# Laticyclic Hyperconjugative Interactions involving a Relay of $CH_2$ or $CH_2CH_2$ Units. A New and Important Mechanism for Transmitting Interactions over Large Distances

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The results of *ab initio* MO calculations (STO-3G basis set) on the complexes (**14**) and (**15**) are reported. The $CH_4$ groups in (**14a**; $n$ = 1—3) and (**15a**; $n$ = 1—4) markedly affect the π levels of these systems by a process termed laticyclic hyperconjugation. Calculations on (**14b**—**e**) and (**15b**—**e**) reveal that hyperconjugative interactions in (**14a**) and (**15a**) can be as large as conjugation involving nonbonding orbitals, π MOs, or vacant *p* orbitals. The relevance of the role that hyperconjugation might play in long-range interactions is discussed. It is concluded that the efficacy of such interactions in molecules might very well depend critically on the presence of hyperconjugation and through-bond effects.

Recent photoelectron (p.e.) spectroscopic studies carried out on (**1**) and (**2**), the first two members of the norbornylogous series of compounds (**3**), revealed the presence of large π,π splitting energies, $\Delta E_\pi$, in these molecules of 0.52 and 0.29 eV, respectively.[1,2] These splittings are much too large to be accounted for exclusively in terms of π orbitals interacting through six bonds in (**1**) (π-OIT-6-B) and through eight bonds in (**2**) (π-OIT-8-B).[1,3] Indeed the contribution of π-OIT-6-B towards the $\Delta E_\pi$ value observed for (**1**) was estimated to be $<0.2$ eV on the grounds that this was the value of $\Delta E_\pi$ obtained from the p.e. spectrum of (**4**), a molecule structurally related to (**1**) but which lacks the central methylene bridge.[1] Using this estimated value for π-OIT-6-B in (**1**), together with the known dependence of OIT-$n$-B on the value of $n$ for a related series of compounds,[3] leads to a value of $\Delta E_\pi < 0.1$ eV for π-OIT-8-B in (**2**).

The major contributions to $\Delta E_\pi$ in (**1**) and (**2**), which amount to *ca.* 0.35 and 0.20 eV respectively, were attributed to the operation of hyperconjugative interactions between the π MOs in these molecules and the pseudo-π ($_\psi\pi$) orbitals of the intervening methylene groups.[1]

This type of hyperconjugation is interesting in that the interacting π- and $_\psi\pi$-ribbons in (**1**) and (**2**) display the laticyclic topology,[4] shown by (**5**) and (**6**), respectively. It is proposed to call this type of hyperconjugation (π, *n*, π)-*laticyclic hyperconjugation* where the symbols in parentheses refer to the sequence of the ribbons and the number, $n$, of hyperconjugating ribbons. For example in (**2**) $n = 2$ and the ribbon sequence is: a single π MO followed by two methylene $_\psi\pi$-ribbons, followed by another π MO. Of course two π MOs are not required to generate laticyclic hyperconjugation; for example (**7**) is illustrative of (π,*n*)-laticyclic hyperconjugation.

Further application of the elegant Goldstein–Hoffmann topologically based classification of π-ribbon interactions[4] to hyperconjugation leads to the pericyclic, spirocyclic, and longicyclic varieties. There is no experimental evidence for the existence of the latter two types of hyperconjugation although norbornadiene could in principle host (π,1,π)-longicyclic hyperconjugative interactions as shown by (**8**). However, this effect is probably swamped by larger hyperconjugative interactions involving the C–C bonds of the six-membered ring in norbornadiene.[5] In contrast, examples of pericyclic hyperconjugation abound. For example the observed $\Delta E_\pi$ value of 1.0 eV[6] for cyclohexa-1,4-diene can be attributed to (π,1,π,1)-pericyclic hyperconjugation. This interaction has been previously referred to simply as an example of OITB[7] which, of course, is quite correct. Our notation provides additional information concerning the topological arrangement of the interacting orbitals. As a final example of pericyclic hyperconjugation we may cite compound (**10**) whose measured $\Delta E_\pi$ value of 0.87 eV[5] is a result of (π,4,π,4)-pericyclic hyperconjugation, where the numerals enclosed within the parentheses refer to the two sets of four hyperconjugating C–C bonds. An alternative description of this interaction, which will continue to be used, is π-OIT-4-B.

The magnitude of the observed $\Delta E_\pi$ value for (**2**)[2] raises the exciting possibility of (π,*n*,π)-laticyclic hyperconjugation in (**3**) extending over more than two methylene groups, *i.e.* (**3**; $n > 2$). This possibility, together with other aspects of laticyclic hyperconjugation, has been explored using *ab initio* MO theory the results of which form the basis of this paper. In addition laticyclic *conjugative* interactions in the structures (**11**)—(**13**), in which the hyperconjugating methylene relays of (**3**) are replaced by π groups, were investigated in order to assess the importance of laticyclic hyperconjugative *versus* conjugative interactions.

It is emphasised that the criterion for gauging the magnitude and importance of the laticyclic interactions in this paper is based on the *amount by which* the π levels of the double bonds are shifted relative to an appropriately chosen π basis level and *not* on overall energy changes which accompany the interactions. The reason for this choice is that in (**3**), (**11**), and (**12**) the dominant orbital interactions will be between those that are doubly occupied and which will lead, therefore, to overall destabilization of the system. Since other factors also contribute to the overall destabilization it would be very difficult to extract from this the laticyclic hyperconjugative contribution.

*The Model.*—The model structures chosen for the calculations are the ethene-$(XH_2)_n$ complex, shown by (**14**), and the ethene-$(XH_2)_n$-ethene complex (**15**). These complexes are expected to reveal the same degree of laticyclic interactions between $(XH_2)_n$ and the ethene group(s) as between the corresponding groups in the 'real' molecules such as (**3**), (**11**), and (**12**), whilst eliminating the additional through-bond effects involving the carbon framework that are present in the latter molecules. The calculations were carried out using GAUSSIAN 70.[8,‡] The

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‡ The program was modified to run on the Honeywell level 66/60 computer by D. Spangler, University of Kansas.

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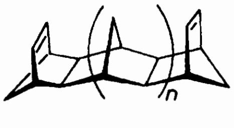
**(2)**



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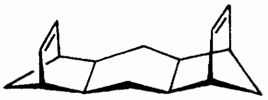

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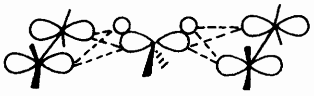

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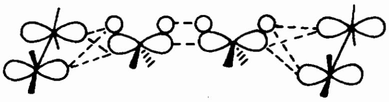

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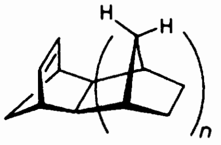

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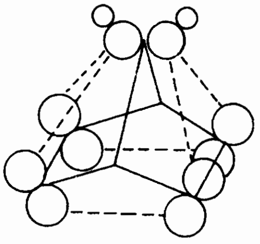

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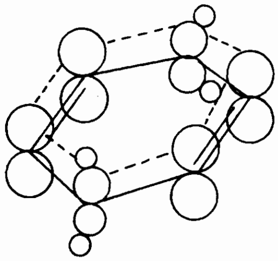

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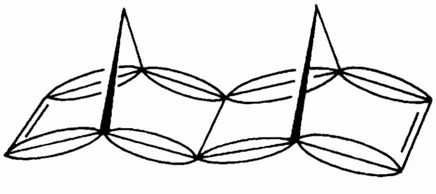

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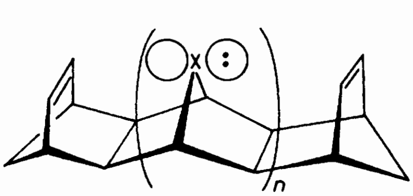
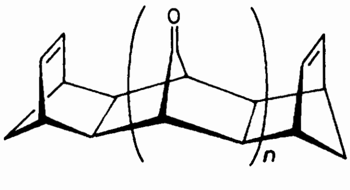


**(11)**

a; X = O
b; X = S



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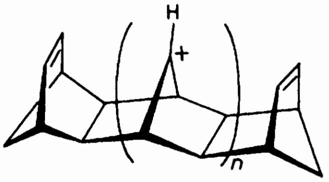

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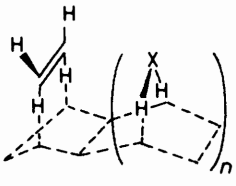

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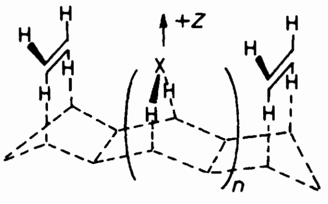


**(15)**

a; X = $CH_2$
b; X = O
c; X = S
d; X = C=O
e; X = $\overset{+}{C}$—H

STO-3G basis set[9] was employed for all calculations since it has been demonstrated to give reliable $\Delta E_\pi$ values for structurally related systems.[5,10] STO-3G-optimised geometries for the molecular fragments of **(14)** and **(15)** were used. This choice was reasonable since calculations on (**15a**; $n = 1$) using geometries more appropriate to the fragments as they would appear in the norbornenyl framework gave a $\Delta E_\pi$ value virtually identical with that obtained using optimised geometries.

The separation between the centres of adjacent groups in **(14)** and **(15)** was set at 3.1 Å which corresponds to the experimentally determined value for the $CH_2$ double bond distance in aldrin.[11] Molecular mechanics calculations also indicate that the adjacent methylene bridges in (**3**; $n > 2$) are separated by *ca.* 3.1 Å.[2] Finally the heavy atoms of $(XH_2)_n$ of **(15)** were constrained to lie in the plane containing the four carbon atoms of the double bonds in accord with the results of molecular mechanics calculations.[2]

## Results and Discussion

The $\pi$ levels of the double bonds in **(14)** and **(15)**, together with the derived $\Delta E_\pi$ values for **(15)**, are listed in the Table. The first entry of the Table gives the $\pi$ MO energy of an isolated ethylene molecule which serves as a reference. Positive values of $\Delta E_\pi$ mean that the two $\pi \pm \pi$ levels follow the natural sequence, that is $E_{\pi-\pi} > E_{\pi+\pi}$.

Before discussing the data in detail it should be pointed out that, because of the large distance separating the ethylene molecules in **(15)**, ranging from 6.2 ($n = 1$) to 15.5 Å ($n = 4$), any contributions to the $\Delta E_\pi$ values resulting from *direct* through-space interactions between the ethylene fragments may be neglected. This point was readily verified: the calculated splitting energy for (**15a**; $n = 1$) disappeared upon removal of the methane fragment.

*Laticyclic Hyperconjugation involving* $CH_2$ $_\psi\pi$ *Ribbons.*—The

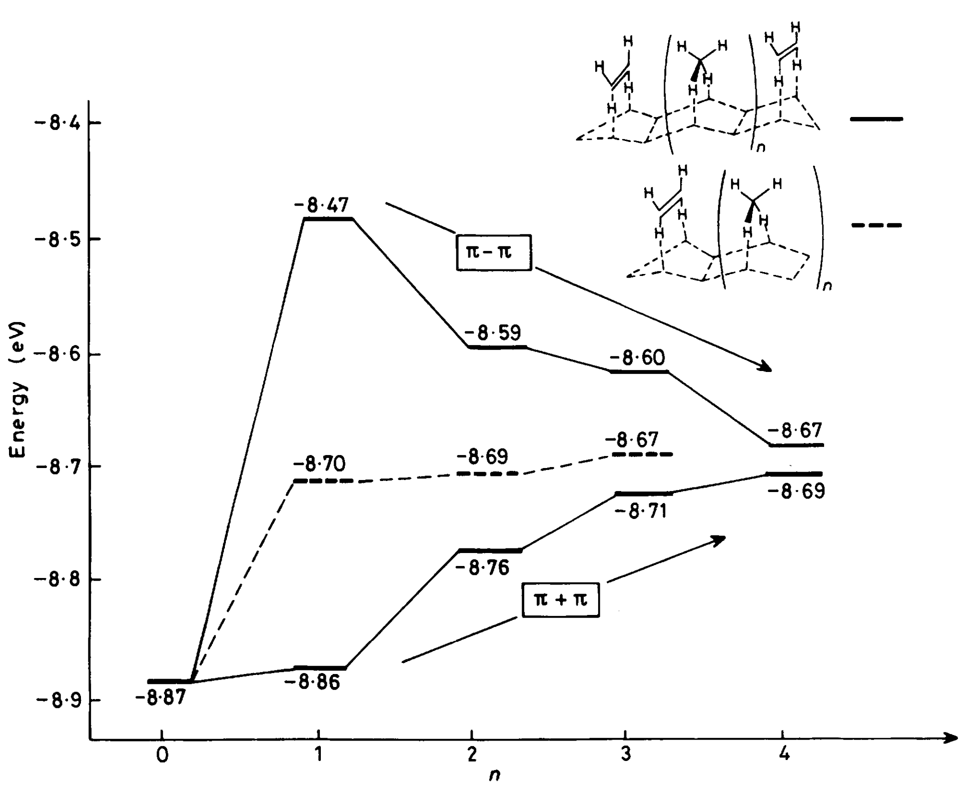


**Figure 1.** STO-3G-calculated π ± π levels of (**15a**) and π level of (**14a**) as a function of *n*, the number of intervening methane units.

**Table.** π Orbital energies, $E_{\pi\pm\pi}$, and $\Delta E_\pi$ values for the double bonds of (**14**) and (**15**)

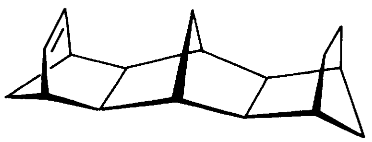
| Entry | Structure | $E_{\pi+\pi}$/eV | $E_{\pi-\pi}$/eV | $\Delta E_\pi$/eV |
|---|---|---|---|---|
| 1 | (**14a**; $n = 0$) | −8.87 | | |
| 2 | (**14a**; $n = 1$) | −8.70 | | |
| 3 | (**14a**; $n = 2$) | −8.69 | | |
| 4 | (**14a**; $n = 3$) | −8.67 | | |
| 5 | (**15a**; $n = 1$) | −8.86 | −8.47 | 0.39 |
| 6 | (**15a**; $n = 2$) | −8.76 | −8.59 | 0.17 |
| 7 | (**15a**; $n = 3$) | −8.71 | −8.60 | 0.11 |
| 8 | (**15a**; $n = 4$) | −8.69 | −8.67 | 0.02 |
| 9 | (**14b**; $n = 1$) | −8.67 | | |
| 10 | (**15b**; $n = 1$) | −8.74 | −8.59 | 0.15 |
| 11 | (**15b**; $n = 2$) | −8.65 | −8.64 | 0.01 |
| 12 | (**14c**; $n = 1$) | −9.12 | | |
| 13 | (**15c**; $n = 1$) | −8.66 | −9.36 | −0.70 |
| 14 | (**15c**; $n = 2$) | −9.32 | −8.89 | 0.43 |
| 15 | (**15c**; $n = 3$) | −9.01 | −9.30 | −0.29 |
| 16 | (**14d**; $n = 1$) | −8.89 | | |
| 17 | (**15d**; $n = 1$) | −8.94 | −8.81 | 0.13 |
| 18 | (**15d**; $n = 2$) | −8.84 | −8.80 | 0.04 |
| 19 | (**14e**; $n = 1$) | −13.71 | | |
| 20 | (**15e**; $n = 1$) | −13.22 | −13.66 | −0.44 |
| 21 | (**15e**; $n = 2$) | −16.34 | −16.17 | 0.17 |

π levels of (**14a**) and (**15a**) as a function of *n*, the number of intervening methane groups, are shown in Figure 1. The calculated $\Delta E_\pi$ values of 0.39 and 0.17 eV for (**15a**; $n = 1$) and (**15a**; $n = 2$) respectively reflect the extent of laticyclic hyperconjugation in compounds (**1**) and (**2**). The experimentally determined estimates are 0.35 and 0.20 eV for (**1**) and (**2**), respectively. The agreement between the two sets of values is remarkable and it serves to reinforce our confidence in the reliability of the model calculations. Parenthetically we mention that in comparing SCF MO energies, or their differences, with those 'obtained' experimentally by p.e. spectroscopy we are assuming the validity of Koopmans' theorem,[12] that is, an experimental $I_p$ is assumed equal to the negative of the corresponding occupied orbital energy.

Three important points emerge from an inspection of Figure 1. First, the π levels for (**14a**) and (**15a**) were all found to be elevated relative to that of the isolated ethylene molecule. Second, the π level of the monoene (**14a**) is very nearly coincident with the centroid of the two π levels of the corresponding diene (**15a**) for $n = 1$—3. Corroborative evidence for this result is provided by the π $I_p$ data for (**1**) and the monoene (**16**):[1] 8.24 and 8.76 eV (centroid = 8.50 eV) for (**1**) and 8.51 eV for (**16**). Third, although $\Delta E_\pi$ for (**15a**) steadily diminishes with increasing values of *n*, finally becoming negligible for $n = 4$, the two π levels converge to a limit (*ca.* −8.67 eV) which is *appreciably higher* (by 0.2 eV) than that of an isolated ethylene molecule. It must therefore follow that, notwithstanding the small $\Delta E_\pi$ value, laticyclic hyperconjugation in (**15a**; $n = 4$) is appreciable. These points may be understood in terms of the following perturbational MO model which was found to be useful in treating through-bond effects.[3,5,10]

To a very good approximation we need only consider those interactions between the ethylene π MOs and the low lying occupied ${}_\psi\pi$ ribbons of the methane groups, as indicated by (**17**); any contributions from the virtual ${}_\psi\pi^*$ MOs of the methane groups must be very small on account of the very large calculated $\pi,{}_\psi\pi^*$ energy gap of *ca.* 29 eV compared with *ca.* 5 eV for the $\pi,{}_\psi\pi$ separation. This lack of ${}_\psi\pi^*$ involvement in the interactions accounts for the resulting *elevation* of the π levels of (**14a**) and (**15a**) mentioned in the first point above.

The basis orbitals, and the regions where they interact, are shown by (**17**) for the case of double bonds mixing with *n* $CH_4$ units. Each $CH_4$ unit is assumed to contribute one ${}_\psi\pi$ ribbon as shown. Of course other methane orbitals can, and do,



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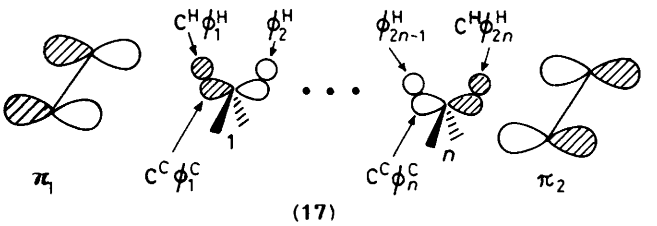

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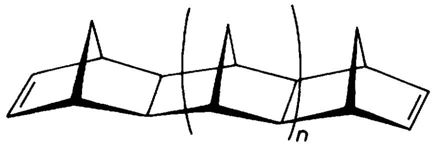

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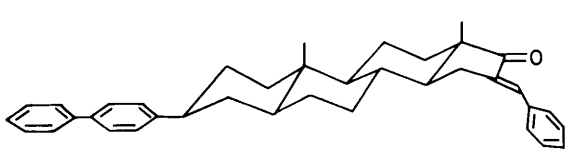

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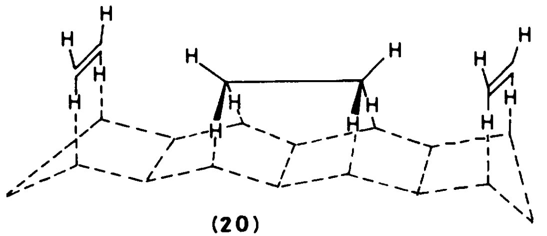

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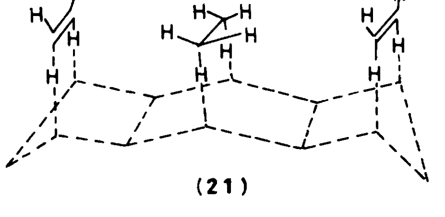

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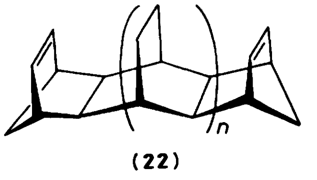

**(22)**

contribute to the interaction; however, their exclusion will not harm the overall argument. Mixing of the $n$ $_{\psi}\pi$ ribbons leads to the formation of the same number of delocalised basis '$_{\psi}\pi$' ribbons whose symmetries may be easily derived using perturbational MO (PMO) theory. The STO-3G energies and coefficients of these basis ribbons for $(CH_4)$, $n$ = 1—4, are shown in Figure 2. The symmetries of these orbitals are classified with respect to the plane of symmetry bisecting, and perpendicular to, the internuclear C–C axis.

The following result of one-electron PMO theory is relevant to the ensuing discussion: if two degenerate and identical MOs, $\varphi_1$ and $\varphi_2$, interact with another MO, $\Psi$, at separate but symmetry-related points then the energy change upon mixing only one of the $\varphi$ orbitals with $\Psi$ is one half that accompanying the mixing of the appropriate symmetry-adapted pair $1/(\sqrt{2})(\varphi_1 \pm \varphi_2)$ with $\Psi$. This result is easily verified using **(17)** in which the $\pi_1$ and $\pi_2$ MOs mix with the $_{\psi}\pi$ ribbon at the two pairs of orbitals $\varphi_1{}^H$, $\varphi_1{}^C$ and $\varphi_{2n}{}^H$, $\varphi_n{}^C$, respectively. The symmetry of the ribbon is such that the coefficients, $C^H$, of the two hydrogen orbitals are equal as are those, $C^C$, of the carbon atoms. The mixing of only one $\pi$ MO, say $\pi_1$, with the $_{\psi}\pi$ ribbon results in an increase in the energy of this MO given to the second-order by relation (1)

$$\delta E_\pi \propto <\pi_1|\mathcal{H}|(C^H\varphi_1{}^H + C^C\varphi_1{}^C)>^2/\Delta \qquad (1)$$

where $\mathcal{H}$ is the Hamiltonian of the mixing and $\Delta$ is the energy gap separating the $\pi$ and $_{\psi}\pi$ levels. The second-order energy change accompanying the mixing of the $(\pi_1 + \pi_2)$ symmetry-adapted combination with the $_{\psi}\pi$ is given by relation (2). The constants of

$$\delta E_{\pi+\pi} \propto <1/\sqrt{2}\,(\pi_1 + \pi_2)|\mathcal{H}|(C^H\varphi_1{}^H + C^C\varphi_1{}^C + C^H\varphi_{2n}{}^H + C^C\varphi_n{}^C)>^2/\Delta \quad (2)$$

proportionality in equations (1) and (2) are identical as are the denominators (it is assumed that OITS between $\pi_1$ and $\pi_2$ are negligible). Expansion of equation (2) leads to the desired result, *i.e.* $\delta E_{\pi+\pi} = 2\delta E_\pi$.

This result is easily generalised to cover the situation of the $\pi$ MOs mixing with several $_{\psi}\pi$ ribbons, some of which are symmetric (S) and some antisymmetric (A). A single $\pi$ MO will, of course, mix with all the $_{\psi}\pi$ orbitals as there are no symmetry constraints here. The total change in energy of the $\pi$ MO is given by summing the second-order perturbations due to its interaction with all the $_{\psi}\pi$ MOs and may be represented as the sum $(X_A + X_S)$ where $X_i$ represents the total energy change due to all second-order terms involving the $_{\psi}\pi$ orbitals of the specified symmetry ($i$ = A or S). The energy changes accompanying interactions between the $_{\psi}\pi$ orbitals with symmetric $(\pi + \pi)$ combination [see **(17)**] and the antisymmetric $(\pi - \pi)$ pair are respective $2X_s$ and $2X_A$. In other words, the resulting level of a single $\pi$ MO will always lie midway between the levels of the two symmetry-adapted $(\pi \pm \pi)$ pairs of MOs after interaction.* This result, which forms the basis of the recently proposed model for OITB,[3,5,10] also nicely explains the $\pi$ level position of a monoene in relation to the $(\pi \pm \pi)$ levels of the corresponding diene as observed for **(16)** and **(1)**[1] and as calculated for **(14a**; $n$ = 1—3) and **(15a**; $n$ = 1—3) (see point two above and Figure 2).

The trends in the $(\pi \pm \pi)$ levels of **(15a)** as a function of $n$ are readily understood in terms of equation (2) and the MO data for the $_{\psi}\pi$ MOs of $(CH_4)_n$, shown in Figure 2. For the case of $n$ = 1 there is only a single $_{\psi}\pi$ orbital. Consequently only the antisymmetric $(\pi - \pi)$ combination can mix with this orbital. The magnitude of this ($\pi$,1,$\pi$)-laticyclic hyperconjugation is calculated to be 0.40 eV relative to the $\pi$ basis of ethylene (Figure 2). The symmetric $(\pi + \pi)$ combination cannot mix with the $_{\psi}\pi$ orbital; this level consequently suffers no laticyclic hyperconjugation and is therefore coincident with the $\pi$ basis level. Calculations fully support this analysis (Figure 2). The calculated splitting energy, $\Delta E_\pi$, is due therefore almost exclusively to hyperconjugation in the $(\pi - \pi)$ MO.

For structures having more than one methane group there are two high lying $_{\psi}\pi$ orbitals of $(CH_4)_n$ ($n > 1$) which shall be

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* This conclusion holds for all types of interacting orbitals, *e.g.* $\sigma, \pi, \pi^*$ *etc.*

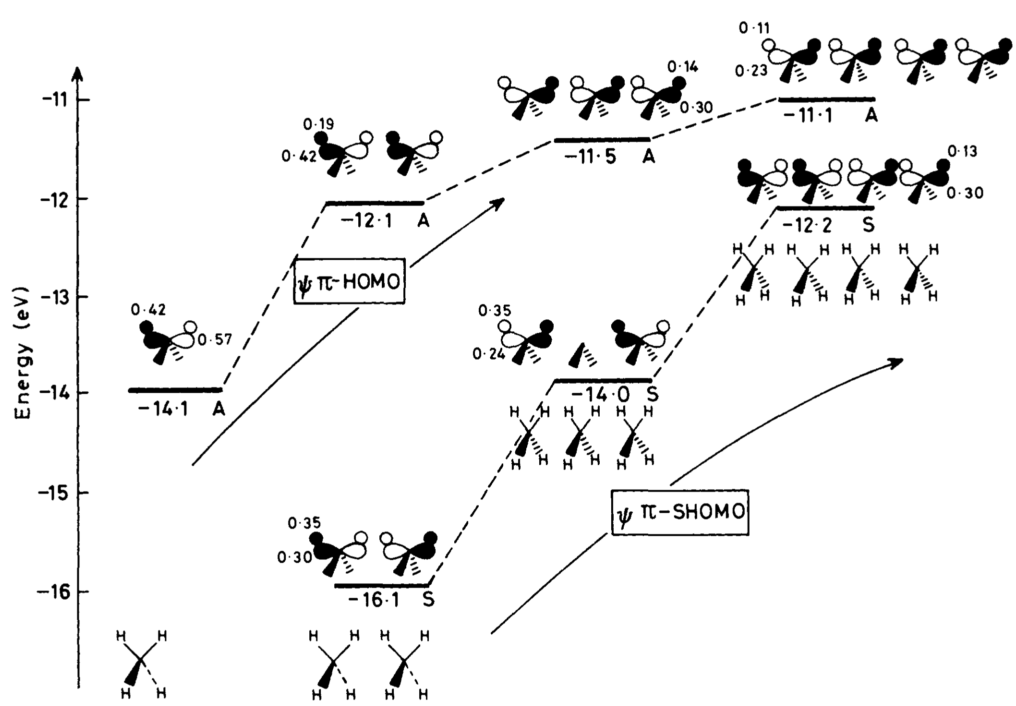

**Figure 2.** STO-3G energies and coefficients of the HOMO and SHOMO of $(CH_4)_n$ in which the adjacent $CH_4$ groups are placed 3.1 Å apart centre to centre

called $_{\psi}\pi$-HOMO and $_{\psi}\pi$-SHOMO (second HOMO). These orbitals have opposite symmetries with the $_{\psi}\pi$-HOMO always being antisymmetric (see Figure 2). Both $(\pi - \pi)$ and $(\pi + \pi)$ levels are thereby raised as a result of their respective interactions with $_{\psi}\pi$-HOMO and $_{\psi}\pi$-SHOMO. The $_{\psi}\pi$-HOMO is predicted to hyperconjugate more strongly than the $_{\psi}\pi$-SHOMO for all values of $n > 1$ because its greater energy and larger $\varphi^H$ and $\varphi^C$ orbital coefficients, compared with those of the $_{\psi}\pi$-SHOMO, will lead to stronger interactions [*i.e.* see equation (2)]. The natural sequence of levels, *i.e.* $(\pi - \pi) > (\pi + \pi)$, is therefore predicted for (**15a**) and this is confirmed by calculations.

However, the data of Figure 2 indicate that, for increasing values of $n$, the ratio of the square of the orbital coefficients of a ribbon to the energy gap, $\Delta$, between that ribbon and the ethylene π basis orbital *decreases* for the $_{\psi}\pi$-HOMO but *increases* for the $_{\psi}\pi$-SHOMO. From the form of equation (2) it follows, therefore, that the $(\pi - \pi)$ level of (**15a**) should fall with increasing values of $n$ whereas the corresponding $(\pi + \pi)$ level should increase. Calculations not only confirm this trend but they also indicate that the two levels finally converge for $n = 4$, *i.e.* $\Delta E_\pi = 0.02$ eV for this case.

On the basis of these calculations it is predicted that the diene (**3**; $n = 3$) should give the rise to an observable $\Delta E_\pi$ of *ca.* 0.11 eV * but that the higher members of the series will give rise to a single π $I_p$ band in their p.e. spectra, *i.e.* $\Delta E_\pi = 0$. However, it is stressed that appreciable $(\pi,n,\pi)$-laticyclic hyperconjugative interactions should still be present in these higher homologues (**3**; $n > 3$); it just happens that both $(\pi \pm \pi)$ levels suffer the same degree of hyperconjugative destabilization which would seem to be *ca.* 0.2 eV, judging from the value calculated for (**15a**; $n = 4$) (relative to the ethylene π basis orbital). An experimental estimate of the magnitude of these hyperconjugative interactions in (**3**) can be made through comparison of their π $I_p$s with the $(\pi + \pi)$ $I_p$ of (**1**) since the latter value should closely resemble that of the ethylene π basis orbital.† Thus, from the π $I_p$ data for (**2**),[2] laticyclic hyperconjugation raises the $(\pi - \pi)$ and $(\pi + \pi)$ levels in this molecule by *ca.* 0.45 and 0.16 eV, respectively.

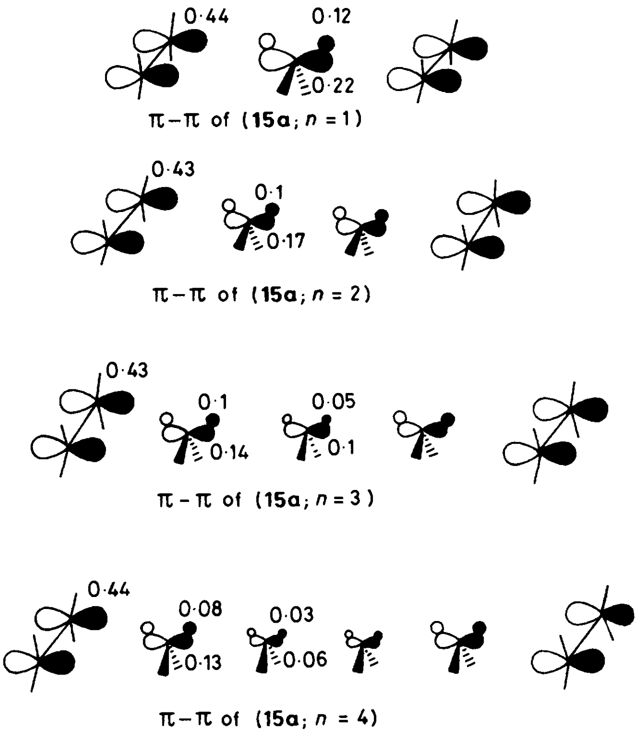

**Figure 3.** STO-3G orbital shapes and coefficients of the $(\pi - \pi)$ of (**15a**) for $n = 1$—4

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* Compound (**3**; $n = 3$) is currently being synthesized in order to test this prediction.

† The $(\pi + \pi)$ level of (**1**) will be slightly raised, relative to the π basis, because of the known presence of OIT-6-B effects in this molecule.[1]

The importance of hyperconjugation in (**3**) can be gauged from the eigenvectors of the ($\pi \pm \pi$) MOs of (**15a**). Those of the ($\pi - \pi$) MO for the first four homologues of (**15a**) are shown in Figure 3. It can be seen that, although the degree of $\pi, {}_{\heartsuit}\pi$ mixing does diminish with increasing values of *n* (as indicated by the relative sizes of the orbital coefficients) it does so sufficiently slowly to remain sufficiently impressive even for (**15a**; $n = 4$).

This result is important as it indicates that the occupied $\pi$ MOs of two groups, *i.e.* double bonds, aromatic rings, *etc.*, are able to 'communicate' with each other over very large distances (>16 Å) through an intervening relay of hyperconjugating groups. The significance of this effect will be most evident in long-range electron-transfer reactions where it provides a mechanism for efficient electron exchange between two remote sites, through the connecting relays, without having to invoke long-range electron-tunnelling effects.[13] An ideal study in this respect would be to determine the rates of positive hole migration between the two $\pi$-systems of cation radicals of compounds such as (**3**), in which the double bonds are replaced by aromatic rings, as a function of *n*.

From the above analysis it seems reasonable to predict that hyperconjugative interactions of the 'classical' through-bond type,[3] *i.e.* OIT-*n*-B, which are prevalent in the lower members of the series of norbornylogues (**18**; $n = 0,1$), should be significant for much larger values of *n*. Thus the interesting observation of extremely rapid intramolecular electron transfer between donor and acceptor groups in the anion radicals of compounds such as (**19**)[13] could very well be due to OIT-9-B rather than to the proposed[13] long-range electron-tunnelling mechanism.

($\pi^*,n,\pi^*$)-Laticyclic hyperconjugation in (**3**), (**7**), (**14a**), and (**15a**), involving the $\pi^*$ MOs of these species, should be absent owing to the different symmetries of the $\pi^*$ and ${}_{\heartsuit}\pi$ (and ${}_{\heartsuit}\pi^*$) orbitals with respect to the plane of symmetry bisecting the double bonds. This is borne out by calculations: the $\pi^*$ levels of (**14a**) and (**15a**) were all found to lie within 0.04 eV of the $\pi^*$ levels of ethylene. Long-range electron-transfer reactions in the *anion* radicals of compounds such as (**3**) should therefore receive little assistance from the intervening methylene groups. Accordingly such processes should be less facile than those involving the corresponding *cation* radicals.

The dependence of the strength of laticyclic hyperconjugative interactions in (**15a**) on the double bond $\cdots CH_4$ and the adjacent $CH_4 \cdots CH_4$ distances was investigated. Not surprisingly, the interactions decayed rapidly with increasing double bond $\cdots CH_4$ separation, being negligible for distances >3.6 Å. Increasing the $CH_4 \cdots CH_4$ distance beyond 3.5 Å in (**15a**; $n = 2$) essentially generated two separate fragments (**14a**; $n = 1$), each exhibiting ($\pi$,1)-hyperconjugation identical in magnitude to that calculated for (**14a**; $n = 1$). Finally the $CH_4$ group of (**15a**; $n = 1$) was moved out of the plane defined by the four carbon atoms of the double bonds. The hyperconjugative interactions were halved upon an upward translation of the methane molecule by 0.6 Å, in the direction of the positive *z*-axis [see (**15a**)], but remained unaltered by a 0.6 Å shift in the downward direction, *i.e.* along the negative *z*-axis. These results may be understood in terms of the changing overlaps between the $\pi$ MOs with the $\varphi^H$ and $\varphi^C$ orbitals of the ${}_{\heartsuit}\pi$ ribbon [*e.g.* see (**17**)] which accompany the out-of-plane movement of the methane molecule: Both $\pi, \varphi^C$ and $\pi, \varphi^H$ overlaps are reduced by an upward translation and the resulting degree of hyperconjugation must diminish accordingly. However, downward translation produces a decrease in the $\pi, \varphi^C$ overlap but an increase in the $\pi, \varphi^H$ overlap. Presumably these two effects cancel and the resulting hyperconjugation remains unaffected providing the methane molecule is moved no more than 0.6 Å, which represents the point of closest approach of the two methane hydrogen atoms involved in the hyperconjugation to the double bonds. Indeed calculations do reveal the expected diminution of hyperconjugation for out-of-plane movement exceeding 0.6 Å.

It is concluded from the above results that the optimal geometric features that are needed for maximising ($\pi,n,\pi$)-laticyclic hyperconjugation involving $CH_2$ groups are embodied in the series of compounds (**3**; $n = 1,2 \cdots$).

*Laticyclic Hyperconjugation involving* $CH_2CH_2$ ${}_{\heartsuit}\pi$ *Ribbons.*—Hyperconjugative interactions in the ethene–ethane–ethene complex was investigated for the two structures shown by (**20**) and (**21**). The ($\pi \pm \pi$) levels for (**20**) were found to be virtually identical with those for (**15a**; $n = 2$) with the exception that the level sequence is now reversed *i.e.* ($\pi + \pi$) > ($\pi - \pi$). Hyperconjugation involving $\pi^*$ MOs is absent in (**20**). The behaviour of (**21**) strongly resembled that of (**15a**; $n = 1$) in that their ($\pi \pm \pi$) levels were very similar. The complex (**21**) is unusual, however, in that it was the only system to be studied which revealed strong hyperconjugative interactions in the $\pi^*$ MO manifold; $\Delta E_{\pi^*} = 0.3$ eV. All these results are readily understood in terms of the PMO procedure described above and the known[14] MOs of ethane and so will not be further elaborated.

The only real advantage that ethane has over methane in terms of hyperconjugating ability is that the former molecule is able to interact with $\pi^*$ MOs in geometries represented by (**21**). In this respect long-range electron-transfer studies in anion radicals of the series of compounds (**22**) should be worthy of experimental study.

*Laticyclic Conjugation.*—Conjugation through $XH_2$ units, where X contributes either a *p* or a $\pi$ orbital, was explored for (**14b—e**) and (**15b—e**) and the results are given in the Table. For all cases except that involving the methyl cation the $\pi$ energy of the monoene (**14b—d**) is approximately equal to the centroid of the ($\pi \pm \pi$) levels of the corresponding diene (**15b—d**), presumably for the same reason that was advanced to account for the related behaviour of the methane complexes (**14a**) and (**15a**). This relationship breaks down for (**14e**) and (**15e**) because of the overwhelming presence of the polarizing effects of the positive charge; these are responsible for the lowering of all $\pi$ levels in both complexes by *ca.* 4 eV, relative to the $\pi$ level of ethylene.

For the water complexes (**15b**; $n = 1,2$) the $\Delta E_\pi$ values are less than those calculated for the corresponding methane systems. However, this is due not only to reduced conjugative interactions in the ($\pi - \pi$) level of (**15b**; $n = 1,2$) but also to increased conjugation in the ($\pi + \pi$) MO of these complexes through mixing with the oxygen nonbonding orbital, $n_z$, which points in the *z* direction [see (**15**)].

Likewise the ($\pi + \pi$) level in the $H_2S$ complex (**15c**; $n = 1$) is raised by 0.22 eV through mixing with the lower lying sulphur $n_z$ orbital. The ($\pi - \pi$) level, however, is *depressed* (by 0.49 eV) because the sulphur *p* orbital with which it mixes [see (**11**)] has a greater energy (*ca.* −7.6 eV) than that of the ethylene $\pi$ MO. The resulting inverted sequence of levels for (**15c**; $n = 1$), *i.e.* ($\pi + \pi$) > ($\pi - \pi$), is therefore explained. The symmetries of the HOMO and SHOMO of the *p* orbitals of $(H_2S)_n$ follow the same pattern as the corresponding orbitals of $(CH_4)_n$ of Figure 1. However, both HOMO and SHOMO levels of $(H_2S)_n$ are calculated to lie above that of the ethylene $\pi$ level. This means that, not only will both ($\pi \pm \pi$) levels of (**15c**) be *depressed* upon mixing with the sulphur orbitals, but the level less affected, that is the resulting $\pi$ level of higher energy, will have the symmetry of the $(H_2S)_n$ HOMO. The level sequence of (**15c**; $n = 1$—3) therefore follows.

The $\Delta E_\pi$ values for (**15c**; $n = 1$—3) are considerably larger than those calculated for any of the other corresponding complexes as are the actual conjugative interactions as measured by the maximum shift in a level for each complex. This is due to the comparatively large size of the sulphur $3p$ orbital and to the narrow sulphur $3p$—ethylene $\pi$ energy gap of *ca.* 1.4 eV.

Although attention has been found on the $(\pi \pm \pi)$ levels in (**15**) these are not the highest occupied MOs of (**15c**; $n = 1$—3). In fact the highest $n$ occupied MOs of this series are more properly identified as the $n$ MOs formed from the sulphur $3p$ orbitals of $(H_2S)_n$. As expected these orbitals also experience large energy changes upon mixing with the two $(\pi \pm \pi)$ levels. For example the HOMO of each member of the series (**15c**; $n = 1$—3) is *raised* by 0.91 ($n = 1$), 0.54 ($n = 2$), and 0.27 eV ($n = 3$) relative to that of the corresponding member of the series $(H_2S)_n$.

The carbonyl group appears not to be a good conjugating group in (**15d**; $n = 1,2$) as the $(\pi \pm \pi)$ level shifts and the $\Delta E_\pi$ values are small. This is due not to any lack of conjugating ability on the part of the carbonyl group but to the opposing influence of the $\pi$ and $\pi^*$ MOs of that group on the $(\pi - \pi)$ level: the former MO (energy $-9.6$ eV) tends to *raise* that level whereas the latter MO (energy 7.7 eV) has the opposite tendency. In fact the $(\pi - \pi)$ MO of (**15d**; $n = 1$) does show considerable admixture of the carbonyl $\pi$-type MOs.*

The methyl cation induces very large energy changes of *ca.* 4 eV in both $(\pi \pm \pi)$ levels of (**15e**; $n = 1$). Because the symmetric $(\pi + \pi)$ MO of (**15e**; $n = 1$) contains no contribution from the methyl cation the energy change associated with this MO must be caused by the polarizing influence of the positive charge. The $\Delta E_\pi$ value may therefore be taken as a measure of the laticyclic conjugation in this complex. The negative sign of this quantity is due to the antisymmetric vacant $p$ orbital of the methyl cation having a higher energy ($-6.4$ eV) than that of the ethylene $\pi$ MO. The $(\pi - \pi)$ level is therefore depressed relative to the $(\pi + \pi)$ level.

Level shifting due to laticyclic conjugation in (**15e**; $n = 2$) is difficult to assess because conjugation and electrostatic interactions now affect both levels.† All that can be safely said is that the difference in the extent of conjugation operating in the two $(\pi \pm \pi)$ levels amounts to *ca.* 0.17 eV.

Laticyclic conjugation involving the $\pi^*$ orbitals of the ethylene groups of (**15b**—**e**) does not occur for symmetry reasons.

*Concluding Remarks.*—The most remarkable result of these studies is the ability of a relay of $CH_2$ groups, having a geometrical relationship described by (**14a**) and (**15a**), to participate in $(\pi,n)$- and $(\pi,n,\pi)$-laticyclic hyperconjugation. Indeed such interactions arising therefrom are large even for $n = 4$, *i.e.* when the double bonds are separated by *ca.* 16.5 Å! Results of experimental studies on the series of compounds (**3**; $n = 1,2$), which embody the structural features of (**15a**; $n = 1,2$) vindicate the quality of our model calculations.

It is predicted that these interactions should play a very important role in long-range electron-transfer reactions in cation radicals of molecules containing $\pi$ systems placed in suitable juxtaposition to $CH_2$ groups.

The $CH_2CH_2$ group is also able to hyperconjugate effectively, not only with $\pi$ MOs, but also with $\pi^*$ orbitals when placed in the orientation shown by (**21**). Molecules such as (**22**) therefore provide an opportunity for studying long-range electron-transfer reactions in anion radicals.

Surprisingly, $(\pi,n,\pi)$-laticyclic hyperconjugation interactions can be as large as, and sometimes larger than, conjugation involving relaying nonbonding orbitals, $\pi$ MOs, or vacant $p$ orbitals, *e.g.* (**15a**) *versus* (**15b**—**e**). Conjugative interactions in (**15c**) are, however, very large. In this respect, of the unknown series of compounds, (**11a**), (**11b**), and (**12**), the synthesis of (**11b**) would be particularly worthwhile.

On a more general note, these studies, together with those carried out on OITB,[3] bring into serious doubt the validity of the adage that simple methylene chains, and other saturated moieties which connect chromophoric or functional groups, serve merely as 'insulators' or 'spacers' and play no role in the interactions between those groups.

Quite the contrary, it is believed that the interconnecting framework linking functional groups plays a vital role in most, if not all, long-range interactions and that more attention should be paid to their possible involvement in future investigations.

Indeed the results of recent and elegant photoinduced long-range electron-transfer studies on bichromophoric molecules carried out by Verhoeven and his co-workers have been interpreted in terms of through-bond orbital interactions.[15,16] The involvement of similar interactions in the long-range electron-transfer reactions observed in the anion radicals such as (**19**)[13] should not be dismissed in the absence of more concrete evidence.

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* The coefficients of the atomic orbitals of the ethylene carbon atom, the formaldehyde carbon atom, and the oxygen atom are 0.43, 0.14, and 0.23 respectively. The net overlap between the ethylene and formaldehyde orbitals in this MO is antibonding, and that between C and O of formaldehyde bonding.

† The coefficients of the carbon $p$ orbitals of the $CH_3^+$ groups in the $(\pi - \pi)$ and $(\pi + \pi)$ MOs are 0.2 and 0.26 respectively; the ethylenic carbon atomic orbital coefficients are *ca.* 0.42 in both MOs.