydrogenation of tropone over platinum-in-acetic acid proceeded with the absorption of 92% of the theoretical amount of hydrogen, calculated on the basis of 4 molar equivalents. However, the clean absorption of 3 molar equivalents of hydrogen was observed over palladium supported on barium sulfate, and the results reported for tropone were obtained in acetic acid with this catalyst. All runs in which palladium was used were carried out in the following manner. The calorimeter containing the solvent, catalyst and an evacuated ampoule containing tropone was flushed with hydrogen according to the previously described procedure.[3] After absorption of hydrogen by the catalyst was complete and thermal equilibrium had been established, the hydrogenation reaction was initiated by breaking the ampoule of tropone. The final results were corrected for the heat of solution of tropone (−0.14 ± 0.01 kcal./mole), which was determined separately, and thus are referable to the dissolved state.

Materials.—A sample of **cycloöctatetraene** obtained from the General Aniline and Film Corp. was purified by conversion into the silver nitrate complex, m.p. 173° dec., as described by Cope and Hochstein.[4] Regeneration and fractionation afforded a sample boiling at 141–141.5° (19 mm.), n^{25}D 1.5350. Examination of the infrared spectrum of this material for the styrene band at 11.08 μ gave no evidence for contamination by the latter substance.

1,3,5-Cycloöctatriene was prepared by the procedure of Cope and Hochstein[4]; n^{24}D 1.5248.

Azulene was synthesized as described by Doering, Mayer and DePuy.[5] The sample employed for hydrogenation, m.p. 99–100°, was purified by chromatography on alumina.

Solutions of **heptafulvene** in Diethylcarbitol were freshly prepared for each run by the method of Wiley.[6] The heptafulvene was collected in a trap containing small amounts of Diethylcarbitol cooled to −40°. The resulting solutions were then made up to 275 ml. and were hydrogenated at once. The stability of heptafulvene in Diethylcarbitol was established by the negligible decrease of the extinction coefficient of the absorption band at 405 mμ over a period of 24 hr. at room temperature.

Heptafulvalene, m.p. 121–122°, was prepared by the method of Mayer.[7]

Dihydroheptafulvalene, m.p. 61°, was obtained by the procedure of Doering and Knox.[8]

Tropone was synthesized as described by Doering and Detert[9] and was purified by recrystallization and evaporative distillation; n^{25}D 1.6155, m.p. −5°.

For reductions in Diethylcarbitol (diethylene glycol diethyl ether) the solvent was purified by (a) distillation at 10 mm. (b.p. 85–86°), (b) treatment with lithium aluminum hydride at 50° for 4 days and distillation at 2–3 mm. (b.p. 65–66°) and (c) distillation through a 24-inch helix-packed column under nitrogen at 37 mm. (b.p. 100°). The product was collected in 350-ml. fractions which were sealed at once under nitrogen in Pyrex flasks, m.p. −46 to −45°.

Results and Discussion

The results obtained in the present investigation are given in Table I. For the evaluation of resonance energies[10] from heats of hydrogenation, the measurements should ideally be carried out in the gas phase. The fact that the values reported here were obtained in solution therefore constitutes an obvious disadvantage, since corrections for solvent–solute interactions involving both the unsaturated derivatives and the hydrogenation products require thermodynamic data that are not generally available. The uncertainties that are introduced by the solvation problem, however, would appear to be small in view of evidence that has been cited previously.[3] Thus calculation of the resonance energy of cycloheptatriene from the gas phase data of Kistiakowsky[11] gives a value of 6.7 kcal./mole, based on a reference standard equal to three times the heat of hydrogenation of cycloheptene. The same method of calculation applied to the measurements made in acetic acid furnishes a comparison value of 7.1 kcal./mole. In any event, ambiguities that arise from uncertainties in the formulation of appropriate "non-resonating" models undoubtedly constitute a more important source of difficulty than do solvent-solute interactions, at least in the case of relatively non-polar molecules.

Cycloöctatetraene.—Cycloöctatetraene is one of the earliest molecules to derive its importance from a potential bearing on the theory of aromatic

TABLE I

HEATS OF HYDROGENATION IN SOLUTION[a]

Compound	Mmoles	Catalyst, mg.	$-\Delta H$(25°, kcal./mole
Cycloöctatetraene	1.259	100.2	97.96
	1.307	100.0	97.96
		Average	97.96 ± 0.05[b]
1,3,5-Cycloöctatriene	1.553	100.2	72.63
	1.315	98.8	72.06
	1.648	98.8	72.39
		Average	72.36 ± 0.26
Azulene	0.8103	99.8	98.75
	0.8007	99.7	99.20
		Average	98.98 ± 0.13
Heptafulvene[c]	1.614	100.2	93.24
	1.560	100.5	92.08
	1.555	100.5	92.56
		Average	92.63 ± 0.41
Heptafulvalene[c]	4.176[d]	110.0	130.86[e]
	4.189[d]	100.5	130.68[e]
		Average	130.77 ± 0.13[e]
Dihydroheptafulvalene	0.7347	99.0	138.90
	0.7593	99.3	138.72
		Average	138.81 ± 0.20
Tropone[f]	0.9813	Pd–$BaSO_4$	67.75
	0.8417	Pd–$BaSO_4$	67.89
	1.938	Pd–$BaSO_4$	67.09
		Average	67.58 ± 0.30

[a] Except in the cases indicated, all hydrogenations were carried out in acetic acid with a platinum oxide catalyst. [b] Deviations include uncertainty in the heat of hydrogenation of the platinum oxide. [c] Hydrogenations of heptafulvene and of heptafulvalene were carried out with Diethylcarbitol as the solvent. [d] Millimoles of *hydrogen* absorbed. [e] These values are based upon the absorption of 6 molar equivalents of hydrogen (see Discussion). [f] Tropone was reduced over 1.0-g. samples of a 5% palladium-on-barium sulfate catalyst. In these experiments the catalyst was equilibrated with hydrogen, and the hydrogenation reaction was initiated by solution of the tropone. The results are corrected for the heat of solution of tropone in acetic acid.

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(4) A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

(5) W. von E. Doering, J. R. Mayer and C. H. DePuy, *ibid.*, **75**, 2386 (1953).

(6) D. W. Wiley, Ph.D. Dissertation, Yale University, Sept., 1954.

(7) J. R. Mayer, Ph.D. Dissertation, Yale University, May, 1955.

(8) W. von E. Doering and L. H. Knox, THIS JOURNAL, **79**, 352 (1957).

(9) W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

(10) As used throughout this paper, "resonance energy" is defined as the difference between the measured heat of hydrogenation (reaction) of a given compound and that estimated for one or more reasonable models. It should be emphasized that resonance energy is not an intrinsic property of a molecule but that it depends on, and varies with, the choice of the model.

(11) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61**, 1868 (1939).

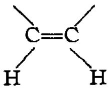
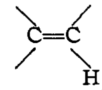
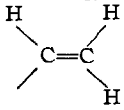
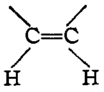
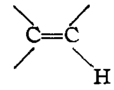
character.[12] The conformation and resonance energy of this substance have been subjects of considerable controversy in recent years. Although a large body of evidence has been variously interpreted in favor of the "tub" structure on the one hand and the "crown" structure on the other,[13] it is now generally agreed that cycloöctatetraene exists in the "tub" form.[14] This structure allows each olefinic linkage to assume a strainless, planar configuration with C=C—C angles approximating 120° but with angles between adjacent double bonds of nearly 90° owing to rotation about the intervening C-C single bonds. Conjugative stabilization in such a non-planar molecule should be largely suppressed, and the resonance energy would therefore be expected to be small.[15] Support for this conclusion is provided by the X-ray analyses of Kaufman, Fankuchen and Mark[16] which show that in the crystal the carbon–carbon bond lengths are alternately 1.54 and 1.34 Å. as in paraffinic and olefinic substances, respectively. This result contrasts with the single value of 1.39 Å. reported for the carbon–carbon distances in benzene.[17]

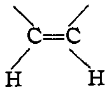
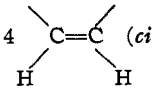
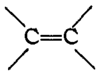
Following publication of data on the heat of formation of cycloöctatetraene[18] shortly after World War II, Pink and Ubbelohde[19] calculated a resonance energy of 25.3 kcal./mole for this substance. This result is inconsistent with the chemical properties of cycloöctatetraene, in particular with its ready conversion into derivatives of bicyclo-[4,2,0]octadiene,[20] and a considerably lower value was subsequently suggested by Person, Pimentel and Pitzer[14a] on the basis of conventional calculations employing the 1950 combustion data of Prosen, Johnson and Rossini[21] and bond energies (4 C=C, 4 C—C and 8 C—H bonds) given by Pitzer.[22] An alternative method of treatment of the Rossini data, however, furnishes a still lower and, we believe, more reliable result.

The heat of isomerization of cycloöctatetraene into styrene (gas phase) derived from Rossini's results is −36.3 kcal./mole.[21,23] Taking 36.9 kcal./mole as the resonance energy of styrene[24] and 72.5 kcal./mole as the heat of formation of "non-resonating" styrene, calculated by Franklin's method of group equivalents (Table II),[25] the heat of formation of styrene can be expressed as 35.6 kcal./mole.

TABLE II

CALCULATION OF HEATS OF FORMATION (NON-RESONATING STRUCTURES)[25]

	Styrene	ΔH_f
2	 (*cis*)	37.8
1		20.2
1		15.0
1	C_6-ring corrn.	−0.5
	Total	72.5
	Azulene	
3	 (*cis*)	56.6
2		40.4
1	C_5-ring corrn.	5.7
	Total	102.7

	Cycloöctatetraene	ΔH_f
4	 (*cis*)	75.5
	Total	75.5
	Naphthalene	
4	 (*cis*)	75.5
1		24.6
2	C_6-ring corrn.	−1.0
	Total	99.1

From this result and from the isomerization data it follows that the heat of formation of cycloöctatetraene is 71.9 kcal./mole. Calculation of the heat of formation of "non-resonating" cycloöctatetraene by the Franklin method[25] gives a value of 75.5 kcal./mole (Table II), and resonance stabilization of this molecule is hence estimated to be of the order of 3.6 kcal./mole. The result obtained by this procedure is in good agreement with the value of 4.8 kcal./mole recently derived by Springall, White and Cass[26] from heat of combustion data and selected average bond energies.

Since all of the values thus far reported for resonance energy in the cycloöctatetraene system are based upon combustion experiments, determination of this quantity by an independent method seemed most desirable. The heat of hydrogenation of cycloöctatetraene was accordingly measured in acetic acid solution at 25° and was found to be −97.96 ± 0.05 kcal./mole (Table I).

Assuming the superficially reasonable reference standard of four times the heat of hydrogenation

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[12] R. Willstätter and E. Waser, *Ber.*, **44**, 3423 (1911); R. Willstätter and M. Heidelberger, *ibid.*, **46**, 517 (1913).

[13] *Cf.* O. Bastiansen, O. Hassel and A. Langseth, *Nature*, **160**, 128 (1947); E. R. Lippincott, R. C. Lord and R. S. McDonald, THIS JOURNAL, **73**, 3370 (1951).

[14] (a) W. B. Person, G. C. Pimentel and K. S. Pitzer, *ibid.*, **74**, 3437 (1952); (b) I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

[15] An approximate valence-bond treatment of *planar* cycloöctatetraene (G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, p. 142) gives a resonance energy of 39 kcal./mole.

[16] H. S. Kaufman, I. Fankuchen and H. Mark, *J. Chem. Phys.*, **15**, 414 (1947); *Nature*, **161**, 165 (1948).

[17] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[18] W. Reppe, B.I.O.S. Final Report, No. 137, Item No. 28, H. M. Stationery Office, London, 1945, p. 3.

[19] R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948).

[20] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[21] E. J. Prosen, W. H. Johnson and F. D. Rossini, THIS JOURNAL, **72**, 626 (1950). The heat of formation of cycloöctatetraene (liq., 25°) is given as +60.82 ± 0.32 kcal./mole. A value of 40 kcal./mole was employed by Pink and Ubbelohde (reference 19).

[22] K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

[23] The liquid phase value is −36.1 kcal./mole. Correction of this quantity to the vapor phase has been made for the sake of consistency only, from the data of D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffmann, *ibid.*, **71**, 1634 (1949), and K. S. Pitzer, L. Guttman and E. F. Westrum, *ibid.*, **68**, 2209 (1946).

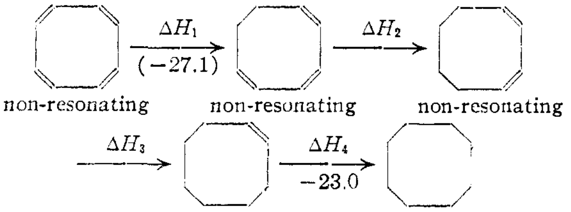
[24] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, p. 80. The value cited by Wheland is obtained from Kistiakowsky's hydrogenation data.

[25] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); THIS JOURNAL, **72**, 4278 (1950).

[26] H. D. Springall, T. R. White and R. C. Cass, *Trans. Faraday Soc.*, **50**, 815 (1954).

of *cis*-cyclooöctene (−22.98 ± 0.10 kcal./mole),[27] the resonance energy calculated for cyclooöctatetraene is *negative* and equal to −6.0 kcal./mole. It will be noted, however, that owing to severe repulsions between non-bonded atoms in cyclooöctane,[11,27] the heat of hydrogenation of *cis*-cyclooctene is considerably lower than that of cyclohexene (−27.10 kcal./mole),[3] which furnishes a reduction product in which non-bonded interactions are minimized.[28] Since the repulsions that are introduced in the last of the four hypothetical steps in the hydrogenation of "non-resonating" cyclooctatetraene (Chart I) are undoubtedly greater than those introduced in the earlier stages, the use of ΔH_4 to represent the heat of all four steps is a poor choice, which leads to an unreasonably low prediction. In order to correct for this effect, the cyclohexene value (−27.1 kcal./mole) has been assigned to ΔH_1 on the grounds that the heat of hydrogenation of the first double bond of the model should closely approximate that of a representative, *cis*-disubstituted olefin. An average of this figure and that obtained experimentally for ΔH_4 (−23.0 kcal./mole) gives an average heat of hydrogenation for all four double bonds of −25.1 kcal./mole. The resonance energy calculated for cyclooöctatetraene on the basis of these assumptions is 2.4 kcal./mole, a result that agrees reasonably well with the lower values derived from combustion data.

CHART I



As a further check on the magnitude of the cyclooctatetraene resonance, the heat of hydrogenation of cyclooöctatetraene has been compared with that of 1,3,5-cyclooöctatriene in analogy with the procedure followed by Kistiakowsky and his associates[2a] in their treatment of the resonance energy of benzene. By subtracting the heat of hydrogenation of 1,3-cyclohexadiene to cyclohexane from that of benzene to the same product, the heat of the reaction benzene + H_2 → 1,3-cyclohexadiene can be calculated. This change is *endothermic* to the extent of 5.6 kcal./mole, as compared with the hydrogenation of an unconjugated, *cis*-disubstituted double bond, *exothermic*, −28.6 kcal./mole (gas phase). The reduction in heat evolution of 34.2 kcal./mole observed in this case represents the increase in stabilization resulting from introduction of a third double bond into the 1,3-cyclohexadiene molecule and is defined[10] as the resonance energy of benzene relative to the cyclohexene—1,3-cyclohexadiene model.[29]

Returning now to the question of cyclooöctatetraene, it follows that a quantitative measure of the aromatic character of this substance can be gained from the extent to which the heat change for the process cyclooöctatetraene + H_2 → 1,3,5-cyclooöctatriene deviates from the standard value of −27.1 kcal./mole (solution). The quantity calculated for this transformation from the heats of hydrogenation of cyclooöctatetraene and of 1,3,5-cyclooöctatriene to cyclooöctane is −25.6 kcal./mole. The discrepancy in this case is hence only 1.5 kcal./mole, a value that is comparable in magnitude to the resonance energy of simple conjugated dienes.

With reference to the triene problem it is interesting to note that the heat of hydrogenation of 1,3,5-cyclooöctatriene (−72.4 kcal./mole) is *higher* than that of 1,3,5-cycloheptatriene (tropilidene) (−70.5 kcal./mole) despite the fact that the heat of hydrogenation of *cis*-cyclooöctene is *lower* than that of cycloheptene by almost 3 kcal.[3,27] The resonance energy of 1,3,5-cyclooöctatriene (0.9 kcal./mole) is obtained directly as the difference between the resonance energy of cyclooöctatetraene (2.4 kcal./mole) and the contribution of the fourth double bond (1.5 kcal./mole). The stabilization of tropilidene is 9.8 kcal./mole based on Kistiakowsky's data[11] or 9.0 kcal./mole based on the solution data,[3] both figures being referable to a "non-resonating" model in which cyclohexene is used for the first double bond, cycloheptene for the third and an average of the two for the second.

The negligible resonance energy of 1,3,5-cyclooctatriene probably is due to its non-planar structure. By analogy one can assume that a non-planar cycloheptatriene structure for tropilidene would also lead to little or no resonance energy. The fact that tropilidene has a relatively high degree of stabilization is in better accord with a planar conformation.[30] It should be mentioned that such an arrangement involves considerable angular strain, of which no account is taken in formulation of the comparison standard. This inadequacy of the model serves to lower the calculated resonance energy.[31]

Azulene.—In view of widespread interest in the properties of non-benzenoid aromatic compounds, we have measured the heat of hydrogenation of azulene. This substance undergoes rapid reduction in acetic acid with clean absorption of five molar equivalents of hydrogen and furnishes a ΔH value of −98.98 ± 0.13 kcal./mole. Simple calculations based on

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(27) R. B. Turner and W. R. Meador, THIS JOURNAL, **79**, 4133 (1957).

(28) In this connection cyclohexene is regarded as a typical unstrained, *cis*-disubstituted olefin, the hydrogenation of which is uncomplicated by the steric repulsion problem. It will be recalled that the gas phase values obtained for cyclohexene and for *cis*-butene (−28.6 kcal./mole) by G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935) and **58**, 137 (1936), are identical.

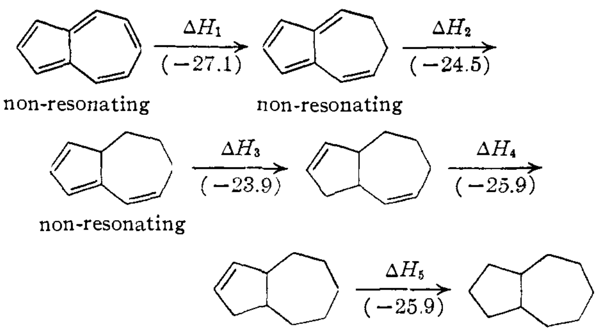
(29) The value of 36.0 kcal./mole for the resonance energy of benzene is based on a model consisting of three molecules of cyclohexene and differs from the figure given above by the resonance energy of 1,3-cyclohexadiene (1.8 kcal./mole).

(30) For additional discussion of this problem see W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, THIS JOURNAL, **78**, 5448 (1956). The resonance energy obtained in the present investigation compares favorably with that calculated by Wheland (reference 24, p. 132) for planar cycloheptatriene. The recent suggestion of M. V. Evans and R. C. Lord, "Abstracts of Papers," 130th Meeting, American Chemical Society, Atlantic City, N. J., Sept. 16, 1956, p. 41R, that tropilidene is bicyclo[3,2,0]heptadiene-1,5 is at variance with results of E. Vogel (private communication) which indicate that a synthetic product of this structure is not identical with tropilidene.

(31) A similar problem is encountered in the case of benzene, since the actual molecule possesses compressional energy not found in the cyclohexene model.

twice the heat of hydrogenation of cyclopentene (−25.9 kcal./mole)[32] and three times the heat of hydrogenation of cycloheptene (−25.9 kcal./mole)[3] give a resonance energy of 30.5 kcal./mole for this substance. Correction for steric repulsion effects is more difficult in this instance than in the cycloöctatetraene case, and the situation is further complicated by the presence in azulene of two trisubstituted double bonds at bridge head positions. The treatment that follows must, therefore, be regarded as a very crude approximation at best.

CHART II



The heat of hydrogenation of the non-resonating model is again obtained as the summation of heats evolved in a hypothetical reduction process (Chart II). The cyclohexene value (−27.1 kcal./mole) is assumed for ΔH_1, and the cycloheptene and cyclopentene[32] figures have been taken for ΔH_4 and ΔH_5, respectively.[33] The heats of hydrogenation ΔH_2 and ΔH_3 present a special problem, and the values that have been chosen, −24.5 kcal./mole for ΔH_2 and −23.9 kcal./mole for ΔH_3, are based upon averages of the heats of hydrogenation of 1-methylcycloheptene and ethylidenecyclopentane and of 1-methylcyclopentene and methylenecycloheptane,[34] respectively, after correction of the methylenecycloheptane value for the substitution effect.[35] The heat of hydrogenation of the non-resonating model is then −127.3 kcal./mole, and the estimated resonance energy of azulene is 28.3 kcal./mole.[36] Since azulene possesses a dipole moment of approximately 1.0 *D*,[37] solvation energy should be larger in this case than in the case of non-polar molecules. "Resonance energy" calculated from solution data thus includes a factor for solvation.

In 1947, Heilbronner and Wieland[38] reported a value of 46 kcal./mole for the resonance energy of azulene, derived from consideration of: (a) the difference in heats of combustion of the isomer guaiazulene and cadalene (−29.6 ± 2.1 kcal./mole),[39] taken also as the difference in heats of formation of the isomeric pair azulene and naphthalene; (b) the heat of formation of naphthalene (solid state); (c) the heat of sublimation of carbon; (d) the heat of sublimation of azulene and (e) various bond energies given by Pauling.[40]

An equivalent, but more direct, evaluation of the azulene resonance can be made on the basis of the following relationships, in which all quantities refer to the vapor phase.

(1) ΔH_f (non-resonating naphthalene) − R.E. (naphthalene) = ΔH_f (naphthalene)
(2) ΔH_f (naphthalene) + $\Delta H_{\text{isom.}}$ (azulene → naphthalene) = ΔH_f (azulene)
(3) ΔH_f (non-resonating azulene) − ΔH_f (azulene) = R.E. (azulene)
(4) R.E. (azulene) = R.E. (naphthalene) + ΔH_f (non-resonating azulene) − ΔH_f (non-resonating naphthalene) − $\Delta H_{\text{isom.}}$ (azulene → naphthalene)

The heats of formation (ΔH_f) of non-resonating molecules of azulene and of naphthalene determined by Franklin's method of group equivalents[25] (Table II) are 102.7 and 99.1 kcal./mole, respectively. The heat of isomerization of azulene into naphthalene, corrected for the difference in heats of vaporization of these two substances,[38] is 33.2 kcal./mole, and it follows that R.E. (azulene) = R.E. (naphthalene) −29.6 kcal. Assuming Pauling's value of 75 kcal./mole for the resonance energy of naphthalene,[41] the resonance energy calculated for azulene by this method is 45.6 kcal./mole. However, evidence that has accumulated during the past few years suggests that the Pauling resonance energies are high. Franklin[25] has given a value of 62 kcal./mole for the resonance energy of naphthalene, and values of 60, 61 and 52.6 kcal./mole have resulted from revised calculations by the valence-bond and molecular-orbital methods.[42] A new experimental value recently has been obtained by Linstead and Jackman,[43] who have investigated the heats of *dehydrogenation* of various hydroaromatic systems by tetrachloro-*o*-benzoquinone. By comparison of the heat changes accompanying the conversions of 1,4-cyclohexadiene into benzene and of 1,4-dihydronaphthalene into naphthalene and assumption of Kistiakowsky's value of 36.0 kcal./mole for the benzene resonance, a tentative value of 67.6 ± 2 kcal. has been obtained for the resonance energy of naphthalene.

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[32] This solution value for cyclopentene is approximate and was obtained by subtracting 1.0 kcal., an average value for the discrepancy between our solution results and Kistiakowsky's gas phase data (see Table II, reference 3), from the gas phase value for cyclopentene (reference 2b).

[33] The order in which the various double bonds are considered is immaterial to the present argument.

[34] R. B. Turner and R. H. Garner, in press.

[35] *Cf.* J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937).

[36] G. Berthier and A. Pullman, *Compt. rend.*, **229**, 561 (1949), give a calculated value of 3.082 β (*cf.* benzene, 2.0 β).

[37] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

[38] E. Heilbronner and K. Wieland, *Helv. Chim. Acta*, **30**, 947 (1947).

[39] E. Perottet, W. Taub and E. Briner, *ibid.*, **23**, 1260 (1940).

[40] The cadalene employed in the combustion experiments of Perottet, Taub and Briner (ref. 39) is described as an oil, b.p. 155–157° (12 mm.), d^{20}_4 0.9737, $n^{20}\text{D}$ 1.5572. The physical state of the guaiazulene was not specified, but it is reasonable to suppose that the data for this compound are also referable to the liquid phase. The heat of formation of azulene (solid state), calculated by Heilbronner and Wieland as the sum of the heats of formation of naphthalene (solid) and the heat of isomerization of guaiazulene into cadalene was not corrected for this discrepancy, and inclusion of an approximate correction term derived from the heats of fusion of azulene and of naphthalene (ref. 38) gives a revised resonance energy value of 44 kcal./mole.

[41] L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1944, p. 136.

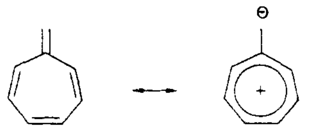
[42] See ref. 24, p. 132.

[43] R. P. Linstead and L. Jackman, private communication.

Recalculation of the resonance energy of azulene employing Franklin's result of 62 kcal./mole for stabilization in the naphthalene system gives a value of 32.4 kcal./mole in reasonable agreement with the results obtained in the present investigation. Conversely, the resonance energy derived for azulene from the hydrogenation data provides independent experimental support for a low value (58 to 60 kcal.) for the resonance energy of naphthalene.

In 1955, the heat of combustion of azulene was measured for the first time by Kováts, Günthard and Plattner, from whose results a value of −34.9 kcal./mole can be calculated for the gas phase heat of isomerization of azulene into naphthalene.[44] The use of this figure and the Franklin value of 62 kcal./mole for the naphthalene resonance in equation 4 leads to a resonance energy of 30.7 kcal./mole for azulene. Direct calculation of the azulene resonance from the heat of combustion data by the Franklin-Wheland method[44a] gives a value of 35.8 kcal./mole.

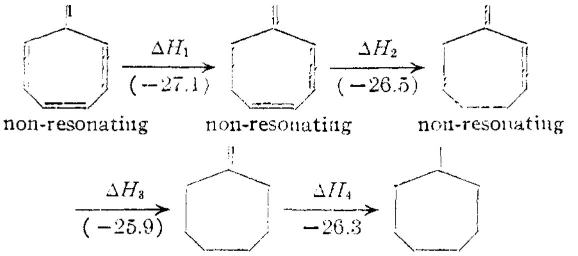
Heptafulvene.—Heptafulvene (I) contains a cyclic system of conjugated double bonds, for which the theoretical treatment of Pullman and Pullman[45] has predicted aromatic properties. Although the substance has never been obtained in pure form, owing to its extreme reactivity, solutions of moderate stability have been prepared.[6] The sensitivity of heptafulvene to acids precluded the use of acetic acid as a solvent for the hydrogenation experiments, which were carried out on freshly prepared samples dissolved in Diethylcarbitol. The amount of material present was determined by the amount of hydrogen absorbed.



Ia Ib

The heat of hydrogenation of heptafulvene is −92.63 ± 0.41 kcal./mole. An approximate evaluation of the heat of hydrogenation of the non-resonating system can be made on the basis of the following assumptions. The standard value of −27.1 kcal./mole is assigned to ΔH_1 of the accompanying reduction sequence (Chart III), and the cycloheptene value (−25.9 kcal./mole) is taken as a reasonable approximation of ΔH_3. An average of these figures gives −26.5 kcal./mole for ΔH_2. ΔH_4 has been determined experimentally and is found to be −26.3 kcal./mole.[34] Summation gives an over-all value of 105.8 kcal./mole and an estimated resonance energy of 13.2 kcal./mole as compared with 36.9 kcal./mole and 2.4 kcal./mole, respectively, for the isomeric compounds styrene and cyclooctatetraene.

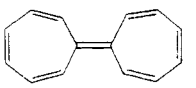
CHART III



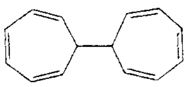
By comparing the heat of hydrogenation of heptafulvene (−92.6 kcal./mole) with that of methylenecycloheptane (−26.3 kcal./mole), a heat change of 66.3 kcal./mole is derived for the reaction, heptafulvene + $3H_2 \rightarrow$ methylenecycloheptane. In terms of the tropilidene model this represents an increase of 4.2 kcal./mole in the resonance energy of the cyclic triene system, which is produced by introduction of the exocyclic double bond.

Theoretical calculations of the resonance energy of heptafulvene by the molecular-orbital and valence-bond methods yield values of 1.994 β and 0.57 α, respectively.[45] In terms of kilocalories, calculated by use of the values for β and α given for benzene, the corresponding figures are 36 and 19 kcal./mole, respectively. A revised value of 16 kcal./mole may be derived from the more refined calculations of Bergmann, *et al.*[46]

Heptafulvalene and Dihydroheptafulvalene.—The resonance energy of heptafulvalene (II), which possesses two conjugated cycloheptatriene rings, has been calculated as 1.496 γ by the molecular-orbital method.[47] A corresponding calculation for the isomeric substance, stilbene, gives a value of 2.446 γ. On the basis of Wheland's value of 77 kcal./mole[42] for stilbene, the resonance energy of heptafulvalene can be expressed as 47 kcal./mole. A considerably lower figure is obtained from the hydrogenation data.



II



III

In view of the instability of heptafulvalene in the presence of acids, the hydrogenation of this substance was carried out in diethylcarbitol as in the case of heptafulvene. Unfortunately reduction proceeded with the absorption of only 95% of the theoretical amount of hydrogen for *six double bonds.* The heat of hydrogenation of this substance (−130.77 ± 0.31 kcal./mole) was thus calculated as six times the heat developed per mole of hydrogen absorbed.[48] The heat of hydrogenation of the non-resonating system was obtained by doubling

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[44] E. Kováts, Hs. H. Günthard and Pl. A. Plattner, *Helv. Chim. Acta*, **38**, 1912 (1955). The values for the heats of combustion (vapor phase, 25°) of azulene and of naphthalene given in line 4 of Table 4 (−1680.7 kcal./mole and −1239.5 kcal./mole) are typographical errors and should read −1280.7 kcal./mole and −1245.8 kcal./mole, respectively. The naphthalene value cited by these authors was obtained from unpublished results of F. D. Rossini.

[44a] Reference 24, p. 94.

[45] B. Pullman and A. Pullman, "Les Théories Électronique de la Chimie Organique," Masson et Cie., Paris, 1952, p. 227.

[46] E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. soc. chim.*, **18**, 684 (1951).

[47] E. D. Bergmann, D. Ginsburg, Y. Hirshberg, M. Mayot, A. Pullman and B. Pullman, *ibid.*, **18**, 697 (1951).

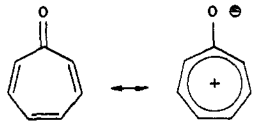
[48] Although the product was not isolated, it is assumed to be cycloheptylidenecycloheptane in view of the known difficulty encountered in reductions of tetrasubstituted olefins under the conditions of these experiments.

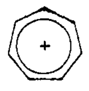
the sum of the values assumed for ΔH_1, ΔH_2 and ΔH_3 in the heptafulvene treatment (−159.0 kcal./mole). The difference between these two figures gives an approximate value of 28 kcal./mole for the resonance energy of heptafulvalene.

Hydrogenation of dihydroheptafulvalene (III) proceeded smoothly in acetic acid solution with absorption of six molar equivalents of hydrogen and a heat evolution of 138.81 ± 0.20 kcal./mole or 69.4 kcal. per cycloheptatriene ring. The latter value is in good agreement with the cycloheptatriene result (−70.5 kcal./mole)[3] if account is taken of non-bonded interactions in the reduction product involving one ring and hydrogen atoms of the other. Comparison of the results obtained for dihydroheptafulvalene and for heptafulvalene (hydrogen uptake, 6 molar equivalents) indicates that the resonance energy involved in the coupling of two cycloheptatriene rings in the latter compound amounts to about 8.0 kcal./mole. It is of interest to note that this figure is approximately twice the value of 4.2 kcal./mole obtained for conjugation of the cycloheptatriene ring and exocyclic double bond in heptafulvene.

Tropone.—Of interest as the oxygen analog of heptafulvene and as the next simpler member of the tropolone system, tropone has been treated theoretically by Brown[49] and has recently been synthesized.[9,50] The basicity of this substance and its chemical stability in acid have led to the formulation of the conjugate acid as a hydroxycycloheptatrienylium ion and to the formulation of tropone itself as cycloheptatrienylium oxide (IV). The considerable stability of the cycloheptatrienylium ion (V), which is regarded as the symmetrical parent of the seven-membered aromatic system, has been clearly demonstrated by Doering and Knox.[51]

The heat of hydrogenation of tropone to cycloheptanone over palladium-on-barium sulfate in acetic acid solution is −67.58 ± 0.30 kcal./mole. Assuming a planar structure for this molecule and using tropilidene (heat of hydrogenation, −70.49 ± 0.39 kcal./mole)[3] as the model for a tropone in which there is no interaction of the carbonyl group with the ring, the extra resonance energy in tropone resulting from this interaction is calculated as 2.9 kcal./mole. Although this stabilization can be rationalized in terms of contributing structures of type IVb, a larger value might have been expected in view of the large resonance energy (3.00 β) calculated for V. It is clear, however, that the stabilization achieved in IVb is accomplished at the expense of considerable electrostatic work of charge separation, which has the effect of reducing the measurable resonance energy.


IVa IVb


V

It should be noted, finally, that the resonance energy associated with coupling of the tropilidene system with a carbonyl group (2.9 kcal./mole) is somewhat less than that derived from coupling with an olefinic linkage (4.2 kcal./mole in heptafulvene). This result finds a parallel in the benzene series where it has been shown that styrene possesses a higher resonance energy (38.2 kcal./mole)[52] than benzaldehyde (35 kcal./mole).[52] A further analogy is provided by the observation that the heat of hydrogenation of pentadiene-1,3 to pentene-1 is 1.1 kcal. lower than that of crotonaldehyde to butyraldehyde.[2c]

HOUSTON, TEX.
NEW HAVEN, CONN.
KATONAH, N. Y.

(49) R. D. Brown, *J. Chem. Soc.*, 2670 (1951).

(50) H. J. Dauben and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951).

(51) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(52) The styrene and benzaldehyde values given here are calculated by comparable methods from combustion data (see ref. 24, pp. 98, 99).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Heats of Hydrogenation. IV. Hydrogenation of Some *cis-* and *trans-*Cycloölefins[1]

BY RICHARD B. TURNER AND W. R. MEADOR

RECEIVED FEBRUARY 25, 1957

The heats of hydrogenation of the *cis-* and *trans-*cycloöctenes, cyclononenes and cyclodecenes have been measured in acetic acid solution at 25°. The values (kcal./mole) obtained for these olefins are as follows: *cis-*cycloöctene, −22.98 ± 0.10, *trans-*cycloöctene, −32.24 ± 0.21; *cis-*cyclononene, −23.62 ± 0.07, *trans-*cyclononene, −26.49 ± 0.14; *cis-*cyclodecene, −20.67 ± 0.08, *trans-*cyclodecene, −24.01 ± 0.09.

The heats of hydrogenation of cyclopentene, cyclohexene, cycloheptene and of *cis-*cycloöctene were measured several years ago in the gas phase by Kistiakowsky and his associates. The results of this work (Table I) were correlated by Conn, Kistiakowsky and Smith,[2] who advanced a consistent interpretation of the data based upon consideration of non-bonded repulsions appearing in the products of the various hydrogenation processes. An important outcome of the investigation was the demonstration that the heat of hydrogenation of cyclopentene is 1.7 kcal./mole *lower* than that of cyclohexene, despite the fact that strain of the cyclopentene double bond is clearly *greater* than that of the olefinic linkage in cyclohexene. Al-

(1) The work reported in this paper was supported by the Eli Lilly Co., Indianapolis.

(2) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61**, 1868 (1939).