A Molecular-orbital Theory of Organic Chemistry. Part VII. The Additivity of Bond Energies in Unconjugated Systems.*

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The problem of additivity of bond energies in unconjugated compounds is discussed. The effect of interactions between localised bonds is calculated by perturbation theory, and it is found that the effect of such interactions vanishes to a first approximation. The second-order effects can to a large extent be absorbed into the empirical bond energies. In this way the additivity of bond energies in such compounds is explained without postulating localisation of electrons in specific bonds. Departures from additivity are satisfactorily interpreted and relations obtained which are shown to be in close agreement with experiment. It is deduced that the important interactions are those between adjacent bonds rather than 1 : 3 interactions of the type postulated in hyperconjugation. The present treatment avoids most of the assumptions made in the usual M.O. treatment and its conclusions should be correspondingly reliable.

IN previous papers of this series (Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3345, 3350, 3353, 3355, 3357) a general molecular-orbital treatment of organic chemistry was discussed and applied to the study of conjugated systems. Here unconjugated systems will be discussed in similar terms.

Unconjugated systems have been little investigated theoretically, and there has been a tendency to regard the bonds in such compounds as being formed by localised pairs of electrons with no significant interaction. This view seems to be supported by the fact that many properties of such compounds are additive functions of the bonds in them: for example, the heats of formation, dipole moments, and molar refractivities.

It has become apparent in recent years that this is too naïve. The electrons in a molecule are not localised in specific bonds but are dispersed to a greater or less extent over the whole molecule. It is true that the resonance theory appears to support bond localisation, but it does so only by virtue of its assumption that the ground states of molecules can be represented adequately in terms of unexcited structures. There is no theoretical justification for this, and it has been shown recently that the practical success of the resonance theory cannot be taken as evidence for the truth of its basic assumptions (Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, 1952, *A*, **214**, 482). The apparent additivity of bond properties then raises an interesting theoretical problem which has not yet been convincingly solved.

Lennard-Jones and his collaborators (*Proc. Roy. Soc.*, 1949, *A*, **198** 1, 14; 1950, *A*, **202**, 155, 166, 323, 336) have examined the situation in unconjugated molecules in terms of the molecular-orbital theory. They found that the usual delocalised molecular orbitals in such a system can be replaced by an equivalent set of orbitals each essentially localised in a single bond. According to them an unconjugated molecule can be regarded in two different but equivalent ways: as a system in which the electrons occupy either delocalised molecular orbitals or localised " equivalent orbitals." The additivity of bond properties follows naturally, but the picture suffers from two defects. First, it does not explain in a simple qualitative manner why similar localised equivalent orbitals are not available in conjugated systems (see Hall, *Proc. Roy. Soc.*, 1950, *A*, **202**, 336, for the equivalent orbital treatment); and secondly, it does not account in any simple way for the second-order deviations from additivity of bond properties in unconjugated systems.

Not only are these second-order deviations appreciable but they also seem to follow definite rules. Platt (*J. Chem. Phys.*, 1947, **15**, 419), found empirically that the heats of formation of paraffins can be expressed with remarkable accuracy by a single set of bond

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* Part VI, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.

energies, together with a set of explicit corrections for structural features such as chain branching

Lennard-Jones and his collaborators have shown that an unconjugated molecule can be represented to a first approximation in terms of localised bonds. In considering such molecules to a higher approximation it is natural to regard the interactions between these localised bonds as small perturbations and to calculate their effect on the ideal localised structure by use of perturbation theory. This programme follows naturally from the earlier papers of this series where similar perturbation methods were used in discussions of the structures and properties of conjugated molecules.

We have taken as the unperturbed system one in which the bonds are represented by simple L.C.A.O. M.O. wave functions. Although these may differ from the equivalent orbitals of Lennard-Jones *et al.*, they serve equally well as a basis for the perturbational treatment; for it can be shown that the net effect of the mutual interaction of the occupied (bonding) orbitals vanishes (Brown and Dewar, *J.*, 1953, 2406). The only interactions that need to be considered are those between occupied (bonding) and unoccupied (antibonding) orbitals.

In this perturbation treatment overlap is necessarily neglected. It would of course be possible to include overlap in a variational treatment of the problem, using the localised molecular orbitals as a basis (cf. Dewar, *Proc. Camb. Phil. Soc.*, 1948, **45**, 648); but such a treatment would be tedious and unsuitable for the present purpose. Moreover, the inclusion of overlap in the simple L.C.A.O. treatment seems to make no appreciable difference, at any rate in the calculation of ground-state energies.

Brown (*J.*, 1953, 2615) considered the problem of localisation from a different but analogous point of view. He used the united-atom concept, expressing the molecular orbitals in a molecule as linear combinations of united-atom orbitals for the individual bonds. The appropriate linear combinations are found by a variation method with inclusion of overlap. This treatment is equivalent to that outlined above, except that only bonding orbitals are used as a basis. The omission of antibonding orbitals greatly simplifies the variational treatment.

If this correspondence between the two treatments is accepted, it is apparent that our approximations are more valid than Brown's. It is unjustifiable in theory to neglect the contribution of antibonding orbitals, since the set of functions used as a basis is then incomplete; and the practical consequences of such an omission are also rather striking. Consider, for example, the analogous treatment of a conjugated or aromatic hydrocarbon, derived by perturbation of one classical structure in which there are localised two-centre π-bonds. The M.O.'s for the molecule can be expressed as linear combinations of the π-M.O.'s of the individual π-bonds in the classical structure, the results being identical with those given by the usual L.C.A.O. M.O. treatment (cf. Dewar, *loc. cit.*, 1948). If, however, only the *bonding* M.O.'s are used as a basis, the total energy of the π-electrons turns out to be the same as in the classical structure; thus, in benzene, only three M.O.'s can be constructed from the bonding π-M.O.'s of a Kekulé structure, and the total energy of these is the same (-3β) as the total energy of the three localised bonding π-M.O.'s in the Kekulé structure. It is obvious therefore that if antibonding orbitals are neglected in this connection, the calculated resonance energies of all hydrocarbons are zero. If one regards an aromatic hydrocarbon as being derived from a classical structure by interaction between the localised π-bonds, it is evident that the interactions leading to resonance stabilisation are those between bonding and antibonding M.O.'s.

Resonance energy in our approximation is indeed a second-order effect, due to the mutual perturbation of bonding and antibonding orbitals. It is therefore impossible to place any confidence in a molecular-orbital treatment where the contribution of antibonding orbitals is neglected. On the other hand no case is known where the omission of overlap leads to serious practical errors in ground-state energies of molecules; and our neglect of this factor should not qualitatively effect our conclusions. The nature of our approximations will be considered in more detail below.

It is curious that the conclusions reached by Brown and by us agree closely in form, although the methods followed are basically dissimilar. However, our method predicts accurate additivity of bond energies to a first approximation, departures from additivity being second-order effects, whereas Brown finds first-order departures from additivity. The experimental evidence seems to suggest that departures from additivity are second-order effects since they are so small.

METHOD AND RESULTS

The interaction between bonds is calculated by use of perturbation theory. In the unperturbed system the electrons occupy a set of localised non-interacting two-centre orbitals. The set of unperturbed orbitals also includes the corresponding antibonding orbitals. It is assumed that all bonds of a given type are similar in the unperturbed state. The energies of the bonding and antibonding M.O.'s between two atoms R, S are written respectively as ε^{+}_{RS}, ε^{-}_{RS}.

First-order Perturbations ; Mutual Interactions of Bonding Orbitals.—First-order perturbations due to interaction of bonds arise only in the case of degeneracy (cf. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341), *i.e.*, when the interacting bonds are similar. First-order perturbations therefore represent a special case of mutual interaction between filled or bonding orbitals. Now it can be shown (cf. Brown and Dewar, *J.*, 1953, 2406) that the total energy of a set of occupied orbitals is unaffected by interactions between them; although such interactions alter the individual energy levels they do not, therefore, alter the total energy of all the orbitals. It follows at once that the heat of formation of a molecule will be an additive function of the individual bond energies, to a first approximation, no matter what interactions arise between the bonds and no matter how large the resulting delocalisation of the electrons in the system. Brown (*loc. cit.*) reached the same conclusion.

Second-order Perturbations.—In a molecule there are commonly a number of bonds of each type (C–H, C–C, etc.). In considering the interactions of such bonds, the individual orbitals ($\phi^{\pm}_{RS}$) of each type should first be replaced by appropriate linear combinations (ψ_{RS}), found by the first-order perturbation theory for degenerate systems; and the second-order perturbations should be calculated by using these perturbed orbitals. This complicated procedure is totally unnecessary if the degenerate levels are all filled, as in the case here, and if only the total energy of the whole set of degenerate levels is required. In that case it can be shown (see Appendix A) that the same result is obtained if the second-order perturbations are calculated by using the set of unperturbed orbitals $\phi^{\pm}_{RS}$ and simply omitting terms with vanishing denominators. Also since mutual interactions between pairs of occupied orbitals cancel (see above), the second-order perturbations reduce to a series of terms of the form :

$$\delta E_{RS.TU} = \left[\int \phi^{+}_{RS} \, . \, P_{RS.TU}\phi^{-}_{TU} \, . \, d\tau\right]^{2}/(\varepsilon^{+}_{RS} - \varepsilon^{-}_{TU}) \quad . \quad . \quad . \quad . \quad (1)$$

where $\delta E_{RS.TU}$ represents the second-order effect on the energy of the bonding orbital ϕ^{+}_{RS} due to interaction with the antibonding orbital ϕ^{-}_{TU} and $P_{RS,TU}$ is the term in the Hamiltonian representing this interaction.

In order to use this expansion some assumption must be made concerning the types of interaction between bonds. It will be assumed that the only interactions of importance are those between nearest-neighbour bonds, *i.e.*, bonds with a common atom such as the R–S and S–T bonds in RST. The total interaction energy in this case will be given by

$$\delta E_{RST} = \frac{\left[\int \phi^{+}_{RS} \, . \, P_{RS,ST}\phi^{-}_{ST} \, . \, d\tau\right]^{2}}{\varepsilon^{+}_{RS} - \varepsilon^{-}_{ST}} + \frac{\left[\int \phi^{+}_{ST} \, . \, P_{ST.RS} \, . \, \phi^{-}_{RS}\right]^{2}}{\varepsilon^{+}_{ST} - \varepsilon^{-}_{RS}}$$

Here δE_{RST}, the R–S–T interaction energy, will be a constant characteristic of the bonds concerned, if, as has been assumed, all bonds of a given type are similar in the unperturbed system and if the stereochemistry of the central atom S is also fixed.

These basic interaction energies can then be regarded as empirical parameters; and the total second-order perturbation energy can be expressed in terms of them simply by counting the number of structures of each type in the molecule.

Application to Paraffins.—In paraffins there are three basic interacting structures, C–C–C, C–C–H, and H–C–H. Denote the corresponding second-order perturbation energies by a, b, c, respectively. The total second-order perturbation energy can be expressed at once in terms of these parameters. This is done for the first five normal hydrocarbons in Table 1, where it is seen that, after ethane, the second-order perturbation increases by a uniform increment ($a + 4b + c$) for each methylene group; this can be shown to hold generally. If it also held for methane–ethane the second-order perturbation energy for methane would be ($2b + 5c - a$).

Suppose the ideal bond energies of localised C–C and C–H bonds to be respectively E°_{CC}, E°_{CH} and define empirical C–C and C–H bond energies E_{CC}, E_{CH} by the relations

$$\left.\begin{aligned} E_{\mathrm{CH}} &= E^{\circ}_{\mathrm{CH}} + \tfrac{1}{4}(2b + 5c - a) \\ E_{\mathrm{CC}} &= E^{\circ}_{\mathrm{CC}} + \tfrac{3}{2}(a + 2b - c) \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Then it is evident that use of these empirical bond energies in calculating heats of formation of normal paraffins other than methane will give values correct to a second approximation. For instance, the calculated heat of formation of propane will be given by

$$\begin{aligned} 2E_{\mathrm{CC}} + 8E_{\mathrm{CH}} &= 2E^{\circ}_{\mathrm{CC}} + 8E^{\circ}_{\mathrm{CH}} + 3(a + 2b - c) + 2(2b + 5c - a) \\ &= 2E^{\circ}_{\mathrm{CC}} + 8E^{\circ}_{\mathrm{CH}} + (a + 10b + 7c) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4) \end{aligned}$$

and the final second-order correction agrees with that given in Table 1.

We can therefore choose empirical bond energies for the C–C and C–H bonds which will give calculated heats of formation for the *n*-paraffins correct to a second approximation. Since the interactions between bonds in paraffins are undoubtedly small, the third-order terms must be very small indeed; the extraordinarily close approximation to additivity shown by heats of formation of *n*-paraffins is not therefore surprising.

TABLE 1. *Total second-order perturbations in normal paraffins.*

Paraffin	Number of structures C–C–C	 C–C–H	 H–C–H	Total perturbation
CH_4	—	—	6	$6c$
C_2H_6	—	6	6	$6b + 6c$
C_3H_8	1	10	7	$a + 10b + 7c$
C_4H_{10}	2	14	8	$2a + 14b + 8c$
C_5H_{12}	3	18	9	$3a + 18b + 9c$

The increment $(a + 4b + c)$ applies in all cases where a paraffin is extended by replacing a primary hydrogen atom by a methyl group. Replacing secondary or tertiary hydrogen gives different increments. The various values are

$$\left.\begin{aligned} \mathrm{R{\cdot}CH_3} &\longrightarrow \mathrm{R{\cdot}CH_2{\cdot}CH_3}; \quad \delta E = a + 4b + c \\ \mathrm{R_2CH_2} &\longrightarrow \mathrm{R_2CH{\cdot}CH_3}; \quad \delta E = 2a + 2b + 2c \\ \mathrm{R_3CH} &\longrightarrow \mathrm{R_3C{\cdot}CH_3}; \quad \delta E = 3a + 3c \end{aligned}\right\} \quad . \; . \; . \; . \quad (5)$$

Now replacement of a secondary hydrogen atom gives a paraffin with a branch or, equivalently, with a tertiary $\geqslant$CH group; comparison with an isomer in which a primary hydrogen atom is replaced by a methyl group shows that the second-order perturbation energies differ by $(a - 2b + c)$. Likewise the difference in total second-order perturbation energies between a normal paraffin and an isomer with a double branch (*i.e.*, with a quaternary carbon atom) is seen to be $3(a - 2b + c)$, or three times the value for a single branch.

The heat of formation, ΔH, of an *iso*paraffin will then be given by

$$\begin{aligned} \Delta H = \Delta H_n + [&(\text{no. of tertiary carbon atoms}) \\ &+ 3(\text{no. of quarternary carbon atoms})](a - 2b + c) \quad . \; . \quad (6) \end{aligned}$$

where ΔH_n is the heat of formation of the isomeric *n*-paraffin. This result agrees exactly with the relations found empirically by Platt (*loc. cit.*). It is difficult to predict theoretically the sign or magnitude of the term $(a - 2b + c)$; in practice it is found to be negative and about 1·3 kcal./mole.

If the bond energies in normal paraffins are additive the heats of formation should also be additive. The heat of formation, ΔH_n, of n-C_nH_{2n+2} should be given by

$$\Delta H_n = A + (n - 1)B \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where $A = 4E_{\mathrm{CH}}$, $B = E_{\mathrm{CC}} + 2E_{\mathrm{CH}}$, and E_{CH}, E_{CC} are the C–H and C–C bond energies. Deviations from this relation are given in Table 2, with $A = -15{\cdot}31$ and $B = -4{\cdot}93$ kcal./mole, values used for the heats of formation at 25° being those given by Prosen and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 263). The deviations are seen to be very small, implying that bond energies are closely additive, except for methane. The abnormal stability of methane cannot be explained in terms of the present treatment; indeed a positive deviation would have been expected. This anomally may be due to the high symmetry of the methane molecule and the absence of bonds about which rotation can take place.

Deviations for singly branched and for *gem.*-branched paraffins are also given in Table 2. Both show systematic negative deviations, the mean deviation for *gem.*-branched paraffins being approximately three times that for singly branched paraffins, as is predicted.

TABLE 2. *Deviations from additivity in heats of formation of unstrained paraffins.*

Hydrocarbon	Deviation from additivity	Hydrocarbon	Deviation from additivity
n-Methane	−2·58	2 : 2-Dimethylpropane	−4·64
n-Ethane	0·00	2 : 2-Dimethylbutane	−4·37
n-Propane	+0·35	2 : 2-Dimethylpentane	−4·40
n-Butane	+0·29	3 : 3-Dimethylpentane	−3·28
n-Pentane	+0·03	2 : 2-Dimethylhexane	−3·89
n-Hexane	+0·00	3 : 3-Dimethylhexane	−2·79
n-Heptane	+0·00		
		Mean	−3·90
2-Methylpropane	−1·35		
2-Methylbutane	−1·89	2 : 4-Dimethylpentane	−3·41
2-Methylpentane	−1·70	2 : 4-Dimethylhexane	−2·62
3-Methylpentane	−1·08	2 : 5-Dimethylhexane	−3·39
2-Methylhexane	−1·71		
3-Methylhexane	−1·07	Mean	−3·14
2-Methylheptane	−1·68		
3-Methylheptane	−1·00		
4-Methylheptane	−0·58		
Mean	−1·34		

As Platt pointed out, the contributions of different branches in poly-branched paraffins are additive provided the branches are well separated; if the branches are close together, steric effects arise. This is seen particularly clearly in compounds with quaternary carbon atoms β to one another, *e.g.*, in poly*iso*butene (Brown and Barbaras, *J. Chem. Phys.*, 1946, **14**, 114) and in homomorphs of di-*tert.*-butylmethane (Brown, *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1).

Data for doubly branched paraffins, with separated branches, given in Table 2, show that additivity holds quite accurately. The steric effects that arise when two or more branches are adjacent are illustrated in Table 3; the second column shows the observed deviations from additivity, and the third the deviations calculated on the assumption that the effects of branches are additive with values of −1·34 and −3·90 kcal./mole for single and *gem.*-branches respectively. The differences, shown in the last column, indicate the importance and magnitude of steric strain effects. Note that strain is significant only when the branches are large, or when at least one quaternary carbon atom is involved; also that additivity holds quite accurately for the cases given in Table 2 where the branches were separated.

TABLE 3. *Deviations from addivity in heats of formation of strained paraffins.*

	Deviation from additivity		
Compound	Obs.	Calc.	Difference
2 : 3-Dimethylbutane	−2·53	−2·68	+0·15
2 : 3-Dimethylpentane	−2·73	−2·68	−0·05
2 : 2 : 3-Trimethylbutane	−4·07	−5·24	+1·17
2 : 3-Dimethylhexane	−1·31	−2·68	+1·37
3 : 4-Dimethylhexane	−1·09	−2·68	+1·59
3-Ethyl-2-methylpentane	−0·66	−2·68	+2·02
2 : 2 : 3-Trimethylpentane	−2·79	−5·24	+2·45
2 : 2 : 4-Trimethylpentane	−3·75	−5·24	+1·49
2 : 3 : 3-Trimethylpentane	−1·91	−5·24	+3·33
2 : 3 : 4-Trimethylpentane	−2·15	−4·02	+1·87
2 : 2 : 3 : 3-Tetramethylbutane	−3·17	−7·80	+4·63

TABLE 4. *Calculated total perturbation energies for olefins.*

Compound	δE	ΔE
$CH_2{=}CH_2$	$2c + 4e$	$a - 2b - 3c + 4e$
$CH_3{\cdot}CH{=}CH_2$	$4b + 4c + d + 3e$	$-2b - 2c + d + 3e$
$(CH_3)_2C{=}CH_2$	$a + 6b + 7c + 2d + 2e$	$-4b + 2d + 2e$
$CH_3{\cdot}CH{=}CH{\cdot}CH_3$	$8b + 6c + 2d + 2e$	$-a - 2b - c + 2d + 2e$
$(CH_3)_2C{=}CH{\cdot}CH_3$	$a + 10b + 9c + 3d + e$	$-a - 4b + c + 3d + e$
$(CH_3)_2C{=}C(CH_3)_2$	$2a + 12b + 12c + 4d$	$-a - 6b + 3c + 4d$

Olefins.—In simple olefins there are two additional types of structures present, C–C=C and H–C=C; let their second-order perturbation energies be d and e respectively. Attention need be focused only on the effect of substitution at the double bond; the CH_2 increment here, as in all homologous series, is known to be constant for extension of a saturated chain. (This conclusion follows from the considerations in the previous section.) Table 4 gives the calculated total second-order perturbation energies (δE) and the corresponding energies (ΔE) that must be ascribed to the C=C bonds in order to use the empirical single bond energies in equation (3). It shows interesting regularities which can be summarized in the expression :

$$\Delta E = \Delta E_0 + (\text{no. of alkyl groups attached to C=C})(c - a + d - e) \\ + (\text{no. of branches})\,(a - 2b + c) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

where ΔE_0 is the value of ΔE for ethylene. The correction for branching in the carbon skeleton is the same as for paraffins [compare equations (5) and (6)]. Since the branching factors are similar, a still simpler expression can be given for the heat of hydrogenation (ΔH) of an olefin to a paraffin, namely,

$$\Delta H = \Delta H_0 + A\ (\text{no. of alkyl substituents}) \quad . \; . \; . \; . \; . \quad (9)$$

where ΔH_0 is the value of ΔH for ethylene and A is a constant.

The data in the third and seventh columns of Table 5 (Kistiakowsky *et al.*, *ibid.*, 1935, **57**, 65, 876; 1936, **58**, 137, 146; 1937, **59**, 831) show only a moderate agreement with equation (9).

TABLE 5. *Calculated and observed heats of hydrogenation of olefins, in kcal./mole.*

Olefin	H (Obs.)	$(H_0 - H)$ (Obs.)	$(H_0 - H)$ (Calc.)	Olefin	H (Obs.)	$(H_0 - H)$ (Obs.)	$(H_0 - H)$ (Calc.)
$CH_2{:}CH_2$	32·58	—	—	Me·CH:CH·Me-*trans*	27·62	4·96	5·0
Me·CH:CH_2	30·12	2·46	2·5	Me·CH:CH·Me-*cis*	28·57	4·01	4·0
Et·CH:CH_2	30·34	2·34		*cyclo*Hexene	28·59	3·99	
C_5H_{11}·CH:CH_2	30·14	2·44		$Me_2C{:}CHMe$	26·92	5·66	5·7
Pr^i·CH:CH_2	30·33	2·26		$Me_2C{:}CMe_2$	26·63	5·95	6·4
Bu^t·CH:CH_2	30·34	2·24					
$Me_2C{:}CH_2$	28·34	4·24	4·2				
MeEtC:CH_2	28·49	4·09					
$MePr^iC{:}CH_2$	28·00	4·58					

However, there are two factors which have so far been neglected. First, there is the steric repulsion between pairs of *cis*-alkyl groups, which is known to be important and accounts for the greater stability of *trans*-but-2-ene when compared with the *cis*-isomer; secondly, there is the tacit assumption that the interactions H–C–H, H–C–C, and C–C–C have the same value regardless of the stereochemistry of the central carbon atom. It is evident that the overlap and so the mutual interaction of these bonds will be less when the bond angle is 120° (in an olefin) than when it has the normal tetrahedral value (in a paraffin). Both these effects will stabilise the paraffin relatively to the olefin. Consequently a correction should be applied to ΔH for each pair of *cis*-alkyl groups, and a second correction for each pair of vicinal alkyl groups. Setting these corrections equal to 1 and 0·8 kcal./mole respectively, and the constant A in equation (9) equal to 2·5 kcal., we obtain the calculated values for ΔH given in the fourth and last column of Table 5. The agreement with experiment could hardly be better.

Other Bonds.—Consider a bond between carbon and some other element X. Denote the second-order perturbations for the groupings C–C–X, H–C–X by f, g respectively. The total second-order perturbation energies for RX with R = methyl, ethyl, *iso*propyl, and *tert.*-butyl are given in the second column of Table 6; and the corresponding second-order perturbation energies that must be included in the C–X bond energy to give additivity are given in the last column. Since extension of the carbon chain at a β-carbon will not affect the C–X bond, these values for the C–X bond are appropriate to methyl, primary alkyl, secondary alkyl, and tertiary alkyl derivatives respectively. Although the expressions look complicated they actually show quite marked regularities. The empirical C–X bond energy (E_{CX}) is given by

TABLE 6. *Perturbation energies for* C–X *bonds.*

Compound	Total second-order perturbation	C–X bond perturbation
CH_3X	$3c + 3f$	$3g - \frac{1}{4}(-3a + 6b + 3c)$
$CH_3{\cdot}CH_2X$	$5b + 4c + f + 2g$	$f + 2g - \frac{1}{4}(a + 2b - 3c)$
$(CH_3)_2CHX$	$a + 8b + 6c + 2f + g$	$2f + g - \frac{1}{4}(a + 6b - c)$
$(CH_3)_3CX$	$3a + 9b + 9c + 3f$	$3f - \frac{1}{4}(-3a + 18b - 9c)$

$$E_{CX} = E^{\circ}_{CX} + A(a - 2b + c) + (\text{no. of }\beta\text{-alkyl groups})\ (f - g - b + c) \quad . \quad (10)$$

where E°_{CX} is the value of E_{CX} for CH_3X, and A is a measure of chain-branching in the corresponding paraffin, being zero for methyl, one for ethyl or *iso*propyl, and two for *tert.*-butyl. The co-factor of A is the same as in the branching term of equation (6).

Equation (10) predicts that there should be a steady increase or decrease in the apparent C–X bond energy along the series, with, superimposed, an increase in bond energy of about 1·3 kcal. on passing from methyl to ethyl and from *iso*propyl to *tert.*-butyl. The latter effect does not appear if one allows specifically for branching; but it should do so in the conventional treatment. The most important point is that the apparent C–X bond energy will be a function of the number of β-carbon atoms; the values appropriate to primary, secondary, and tertiary Alkyl–X should differ, and primary Alkyl–X should differ from CH_3–X.

The branching factor can be eliminated by comparing the heats of formation of the hetero-compounds with those of corresponding paraffins.

The heat (ΔH) of formation (from atoms) of R_3CX, and the corresponding value (ΔH_0) for the paraffin R_3CH, are related by

$$\Delta H - \Delta H_0 = E_{CX} - E_{CH} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where E_{CX} is the apparent C–X bond energy, and E_{CH} the C–H bond energy. The value for the apparent bond energy between carbon and a hetero-atom should according to the present treatment be given by

$$E_{CX} = (E_{CX})_0 + nA \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $(E_{CX})_0$ is the value of E_{CX} for the methane derivative, and n is the number of carbon atoms adjacent to the C–X bond. In the case of carbonyl compounds, the comparison will be between R_2CO and R_2CH_2.

Reliable data are scanty, and the available information is summarised in Table 7. In practice heats of combustion have been used in place of heats of formation; the differences between these will differ from ($\Delta H - \Delta H_0$) for a given series of compounds only by a constant term. The final column gives these differences; and it will be seen that they vary linearly with n, as equation (12) requires.

TABLE 7. *Deviations from additivity of the heats of combustion of alcohols and carbonyl compounds.*

Compound	n	H	H_0	$H_0 - H$		Compound	n	H	H_0	$H_0 - H$	
MeOH	0	182·6	215·4	32·8		CH_2O	0	134·7	215·4	80·7	
EtOH	1	336·8	372·8	36·0	Mean 37·0	Me·CHO ...	1	284·7	372·8	88·1	
Pr^{n}OH	1	493·3	530·2	36·9		Me_2CO ...	2	434·6	530·2	95·6	Mean 97·5
Bu^{n}OH ...	1	650·0	687·7	37·7		Et_2CO	2	746·8	845·1	98·3	
Bu^{i}OH ...	1	649·3	686·4	37·1		MePr^{i}CO ...	2	744·9	843·8	98·9	
Pr^{i}OH	2	489·3	530·2	40·7		Pr$^i_2$CO ...	2	1059·9	1157·3	97·4	
Bu^{t}OH ...	3	643·3	686·4	43·1							

DISCUSSION

In the preceding pages the following conclusions have been reached: (*a*) Interactions between bonds, and the consequent delocalisation of electrons, do not alter total binding energies to a first approximation. (*b*) The second-order interactions are functions of neighbouring bonds in unconjugated systems; they can to a large extent be absorbed into empirical bond energies. In homologous series the compensation can be perfect. The heats of formation of such compounds are linear functions of the numbers of carbon atoms to a very good approximation since the deviations are third-order quantities and usually quite negligible.

Conclusion (*b*) depends on the assumption that the important interactions are nearest-neighbour interactions, and not the 1 : 3 interactions of conventional hyperconjugation * (Mulliken, Rieke, and Brown, *ibid.*, 1941, **63**, 41). Platt (*loc. cit.*) showed that 1 : 3 interactions could not be important if the very accurate thermochemical data on paraffins were to be interpreted satisfactorily; and Altmann (*Proc. Roy. Soc.*, 1951, *A*, **210**, 327, 343) has given reasons for believing that the "conjugation" of alkyl groups with adjacent double bonds is a nearest-neighbour effect. One might add in this connexion that the chemical and spectroscopic evidence suggests strongly that all alkyl groups have a similar

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* But see Appendix B.

and quite large conjugative effect when attached to unsaturated systems; the differences between different alkyl groups are relatively very small. This point is illustrated by the examples given in Table 7. In each case alkyl groups have a large effect, while the differences between different alkyl groups are very much smaller. Yet these cases are cited by Baker (" Hyperconjugation," Oxford Univ. Press, 1952, pp. 37, 44, 50) as good evidence for the importance of hyperconjugation in organic chemistry. We feel that these differences, which are undoubtedly due to hyperconjugation, are better regarded as small second- or third-order effects, and that the main electromeric effects of alkyl groups have some other origin. The main effect of alkyl groups cannot be inductive in nature since inductive effects would not alter heats of formation appreciably. A direct conjugation between adjacent bonds seems the most likely explanation. None of the regularities noted in Table 1 would follow were 1 : 3 interactions included, if only because such interactions would depend on the detailed stereochemistry of the molecule.

According to the views presented here the electrons in unconjugated molecules need not be localised. The additivity of bond energies is ascribed to the vanishing of the net first-order interactions between bonds, and to the possibility of absorbing second-order effects into empirical bond energies. The second-order contribution of a given bond is not, however, a function of that bond only, but depends also on its environment (*i.e.*, the number and kind of adjacent bonds). Strict additivity of bond energies would be expected only in compounds where the environments of the bonds are similar. In the general case it should be necessary to use a different value for the bond energy of a given bond for each different environment, corresponding to the different second-order perturbations that must be absorbed. This situation is recognised in the case of the carbonyl bond. Pauling (" The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1941) gives three different values, corresponding to formaldehyde, other aldehydes, and ketones. But the same should be true of other bonds; and certainly the heats of formation of adjacent C–O or C–F bonds appear to be abnormally large. For instance, the heats of formation of acetals are uniformly 10—14 kcal. greater than those predicted from Pauling's bond energies (Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767); and compounds of the type R_2CF_2 are abnormally stable.

One could in principle look at this problem from a different point of view. One could calculate heats of formation from " ideal " bond energies appropriate to localised bonds and describe the differences between the calculated and the observed heats of formation as resonance energies. This, of course, is the conventional view in the case of olefins where the differences between apparent heats of formation of the C=C bond are ascribed to hyperconjugation. However, similar differences appear in the case of saturated compounds, probably for similar reasons; the effects in olefins and saturated compounds are probably due in each case to interactions between adjacent bonds. The differences in heats of formation are also quite similar; the total range in apparent C=C bond energy in passing from ethylene to tetramethylethylene is about 6 kcal., virtually identical with the average difference in bond energy of the C–O bond between simple ethers and acetals, and much less than the corresponding difference between methanol and *tert.*-butyl alcohol. We have not discussed the values of the interaction terms that arise in this treatment, and experimental data are insufficient to allow them to be evaluated individually. The sign of the branching term in paraffins shows that $(a + c) > 2b$, but otherwise the signs and magnitudes of a, b, and c are indeterminate. Altmann's work (*loc. cit.*) suggests that a is in fact the dominant term in hydrocarbons, and all our results would be consistent with the assumption that interactions with bonds containing hydrogen can be neglected.

APPENDIX A.

In applying perturbation theory to sets of degenerate orthogonal unperturbed eigenfunctions it is usually necessary to replace each set of degenerate eigenfunctions by an appropriate set of linear combinations of those eigenfunctions, the linear combinations being found by first-order perturbation theory; the combinations are then used as a basis in calculating the second-order perturbations. If, however, only the sum of all the second-order perturbations of a degenerate set of eigenfunctions is required, it is legitimate to calculate them by using the original unperturbed eigenfunctions and by omitting terms with vanishing denominators. Only second-order perturbations by eigenfunctions extraneous to the set need be considered, for, as has been pointed out above, the sum of all mutual perturbations of eigenfunctions of the set by one another vanishes.

The theorem need be proved only for the most general case, *viz.*, the total second-order perturbation of one degenerate set of eigenfunctions by a second degenerate set. Denote the two sets by ϕ_r, ψ_s. Let the correct linear combination of these eigenfunctions found by first-order perturbation theory, *i.e.*, Φ_m, Ψ_n, be given by

$$\Phi_m = \sum_r a_{mr}\phi_r \qquad \qquad (13)$$

$$\Psi_n = \sum_s b_{ns}\psi_s \qquad \qquad (14)$$

Let the energies of the various orbitals be

$$\text{of } \phi_m,\ E_m;\ \text{ of } \psi_n,\ F_n;$$
$$\text{of } \Phi_m,\ E_m + \varepsilon_m;\ \text{ of } \Psi_n,\ F_n + \zeta_n$$

where ε_m, ζ_n are first-order perturbations. It has been shown that

$$\sum_m \varepsilon_m = \sum_n \zeta_n = 0$$

The total second-order perturbation, ΔE, to the first set of levels, due to a perturbation operator P, is then given by

$$\Delta E = \sum_m \sum_n \Delta E_{mn} = \sum_m \sum_n \frac{[\int \Phi_m \,.\, P \,.\, \Psi_n \,.\, d\tau]^2}{(E_m + \varepsilon_m) - (F_n + \zeta_n)} \qquad \qquad (15)$$

$$\simeq \sum_m \sum_n \sum_r \sum_s \frac{a^2_{mr} \,.\, b^2_{ns} \,.\, P^2_{rs}}{E_m - F_n} + o(P^2\varepsilon, P^2\zeta)$$

where $P_{rs} = \int \phi_r \,.\, P \,.\, \psi_s d\tau$

Thus to the second-order of small quantities, *i.e.*, to the approximation of second-order perturbation theory,

$$\Delta E = \sum_m \sum_n \sum_r \sum_s \frac{a^2_{mr} b^2_{ns} P^2_{rs}}{E_m - F_n} \qquad \qquad (16)$$

Now if the functions ϕ_r are represented by unit orthogonal vectors in a many-dimensional space, equation (13) expresses the vector representing the function Φ_m in terms of the ϕ_r; the a_{mr} are then direction cosines relating Φ_m to the ϕ_r and the Φ_m form a set of unit orthogonal vectors related to the ϕ_r by (13). It follows at once (cf. Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193, to whom this argument is due) that

$$\sum_m a^2_{mr} = \sum_r a^2_{mr} = 1 \qquad \qquad (17)$$

Likewise

$$\sum_n b^2_{ns} = \sum_s b^2_{ns} = 1 \qquad \qquad (18)$$

Combining equations (16), (17), and (18) and carrying out the summation over m and n, we get

$$\Delta E = \sum_r \sum_s \frac{P^2_{rs}}{E_m - F_n}$$

But this is just the second-order perturbation to the ϕ_r's that would be calculated by using the unperturbed function ϕ_r, ψ_s as a basis, and by neglecting terms representing mutual perturbations of the ϕ_r (which would have vanishing denominators).

Further Refinement of the Treatment.—Although the whole of this treatment has been given in terms of the simple L.C.A.O. M.O. theory, it will be noticed that nowhere in it are simple L.C.A.O. M.O. wave functions or orbital energies. It is evident that the treatment would be quite unaffected if the bond orbitals used as a basis were ideal Hartree–Fock functions. The only approximation made has been the neglect of overlap between different bonds, apart, of course, from those inherent in the use of perturbation methods. Furthermore, the treatment would remain unaffected if the best possible two-electron wave functions were used for the individual bonds, the " antibonding orbitals " now being replaced by two electron wave functions for excited states of the bond.

It is evident therefore that the simplifying assumptions inherent in the present treatment are much less restrictive than those made in current treatments of molecular structure, although for convenience we have formulated it in more familiar terms.

APPENDIX B.

Hyperconjugation is usually assumed to be important only if it involves C–H bonds. In this sense hyperconjugation cannot account for the phenomena we have discussed. If, however, hyperconjugation is of comparable importance for bonds of different types, so that the effect on a given C–C bond in hydrocarbon depends only on the number of adjacent carbon atoms, and not on the groups attached to those atoms, hyperconjugation could replace the adjacent bond interactions postulated in our treatment. In that case, in a hydrocarbon, the H–C–C and H–C–H interactions would be small, and only the C–C–C interaction significant. It is easily seen that none of our conclusions would be affected by this alternative interpretation.

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