Tetrahedron, 1963, Vol. 19, pp. 1175 to 1184. Pergamon Press Ltd. Printed in Northern Ireland

A BOND ENERGY SCHEME—II
STRAIN AND CONJUGATION ENERGIES IN CYCLIC COMPOUNDS

J. D. Cox
National Chemical Laboratory, Teddington, Middlesex

(*Received* 25 *January* 1963)

Abstract—Strain energies in certain cyclic compounds, and conjugation energies in other cyclic compounds with delocalized π-electron systems are estimated with the aid of bond energy terms, of which some have been published and some are derived in the paper. The magnitudes of the strain energies found can in general be understood in terms of likely angular or torsional strain. The magnitudes of the conjugation energies found are appreciably lower than some previous estimates of these energies; attention is drawn to the uncertainties which remain in the calculation of conjugation energies from thermochemical data.

THE thermochemical calculations on benzene derivatives in Part I[1] employed bond energy terms for C—C and C—H bonds which were so chosen that the sum of the bond energy terms equalled the heat of atomization of the compound i.e. the conjugation energy resulting from delocalization of the π-electrons was considered to be distributed among the bonds. However, any attempt to extend this principle to heterocyclic compounds with delocalized π-electron systems would not be satisfactory because some gross assumptions would have to be made, e.g. that $E(C—C)_{bz}$ could be carried over to calculations on heterocyclic compounds. Similarly, whilst the strain energies of destabilized homocyclic compounds can be treated as being distributed among the bonds, treatment of the strain energies of destabilized heterocyclic compounds in this way is unsatisfactory. Hence thermochemical calculations on ring compounds (other than of the benzene series) are best carried out with the aid of bond energy terms derived from open chain compounds. Strain energies are then evaluated as positive differences between experimentally derived values of ΔH_f^0 (g) and calculated ones; conjugation energies in compounds with delocalized π-electrons are evaluated as negative differences between experimental values of ΔH_f^0 (g) and values calculated for the classical structures. The purpose of the present paper is to calculate strain or conjugation energies for a range of cyclic compounds. The treatment differs from other published treatments of this topic because cognizance has here been taken of the facts that (i) the energy of a C—X bond depends on the hybridization state of the carbon atom[1,2], (ii) there are differences in energy between primary, secondary and tertiary C—H bonds,[1,3] and (iii) there are next-nearest-neighbour interaction energies in oxygen-containing compounds.[1]

Derivation of bond energy terms

Before deriving conjugation or strain energies it is necessary to have available certain bond energy terms additional to those presented in Part I. Quantities needed for the calculation of the additional terms were taken from Part I, except for values

---

[1] J. D. Cox, *Tetrahedron* **18**, 1337 (1962).
[2] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959); **11**, 96 (1960).
[3] K. J. Laidler, *Canad. J. Chem.* **34**, 626 (1956).

of E(C_{sp^2}—H) and E(C_{sp^2}—C_{sp^2}) which have been recalculated (see below). The same symbolism is used as in Part I.

Olefines. The bond energy terms for C=C bonds, C_{sp^2}—C_{sp^2} bonds and C_{sp^2}—H bonds which were used in Part I had been taken from the work of Mackle and O'Hare[4], who showed that their values led to good agreement between Q_a (calc.) and Q_a (expt.) for a number of olefines. Substantially better agreement may be secured by recognizing the existence of two types of C_{sp^2}—H bond, viz. a (C_{sp^2}—H)′ bond when *sp*^{2} carbon is substituted by one hydrogen atom only, and a (C_{sp^2}—H)″ bond when *sp*^{2} carbon is substituted by two hydrogen atoms. A consequence of this new method of treating C_{sp^2}—H bonds is that the previously used value of E(C_{sp^2}—C_{sp^2}) needs to be revised.

From ΔH_f^0 (g) for ethylene = +12·5 kcal/mole[5] was derived E(C_{sp^2}—H)″ = 101·2.[*] From ΔH_f^0 (g) for 2-methylpropene = −4·0 kcal/mole[5] was derived E(C_{sp^2}—C_{sp^3}) = 89·6. From ΔH_f^0 (g) for propylene = +4·9 kcal/mole[5] was derived E(C_{sp^2}—H)′ = 100·5.

Calculated values of E(C—X) for C—X bonds in substituted olefines and benzenes are dependent on the values for E(C_{sp^2}—H) and E(C_{sp^2}—C_{sp^3}) used in the calculations. Since values of these two bond energy terms have now been changed from those given in Part I, it follows that values of the dependent bond energy terms should be changed also. However, the changes in the values of E(C_{sp^2}—X) or E(C_{bz}—X) are so small that there seems little point in giving revised values for these quantities until such time as more, or better, experimental values of ΔH_f^0 (g) for substituted olefines and benzenes are available.

In Table 1 experimental values of ΔH_f^0 (g) for the six pentenes, unconjugated pentadiene, and three of the butenes [the value for the fourth butene was used to derive

TABLE 1. CALCULATED AND OBSERVED HEATS OF FORMATION OF MONO-ENES AND DI-ENES

Compound	ΔH_f^0 (g), kcal/mole Calc.	ΔH_f^0 (g), kcal/mole Expt.[5]
Butene-1	−0·1	0·0
cis-Butene-2	−1·7	−1·7
trans-Butene-2	−2·7	−2·7
Pentene-1	−5·0	−5·0
cis-Pentene-2	−6·6	−6·7
trans-Pentene-2	−7·6	−7·6
2-Methylbutene-1	−9·0	−8·7
3-Methylbutene-1	−6·5	−6·9
2-Methylbutene-2	−10·6	−10·2
1,4-Pentadiene	+25·2	+25·2
trans-1,3-Pentadiene	+18·8	+18·7
2-Methyl-1,3-butadiene	+17·4	+18·1

---

[*] Here, and throughout the paper, the unit is kcal.

[4] H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.*, **57**, 1521 (1961).

[5] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh (1953).

$E(C_{sp^2}—C_{sp^3})$] are compared with values calculated from the bond energy terms. The calculated values for *cis*-butene-2, 2-methylbutene-2 and *cis*-pentene-2 contain a +1 kcal contribution to ΔH_f^0 (g), arising from the repulsion energy of the *cis* methyl groups, because it is well established that non-bonded interaction must be allowed for in *cis*-dialkyl ethylenes.[6,7] Excellent agreement between ΔH_f^0 (g) calc. and ΔH_f^0 (g) expt. is found for all the olefines in Table 1. Calculated values of ΔH_f^0 (g) for the seventeen isomeric hexenes are not tabulated, but they are generally in very good agreement with the experimental values.[8] Only in one instance does the difference between ΔH_f^0 (g) calc. and ΔH_f^0 (g) expt. exceed 1 kcal/mole, namely that for 2,3-dimethylbutene-2 (tetramethyl ethylene), where the compound is 1·4 kcal/mole less stable than calculated; since the calculated value already contains an allowance for *cis*-methyl repulsion, it must be concluded that strain due to overcrowding in this molecule is considerable.

Conjugated di-enes. After the establishment of bond energy terms for mono-enes, the problem of deriving a value for $E(C_{sp^2}—C_{sp^2})$ must be faced. By consideration of thermochemical data alone it is not possible to separate $E(C_{sp^2}—C_{sp^2})$ from the conjugation energy of the molecules which contain a $C_{sp^2}—C_{sp^2}$ bond. Dewar and Schmeising[2] have argued, largely from consideration of bond lengths, that the conjugation energy of butadiene is probably less than 1 kcal/mole. As a corollary the $C_{sp^2}—C_{sp^2}$ bond must be particularly strong, and it is this strong bond which is to be regarded as the main source of the stability of conjugated dienes. For purposes of bond energy calculations, a conjugation energy of 1 kcal/mole is small enough to be ignored. Hence, if it be assumed that *the conjugation energy of butadiene is in fact zero*, then a value for $E(C_{sp^2}—C_{sp^2})$ can immediately be derived, and this is the basis of the calculation which follows. $E(C_{sp^2}—C_{sp^2}) = 98·0$ was derived from ΔH_f^0 (g) for butadiene = +26·3 kcal/mole.[5] Experimental values of ΔH_f^0 (g) for two 1,3-conjugated di-enes are compared in Table 1 with values of ΔH_f^0 (g) calculated from the bond energy terms; agreement is quite good.

Oxygen-containing compounds. For calculations on furan and dihydropyran, values of $E(C_{sp^2}—O)$ and $E(C_{sp^2}—H)_o$ are needed. Pilcher *et al.*[9] have published experimental values of ΔH_f^0 (g) of two vinyl ethers and also estimates of the conjugation energies of these ethers. From these data and a value for ΔH_f^0 (g) of ethyl 1-methylvinyl ether (calculated from Kistiakowsky's measurement[10] of the heat of hydrogenation and ΔH_f^0 (g) calc. for ethyl isopropyl ether = −69·0 kcal/mole) the required bond energy terms were derived. Thus $E(C_{sp^2}—O) = 93·95$ was derived from ΔH_f^0 (g) for ethyl 1-methylvinyl ether = −43·9 kcal/mole, with the assumption that the conjugation energy is 2·8 kcal/mole[9] in this compound. $E(C_{sp^2}—H)_o = 99·3$ was derived from ΔH_f^0 (g) for divinyl ether = −3·0 kcal/mole[9], with the assumption that the conjugation energy is 1·4 kcal/mole[9] in this compound.

It should be noted that $E(C_{sp^2}—O) - E(C_{sp^3}—O) = 2·2$, that $E(C_{sp^2}—H)_o - E(C_{sp^3}—H)'_o = 4·9$, that $E(C_{sp^2}—C_{sp^2}) - E(C_{sp^2}—C_{sp^3}) = 4·6$, that $E(C_{sp^2}—H)'' - E(C_{sp^3}—H)'' = 3·7$ and that $E(C_{sp^2}—H)' - E(C_{sp^3}—H)' = 3·9$. It may be

---

[6] C. J. McGinn, *J. Chem. Phys.* **35**, 1511 (1961).

[7] M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York (1956).

[8] H. F. Bartolo and F. D. Rossini, *J. Phys. Chem.* **64**, 1685 (1960).

[9] G. Pilcher, H. A. Skinner, A. S. Pell and A. E. Pope, *Trans. Faraday Soc.* **59**, 316 (1963).

[10] H. A. Skinner, *Modern Aspects of Thermochemistry* ,Royal Institute of Chemistry, London (1958).

surmised that in general $E(C_{sp^2}—X) - E(C_{sp^3}—X) \approx 4$, and this approximation will be used for calculating $E(C_{sp^2}—N)$ and $E(C_{sp^2}—S)$, in the absence of any thermochemical data for N or S substituted olefines.

Nitrogen-containing compounds. In Part I the group energy $E(C_{sp^3}—NH_2) = 275{\cdot}1$ was derived. No attempt was made to break down this group energy into its constituent bond energy terms, but for calculations on nitrogen-containing heterocyclic compounds such a break-down is necessary. Ideally $E(C_{sp^3}—N)$ should be derived from ΔH_f^0 (g) of an aliphatic tertiary amine; $E(N—H)''$ would then follow from the available value of $E(C_{sp^3}—NH_2)$, whilst $E(N—H)'$ would follow from ΔH_f^0 (g) of any secondary amine. However, no *reliable* value of ΔH_f^0 (g) for an aliphatic tertiary amine is available,[11] so that a less rigorous approach must be adopted. It was assumed that $E(N—H)''$ and $E(N—H)'$ were equal. $E(N—H) = 92{\cdot}5$ and $E(C_{sp^3}—N) = 72{\cdot}1$ were then derived simultaneously from ΔH_f^0(g) for n-butylamine $= -22{\cdot}5$ kcal/mole[12], and ΔH_f^0 (g) for diethylamine $= -17{\cdot}0$ kcal/mole.[13] Experimental values of ΔH_f^0 (g) for a few amines are compared in Table 2 with values calculated from the bond energy terms.

$E(C_{sp^2}—N) \approx 76$ was estimated by use of the approximate relationship given above. $E(C{=}N) \approx 134$ was derived from ΔH_f^0 (g) for n-butylisobutyraldimine ≈ -22 kcal/mole,[14] on the assumption that $E(C_{sp^3}—N)$ does not alter when nitrogen is doubly-bonded. $E(N—N) \approx 42$ was derived from ΔH_f^0 (g) for hydrazine $\approx +22$ kcal/mole[15]. The present value for E(N—N) differs slightly from that given by Gunn and Green[15] because they used $E(N—H) = 93{\cdot}4$ (in ammonia) whereas $E(N—H) = 92{\cdot}5$ (in amines) is used here.

TABLE 2. CALCULATED AND EXPERIMENTAL HEATS OF FORMATION OF AMINES

Compound	ΔH_f^0 (g) kcal/mole		Source of expt. value
	Calc.	Expt.	
Methylamine	− 7·8	− 6·7	Rossini[16]
Dimethylamine	− 7·2	− 6·6	Rossini[16]
Ethylamine	−12·7	−11·6	Rossini[16]
s-Butylamine	−24·0	−25·2	Evans[12]
t-Butylamine	−27·3	−28·6	Evans[12]
n-Butyl isobutylamine	−38·2	∼ −42	Bedford[14]

Sulphur-containing compounds. It was shown in Part I that the experimental heats of formation of thiols and sulphides can be reproduced quite well by bond energy terms which make no allowance for next-nearest-neighbour interactions i.e. a C—H bond adjacent to a sulphur atom was considered to have the same energy as the corresponding type

---

[11] L. H. Long and J. F. Sackman, *Trans. Faraday Soc.* 53, 1606 (1957).

[12] F. W. Evans, D. M. Fairbrother and H. A. Skinner, *Trans. Faraday Soc.* 55, 399 (1959).

[13] An unpublished value from the National Bureau of Standards, cited by P. A. Fowell and C. T. Mortimer, *J. Chem. Soc.* 2913, (1959).

[14] A. F. Bedford, P. B. Edmondson and C. T. Mortimer, *J. Chem. Soc.* 2927 (1962).

[15] S. R. Gunn and L. G. Green, *J. Phys. Chem.* 65, 779 (1961).

[16] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards, Washington D.C. (1952).

of C—H bond in a hydrocarbon. There is thus a difference between the methods used for treating sulphur compounds and oxygen compounds, and some justification for neglect of next-nearest-neighbour interactions in sulphur compounds is perhaps desirable. The justification rests chiefly on the fact that the heat of isomerization of n-butanthiol to t-butanthiol (−5·1 kcal/mole[1]) does not differ very significantly from the heat of isomerization of n-pentane to neopentane (−4·7 kcal/mole[5]) or from the heat of isomerization of n-butyl bromide to t-butyl bromide (−5·4 kcal/mole[1]); hence the heats of isomerization of aliphatic thiols can be accounted for in the same way as can the heats of isomerization of aliphatic hydrocarbons i.e. in terms of the energy differences between primary, secondary and tertiary C—H bonds.[3] This situation is in contrast with that prevailing in the aliphatic alcohol series, where the heat of isomerization of n-butanol to t-butanol is −8·8 kcal/mole.[17]

For calculations on thiophenes a value of $E(C_{sp^2}—S)$ was needed. $E(C_{sp^2}—S) \approx 70$ was estimated by use of the approximate relationship $E(C_{sp^2}—X) - E(C_{sp^3}—X) \approx 4$.

Conjugation and strain energies in cyclic compounds

Relevant bond energy terms and bond contributions to molecular heats of formation have been assembled in Table 3. With the aid of these quantities, ΔH_f^0 (g) for a

TABLE 3. A SUMMARY OF BOND ENERGY TERMS AND BOND CONTRIBUTIONS TO MOLECULAR HEATS OF FORMATION (KCAL)

Bond	Bond energy term	Bond contribution to ΔH_f^0 (g)
$C_{sp^3}—C_{sp^3}$	85·0	$+0{\cdot}4_5$
$C_{sp^3}—C_{sp^2}$	89·6	$-4{\cdot}1_5$
$C_{sp^2}—C_{sp^2}$	98·0	$-12{\cdot}5_5$
$(C_{sp^3}—H)'$	96·6	$-1{\cdot}7_8$
$(C_{sp^3}—H)''$	97·5	$-2{\cdot}6_8$
$(C_{sp^3}—H)'''$	98·3	$-3{\cdot}4_8$
$(C_{sp^2}—H)'$	100·5	$-5{\cdot}6_8$
$(C_{sp^2}—H)''$	101·2	$-6{\cdot}3_8$
$(C_{sp^3}—H)'_o$	94·4	$+0{\cdot}4_2$
$(C_{sp^3}—H)''_o$	95·3	$-0{\cdot}4_8$
$(C_{sp^2}—H)_o$	99·3	$-4{\cdot}4_8$
$C_{sp^3}—O$	91·75	$-19{\cdot}2_5$
$C_{sp^2}—O$	93·95	$-21{\cdot}4_6$
$C_{sp^3}—N$	72·1	$+8{\cdot}2_4$
$C_{sp^2}—N$	~76	~ −4
$C_{sp^3}—S$	65·75	$+5{\cdot}4_8$
$C_{sp^2}—S$	~70	~ +1
$C_{sp^3}—C_{co}$	93·1	$-7{\cdot}6_5$
C=C	133·	+37·9
C=O	160·5	$-15{\cdot}5_1$
C=N	~134	~ +27
N—N	~42	~ +33
O—H	107·95	$-26{\cdot}0_9$
N—H	92·5	$-2{\cdot}7_8$
S—H	81·9	$-1{\cdot}3_1$

---

[17] H. A. Skinner and A. Snelson, *Trans. Faraday Soc.* **56**, 1776 (1960).

TABLE 4. CALCULATED AND EXPERIMENTAL HEATS OF FORMATION OF CYCLIC COMPOUNDS

Compound	ΔH_f^0 (g) kcal/mole Calc.	ΔH_f^0 (g) kcal/mole Expt.	ΔH_f^0 (g) expt. $-\Delta H^0$ (g) calc.	Source of expt. value
Cyclopropane	−14·8	+12·7	27·5	Knowlton[18]
Spiropentane	−18·8	+44·2	63·0	Fraser[19]
Cyclobutane	−19·7	+6·4	26·1	Kaarsemaker[20]
Cyclopentane	−24·6	−18·5	6·1	Rossini[5]
Cyclohexane	−29·5	−29·4	0·1	Rossini[5]
Cycloheptane	−34·4	−28·3	6·1	Kaarsemaker[20]
Cycloöctane	−39·4	−29·7	9·7	Kaarsemaker[20]
Cyclononane	−44·3	−31·8	12·5	Kaarsemaker[20]
Cyclopentanol	−64·2	−57·6	6·6	Sellers[21]
Cyclopentanthiol	−16·9	−11·4*	5·5	McCullough[22]
Cyclopentyl methyl sulphide	−20·5	−15·4*	5·1	McCullough[22]
Cyclopentanone	−50·9	−46·3	4·6	Sellers[21]
Cyclohexanol	−69·1	−68·4	0·7	Sellers[21]
Cyclohexanthiol	−21·8	−22·9*	−1·1	McCullough[22]
Cyclohexanone	−55·9	−54·1	1·8	Sellers[21]
Ethylene oxide	−40·0	∼−12	∼28	Rossini[16]
Propylene oxide	−48·6	−22·2	26·4	Sinke[23]
Ethylene imine	+3·5	∼+26	∼23	Nelson[24]
Ethylene sulphide	+0·7	+19·3	18·6	Guthrie[25]
Thiacyclobutane	−4·3	+14·6*	18·9	McCullough[22]
Pyrrolidine	−6·4	−0·9	5·5	Hildenbrand[26]; McCullough[27]
Tetrahydrofuran	−49·8	−43·1	6·7	Cass[28]
1,3-Dioxolan	−79·5	−72·2	7·3	Fletcher[29]
Thiacyclopentane	−9·2	−8·2*	1·0	McCullough[22]
Piperidine	−11·3	−11·3	0	McCullough[30]
Tetrahydropyran	−54·8	−52·6	2·2	Snelson[31]
1,3-Dioxan	−84·4	−81·5	2·9	Snelson[31]
1,4-Dioxan	−80·0	−76·0	4·0	Snelson[31]
5,5′-Spiro bis-1,3-dioxan	−158·0	−154·5	3·5	Fletcher[29]
Thiacyclohexane	−14·1	−15·1*	−1·0	McCullough[22]
Cyclopentene	+3·0	+7·9	4·9	Rossini[5]
1,3-Cyclopentadiene	+26·8	∼+32	∼5	ΔH_h (g) (taken from Skinner[10]) combined with ΔH_f^0 (g) of the appropriate cyclane (taken from this table)
Cyclohexene	−1·9	∼−1	∼1	
1,3-Cyclohexadiene	+21·9	∼+26	∼4	
Cycloheptene	−6·8	∼−2	∼5	
1,3-Cycloheptadiene	+17·0	∼+23	∼6	
1,3,5-Cycloheptatriene	+40·8	∼+45	∼4	
Cycloöctene	−11·7	∼−6	∼6	
Cycloöctatetraene	+55·9	+71·1	15·2	ΔH_f^0 (liq) from Prosen[32]; $\Delta H_{v,25^\circ}$ from Scott.[33]
Dihydropyran	−27·9	−29·9	−2·0	Cass[28]
Benzene	∼+42	+19·8	∼−22	Rossini[5]
Thiophen	∼+43	+27·5	∼−16	Hubbard[34]
2-Methylthiophen	∼+34	+20·2	∼−14	Pennington[35]
3-Methylthiophen	∼+34	+19·9	∼−14	McCullough[36]
Furan	∼0	−8·3	∼−8	Guthrie[37]
Pyrrole	∼+46	∼+31	∼−15	Klages[38]
Pyrazole	∼+70	∼+43	∼−27	Bedford[14]
Imidazole	∼+58	∼+31	∼−27	Bedford[14]
Pyridine	∼+53	+33·6	∼−19	Andon[39]
1,2-Diazine	∼+77	+66·5	∼−10	Tjebbes[40]
1,3-Diazine	∼+65	+47·0	∼−18	Tjebbes[40]
1,4-Diazine	∼+65	+46·9	∼−18	Tjebbes[40]

cyclic compound can be estimated by either of two routes: (i) the bond contributions to molecular heats of formation are summed, or (ii) the bond energy terms are summed and the heats of atomization of the constituent elements[1] are subtracted from the sum. (The result by route (i) will be in the thermochemical convention that an exothermic compound has a negative heat of formation; that by route (ii) will require a change of sign to bring it into the thermochemical convention). Calculated values of ΔH^0 (g) for numerous homocyclic and heterocyclic compounds are compared in Table 4 with the experimental values.

Ring strain in cyclanes and their derivatives. Much has been written about ring strain in cyclanes e.g.[7,20], and the present analysis does nothing to change the familiar picture, if the positive differences in the fourth column of Table 4 are attributed to strain. Thus the values indicate (i) very high strain in cyclopropane and cyclobutane, resulting from distortion of valency angles, (ii) 6 kcal of strain in cyclopentane,

---

* The numerical values in McCullough and Good's paper[22] differ from those in the table because these authors used S_2 (g) as the reference state for sulphur, whereas S (rhombic cryst.) has been employed as the reference state in the present work. Conversion from one reference state to the other was made with the aid of data from W. H. Evans and D. D. Wagman, *J. Res. Nat. Bur. Stand.* **49**, 141 (1952).

† ΔH_h (g) is the heat of hydrogenation of the compound in the gas phase. The measured values[10] of ΔH_h (g) actually referred to 82°C, but they may be taken to refer to 25°C without incurring an error greater than 1 kcal/mole.

[18] J. W. Knowlton and F. D. Rossini, *J. Res. Nat. Bur. Stand.* **43**, 113 (1949).

[19] F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stand.* **54**, 143 (1955).

[20] S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71**, 261 (1952).

[21] P. Sellers and S. Sunner, *Acta. Chem. Scand.* **16**, 46 (1962).

[22] J. P. McCullough and W. D. Good, *J. Phys. Chem.* **65**, 1430 (1961).

[23] G. C. Sinke and D. L. Hildenbrand, *J. Chem. Eng. Data* **7**, 74 (1962).

[24] R. A. Nelson and R. S. Jessup, *J. Res. Nat. Bur. Stand.* **48**, 206 (1952).

[25] G. B. Guthrie, D. W. Scott and G. Waddington, *J. Amer. Chem. Soc.* **74**, 2795 (1952).

[26] D. L. Hildenbrand, G. C. Sinke, R. A. McDonald, W. R. Kramer and D. R. Stull, *J. Chem. Phys.* **31**, 650 (1959).

[27] J. P. McCullough, D. R. Douslin, W. N. Hubbard, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, J. P. Dawson and G. Waddington, *J. Amer. Chem. Soc.* **81**, 5884 (1959).

[28] R. C. Cass, S. E. Fletcher, C. T. Mortimer, H. D. Springall and T. R. White, *J. Chem. Soc.* 1406 (1958).

[29] S. E. Fletcher, C. T. Mortimer and H. D. Springall, *J. Chem. Soc.* 580 (1959).

[30] J. P. McCullough, private communication.

[31] A. Snelson and H. A. Skinner, *Trans. Faraday Soc.* **57**, 2125 (1961).

[32] E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Amer. Chem. Soc.* **72**, 626 (1950).

[33] D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffman, *J. Amer. Chem. Soc.* **71**, 1634 (1949).

[34] W. N. Hubbard, D. W. Scott, F. R. Frow and G. Waddington, *J. Amer. Chem. Soc.* **77**, 5855 (1955).

[35] R. E. Pennington, H. L. Finke, W. N. Hubbard, J. F. Messerly, F. R. Frow, I. A. Hossenlopp and G. Waddington, *J. Amer. Chem. Soc.* **78**, 2055 (1956).

[36] J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, M. E. Gross, R. E. Pennington, J. F. Messerly, W. D. Good and G. Waddington, *J. Amer. Chem. Soc.* **75**, 5075 (1953).

[37] G. B. Guthrie, D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson and G. Waddington, *J. Amer. Chem. Soc.* **74**, 4662 (1952).

[38] F. Klages, *Chem. Ber.* **82**, 358 (1949).

[39] R. J. L. Andon, J. D. Cox, E. F. G. Herington and J. F. Martin, *Trans. Faraday Soc.* **53**, 1074 (1957).

[40] J. Tjebbes, *Acta Chem. Scand.* **16**, 916 (1962).

resulting from repulsion between eclipsed hydrogen atoms (torsional strain), (iii) no strain in cyclohexane, (iv) 6 kcal of strain in cycloheptane and somewhat more strain in cycloöctane and cyclononane. It is noteworthy that the strain energy in spiropentane, which has two C_3 rings, is more than double the strain energy in cyclopropane.

For substituted cyclanes, the present analysis leads to several conclusions: (i) there is a small strain energy in cyclohexanol, the magnitude of which, 0·7 kcal/mole, agrees with the accepted value,[41] viz. 0·6 ± 0·2 kcal/mole. (ii) There is 0·5 kcal/mole more strain in cyclopentanol than in cyclopentane. (iii) There is 1·8 kcal/mole of strain in cyclohexanone, in broad agreement with the finding of Brown *et al.*[42] (based on thermochemical data extant in 1954) but in disagreement with Pitzer and Donath's contention[41] that cyclohexanone is unstrained. (iv) Cyclopentanone apparently has 1·5 kcal/mole less strain than cyclopentane, which may be due to fewer hydrogen-hydrogen repulsions in the ketone than in cyclopentane.

Ring strain in saturated heterocyclic compounds. The strain energies of ethylene and propylene oxides are seen to be (Table 4) nearly the same as the strain energy of cyclopropane, whilst the strain energy of ethylene imine is only a little lower; the strain energy of ethylene sulphide is, however, appreciably less than the strain energy of cyclopropane. A related situation obtains in the four-membered rings, where there is 7 kcal/mole less strain in thiacyclobutane than in cyclobutane itself. Molecular orbital treatments of cyclopropane and cyclobutane, in terms of "bent bonds", have been published,[43] and there is clearly scope for theoretical investigations of the thia analogues, to determine the reason for their smaller strain energies.

Amongst the five-membered rings, the order of strain energies is: 1,3-dioxolan > tetrahydrofuran > cyclopentane > pyrrolidine > thiacyclopentane. The greater strain in the two oxa-compounds relative to cyclopentane may be angular in origin, since a C—O bond is shorter than a C—C bond; but the thermochemical evidence for strain in 1,3-dioxolan conflicts with the view of Lemieux *et al.*[44] that this molecule is substantially free from strain. The slightly smaller strain in pyrrolidine relative to cyclopentane may be due to a lessening of torsional strain in the aza-compound, since there are fewer hydrogen-hydrogen interactions. The strain in thiacyclopentane is quite small; perhaps the relatively long C—S bonds allow the ring to adopt a conformation such that the hydrogens are partially staggered. A similar picture is disclosed by the data for the six-membered rings where the oxa-compound is slightly strained, the dioxa-compounds more so and the aza- and thia-compound are unstrained.

Ring strain in compounds with olefinic unsaturation. The experimentally-derived value of the strain energy for cyclopentene (Table 4) is not immediately comparable with the theoretically calculated value[45] because the latter refers to 0°K, but it seems doubtful whether the experimental and calculated values are reconcilable (cf. cyclopentane[46]). According to the present analysis, the strain energy in cyclopentene is

---

[41] K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.* **81**, 3213 (1959).

[42] H. C. Brown, J. H. Brewster and H. Shechter, *J. Amer. Chem. Soc.* **76**, 467 (1954).

[43] C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.* 2851 (1962).

[44] R. U. Lemieux, J. D. Stevens and R. R. Fraser, *Canad. J. Chem.* **40**, 1955 (1962).

[45] C. W. Beckett, N. K. Freeman and K. S. Pitzer, *J. Amer. Chem. Soc.* **70**, 4227 (1948).

[46] R. Spitzer and H. M. Huffman, *J. Amer. Chem. Soc.* **69**, 211 (1947).

slightly *less* than the strain energy in cyclopentane. This finding is at first sight surprising, but it may be that the insertion of a double bond into the cyclopentane ring is accompanied by only a small increase in angular strain which is outweighed by a reduction in non-bonded interactions between hydrogen atoms, of which there are two fewer in the olefine. The magnitude of the strain energy found in cyclohexene, 1 kcal/mole, is compatible with Pitzer's calculated values.[45,47] Cycloheptene and cycloöctene appear to have slightly less strain energy than the corresponding cyclanes. Cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene and 1,3,5-cycloheptatriene appear to have strain energies which are not greatly different from those of the related cyclic mono-olefines. By contrast, the fully conjugated ring compound cycloöctatetraene is seen to be appreciably strained. Dihydropyran appears to be stabilized to a small extent, rather than strained; the conjugation energy found does not differ significantly from that of the related open chain compound ethyl vinyl ether.[9]

Conjugation energies. It would be appropriate to start this paragraph with a note on nomenclature. The terms "stabilization energy", "hydridization energy", "resonance energy", "delocalization energy" and "conjugation energy" have been used to describe the energy associated with the delocalization of π-electrons. Dewar and Schmeising[2] recommend that this energy should be described as "resonance energy" and that the term "conjugation energy" should be used for the difference between the experimental heat of atomization of a compound and the calculated heat of atomization of the classical structures. *Conjugation energies* are the subject of this section; they should not be equated with resonance energies, for reasons discussed by Dewar and Schmeising.[2]

Calculation of the heat of atomization of the Kekulé forms of benzene requires knowledge of E(C=C), $E(C_{sp^2}—H)'$ and $E(C_{sp^2}—C_{sp^2})$. Whilst values of the first two named bond energy terms may be regarded as satisfactorily established, the value of the last named may not be so regarded; the basis for the present choice of value has been given above. Because the chosen value of $E(C_{sp^2}—C_{sp^2})$ is possibly up to 1 kcal higher than the true value (because the conjugation energy of butadiene may be up to 1 kcal/mole), it follows that the conjugation energies now to be presented are perhaps up to x kcal/mole lower than the true values, where x represents the number of $C_{sp^2}—C_{sp^2}$ bonds in a classical structure.

According to the present scheme, the conjugation energy of benzene is 22 kcal/mole (see the fourth column of Table 4). The conjugation energies of thiophen and its two methyl derivatives are seen to be rather less, and the conjugation energy of furan much less, than the value for benzene. No great difference between the conjugation energies of benzene and thiophen was to have been expected, since the replacement of —CH=CH— by S can be effected with little alteration to the molecular orbitals.[48] With regard to furan, Badger[49] has summarized the evidence for supposing that π-conjugation is much less complete than it is in benzene, but that conjugation nevertheless occurs. Hence the conjugation energy now found for furan, 8 kcal/mole seems not unreasonable.

The calculation of conjugation energies in nitrogen-containing heterocycles is

---

[47] K. S. Pitzer, *Science* **101**, 672 (1945).

[48] A. D. Walsh, *Quart. Revs.* **2**, 73 (1948).

[49] G. M. Badger, *The Chemistry of Heterocyclic Compounds* Academic Press, London (1961).

particularly difficult, because several of the bond energy terms necessary for the calculations are not known with certainty. But, notwithstanding their imprecision, the present calculations serve to show that previous estimates of the conjugation energies of some nitrogen-containing heterocycles,[50,51] based on simpler bond energy schemes, were too high.

The conjugation energy found for pyrrole (Table 4) is intermediate between the values found for benzene and furan, and is close to the value for thiophen. This finding is in accord with Badger's qualitative predictions,[49] which indicates that the uncertainty in the calculation for pyrrole is not large. [The uncertainty in question relates to $E(C_{sp^2}—N)$, the estimated value for which applies to pyramidal nitrogen, whereas the nitrogen atom in pyrrole is trigonal (sp^2) and two of its electrons contribute to the π-bond system.[52] It is interesting to note that the length of a $C_{sp^2}-N$ bond has been shown to be independent of the valence state of the nitrogen atom,[53] so that energy effects accompanying a change of valence of nitrogen would be expected to be small].

The conjugation energy found for pyridine is only a little less than that found for benzene, but the energy term used for the

$$-\overset{|}{C}\ N-$$

bond was that for sp^2 carbon bonded to pyramidal nitrogen whereas in pyridine the nitrogen atom is trigonal and one of its electrons contributes to the π-bond system.[52] Possibly, therefore, the value of the conjugation energy for pyridine in Table 4 is an over-estimate.

The calculation for pyrazole is rendered uncertain by the value used for E(N—N), which strictly applies to pyramidal nitrogen. The calculation for imidazole is rendered uncertain for the reasons given above with respect to pyrrole and pyridine. It must be regarded as coincidental that the conjugation energies for pyrazole and imidazole shown in Table 4 are equal; possibly both values are over-estimates.

The calculation for 1,2-diazine, which applies to the valence bond structure with a N—N single bond, involves a similar uncertainty to that in the calculation for pyrazole. The calculations for 1,3- and 1,4-diazine involve a similar uncertainty to that in the calculation for pyridine. Again, the values of the conjugation energies for the diazines given in Table 4 may be over-estimates.

Acknowledgements—I wish to thank Drs. G. Pilcher and J. P. McCullough for sending me details of their work (on vinyl ethers and piperidine respectively), before its publication.

---

[50] L. Pauling, *The Nature of the Chemical Bond* (3rd Edition), Cornell University Press, Ithaca, N.Y. (1960).

[51] G. W. Wheland, *Resonance in Organic Chemistry* Wiley, New York (1955).

[52] H. Hamano and H. F. Hameka, *Tetrahedron* **18**, 985 (1962).

[53] A. I. Finkel'shtein, *J. Phys. Chem. U.S.S.R.* **35**, 1358 (1961).