THE TWISTING FREQUENCY AND THE BARRIER HEIGHT FOR FREE ROTATION IN ETHYLENE[1]

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By the use of the semiempirical LCAO MO method the variation of the energy of the ethylene molecule, on twisting the plane of one CH_2 group relative to that of the other about the C=C axis, has been computed for each of four important electronic states, and also for the normal state of the ionized molecule. Three empirical parameters were used in the computations. Finally, estimated corrections for electronic interactions were made to the computed curves. The computations were made for each of several plausible sets of values of two of the parameters (those which govern the computed extent of hyperconjugation). For the third parameter, the bond integral β, a value -3 ev. taken from the ultraviolet spectrum was used. It is concluded that the 90°-twisted form of the molecule is more stable by about 1 ev., as a result of hyperconjugation, than it would otherwise be. An important and probably fairly reliable conclusion from the computations is that the potential curve for twisting is nearly a parabolic one, probably with slight *positive* anharmonicity; there are indications of support for this last point in the spectroscopic data. The computed frequencies and barrier heights show reasonable agreement with the most probable observed values. However, we do not wish to stress this agreement so much as the value of the computations as a step toward a better understanding of the possibilities and difficulties of the semiempirical LCAO MO method, and toward the possible determination of a reliable set of empirical parameters for use in other computations.

I. PURPOSES AND METHOD

Some computations made recently on the ethylene molecule furnish an interesting example of the use of the LCAO[2] molecular orbital method in its semiempirical form (*cf.* second preceding paper (7)). The purpose of the computations was twofold. The *first purpose* was to obtain information about the energy of the molecule in several of its important electronic states, not only for the normal planar geometrical configuration but also for configurations with the planes of the CH_2 groups twisted through various angles relative to each other; and, a corollary to this, to obtain information about the twisting frequency, and about the barrier height for thermal *cis–trans* isomerization. Such computations by the semiempirical method require the use of certain parameters for which reasonable values can be assumed in harmony with empirical

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[2] Linear combination of atomic orbitals.

evidence. The present computations were carried through for each of several alternative sets of values of such parameters, chosen within a reasonable range based on previous experience. The *second purpose* of the computations, then, was to compare the results with further experimental evidence, in the hope of narrowing the range of choice of the parameters used, as a step toward an ultimate goal of a single consistent set of parameters suitable for use in computations on other molecules by the semiempirical LCAO MO method. Space here does not permit a discussion of the various limitations and qualifications that must be placed on the hope of attaining such a goal. The work here reported may perhaps best be regarded as an exploratory effort toward a determination of the feasibility of reaching a goal such as that stated.

The point of view used in any MO method is to regard the electronic structure as consisting of a set of electrons each occupying a definite MO (molecular orbital), commonly with two electrons of opposite spin in each MO. Each MO is in principle an eigenfunction of a one-electron Schrödinger equation. The appropriate Schrödinger equation is that for an electron moving in the electric field (i.e., the Hartree self-consistent field) due to all the other electrons and the nuclei.

In the LCAO MO method, the MO's are approximated by setting up linear combinations of known AO's (atomic orbitals) of the atoms concerned. The coefficients in these linear combinations are partly, or sometimes wholly, determined by the symmetry of the molecule. In our example of twisted ethylene, they are partly determined by the symmetry and partly by the solution of certain secular equations into which enter some of the semiempirical parameters already mentioned.

At the same time, the *energy* for each MO is determined from the solutions of the secular equations, with the introduction of one more semiempirical parameter. The total energy of the molecule is obtained, roughly, by adding the *orbital energies* (that is, the energies of the various occupied MO's), counted once for each occupying electron. To obtain the total energy more accurately, allowance must be made for the specific energies of interaction between electrons.

In the present work, a semiempirical computation has been made of the MO orbital energies for the *last six* of the sixteen electrons of ethylene, as a function of the *angle of twist* ϕ. For various trial sets of the semiempirical parameters, the orbital energy has been computed for several points in the range 0° to 90° and corresponding curves for the energy $U(\phi)$ have been plotted; the same curves apply to the range 180° to 90°, and the whole is repeated between 180° and 360°. It was then plausibly assumed that the total energy of the *first ten* ethylene electrons is essentially independent of the angle of twist. Finally, the forms of the integrals for the energies of interaction among the outer electrons were examined, and *estimates* made of the total contribution of these to the variation of the total energy with angle of twist. It was tentatively concluded that this contribution is a semi-order-of-magnitude smaller than that due to the variation of the orbital energy with ϕ.

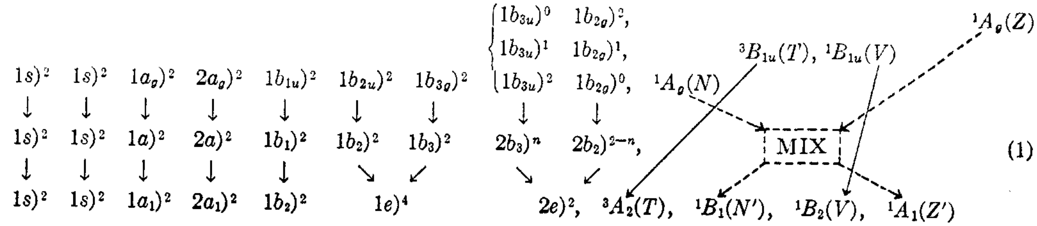
II. PENNEY'S WORK ON ETHYLENE

In 1934, Penney (12) discussed the structure of ethylene, both by the valence-bond AO method and by the LCAO MO method. He demonstrated the stability of the planar form for reasonable assumed values of certain relevant theoretical integrals in the AO method. He set up the secular equations for the LCAO MO method, but did not carry through as complete computations as we have done, and assumed values for the integrals which we believe now not to be empirically justified.[3]

Penney also showed in a second paper (13), that the frequency for twisting oscillations and the barrier height for 90° twisting are given by very simple expressions by the AO method, and from an observed value of the twisting frequency he obtained an empirical value of the double-bond π exchange integral, and also a value for the barrier height. These points will be referred to again later.

III. ELECTRON CONFIGURATIONS OF IMPORTANT ELECTRONIC STATES

In order to understand what happens to the electronic energy levels of ethylene when it is twisted from the planar to the *perpendicular form* (90° twist), it is necessary to consider simultaneously four electronic levels of the planar form, since all go over into states of a single electron configuration of the perpendicular form (5, 6).[4] These are the so-called N, T, V, and Z states of the planar form. Their electron configurations, and the way in which these are correlated with the electron configurations and states of the perpendicular form, can be expressed by the following scheme:



(1)

At the left are given the point-group symmetries (V_h for planar, V for partially twisted, V_h for 90°-twisted ethylene). The electron configurations follow, together with arrows to show how the MO's for one geometrical arrangement go over into those for another. Where two or more MO's belong to the same group-theory species, the one of lower energy is called 1, the next 2, and so on

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[3] W. G. Penney (12) set up the general LCAO MO secular equation for the complete set of MO's of ethylene, for various angles of twist and other distortions, but came to somewhat different conclusions from ours. Also, he concluded that the sixth-order secular equation for the π MO's does not factor for twisted ethylene, whereas we have shown that it does factor into two cubics, one for the b_2 and one for the b_3 MO's (*cf.* our equation 3).

[4] On group-theory nomenclature and electronic structure in the perpendicular form, see especially reference 5.

(for example $1a_g$, $2a_g$). Detailed LCAO approximate forms and a description of bonding properties for the MO's of planar ethylene are given by equations 2–4, and the accompanying text, in the preceding paper on diborane and related compounds (8).

The most notable change on twisting to 90° is the coming together of the non-degenerate b_2 and b_3 MO's of untwisted or partially twisted ethylene into the degenerate $1e$ and $2e$ MO's of perpendicular ethylene. As a result, perpendicular ethylene contains a *half-filled shell* of $2e$ electrons, very similar to the half-filled π_g shell which occurs in the isoelectronic molecule O_2 and (for the D_3 geometrical model only) in the likewise isoelectronic B_2H_6 (8). (On the other hand, the electronic structure of planar ethylene is very similar to that for the bridge model of diborane.) This half-filled $2e$ shell gives rise to four electronic states, which can be shown[4] to be correlated as indicated in scheme 1 with the four states N, T, V, Z of planar ethylene. The states of perpendicular ethylene are here called N', T, V, Z', because a 50-50 mixing of the N and Z eigenfunctions takes place during the twisting to 90°.[4]

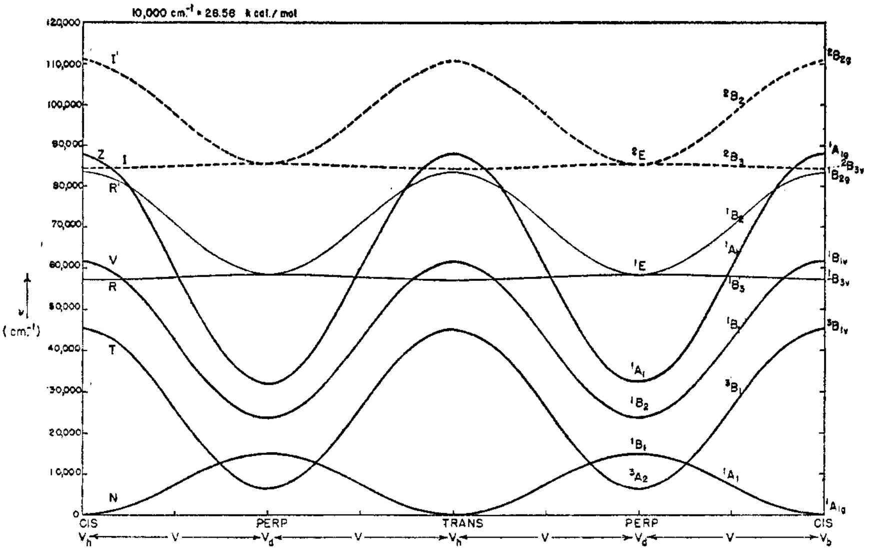

FIG. 1. Electronic states of ethylene molecule (*not based on present computations*). Variation in energy with angle of twist for the theoretically important electronic states N, T, V, Z of ethylene, and for certain excited states R, R' and ionized states I, I'. States N, T, V, R, I are observed states; Z, R', I' are related theoretically predicted states. The curves for N, T, V, R are based on an interpretation of available experimental data combined with qualitative theoretical considerations, as described by R. S. Mulliken (Rev. Modern Phys. **14**, 265 (1942)); the curve for I is drawn of the same shape as for R, in accordance with theory. These curves were drawn before the present computations were made; according to the latter, all the curves should be relatively higher for perpendicular ethylene.

Figure 1 shows qualitatively how the curves of states N, T, V, Z, also those of two other excited states R and R' and of two ionized states I and I', should vary on twisting the molecule. These curves were drawn before the present computations were made; according to the latter, the heights of the curves for perpendicular ethylene are somewhat greater.

As can be seen from an inspection of the forms of the MO's $1a_g$, $2a_g$, and $1b_{1u}$ of planar ethylene as given in equations 3 of the preceding paper, no important change in these MO's is to be expected during twisting. Thus it is reasonable to assume that the total energy of these and the K electrons does not change appreciably as a direct result of twisting. However, if the C=C bond should be lengthened as a result of twisting, the energy of these electrons would be somewhat affected. This point will be considered later; a preliminary check indicates that the effect is small.

We have then to consider just the *last six electrons*, those which occupy MO's which become $1e$ and $2e$ in the 90° form. This problem might be treated in either of two ways: (*1*) consider just the last two electrons, those which become $2e)^2$ in the 90° form, and assume that the next four electrons, which become $1e)^4$ at 90°, do not contribute much to the energy change on twisting; (*2*) consider the last six electrons together. In a computation parallel to the present one, following the approximate-theoretical method (7) in LCAO MO form, Parr and Crawford (11) are using the first of the above-mentioned two approaches. In the present paper we are using the second, following the semiempirical method in LCAO MO form.

By considering all six outer electrons, we take into account the phenomenon of hyperconjugation. This is responsible in planar ethylene for an appreciable energy stabilization of the four next-to-outer electrons (10); and in 90° ethylene for a *further* stabilization of the molecule by strengthened hyperconjugation, involving both the four middle and to some extent the two outer electrons. The existence of hyperconjugation, partially offsetting the loss of bond strength in 90°-twisted ethylene, was first pointed out some time ago, though the word "hyperconjugation" was not then used.[4]

IV. ENERGY RELATIONS FOR NORMAL AND TWISTED MOLECULES

Given below is a comparative tabular outline of theoretical energy relations for the planar and the perpendicular forms of ethylene. Listed are energy formulas for states N, T, V, Z (or N', T, V, Z'), and also for the normal state I of the ethylene positive ion. The latter may be obtained in scheme 1 by removing one electron from $1b_{3u}$ of planar or from $2e$ of perpendicular ethylene. At the foot of the table are also stated (a) some additional theoretical relations, (b) some reasonable assumptions or estimates on the magnitudes of certain theoretical integrals or on relations between these, and (c) some observational data (6) which may be fed into the semiempirical method to supply numerical values for certain theoretical integrals, together with the empirical parameters or relations deduced using these.

In table 1, E represents the total energy of the given state. A represents the (unknown) total energy of the ten inner electrons,[5] which we assume does not

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[5] Plus certain Coulomb and exchange (J and K) interaction terms belonging to the six outer electrons, but whose sum it is reasonable to hope does not vary greatly with the angle of twist.

vary appreciably with the angle of twist. I represents the total *orbital* energy of the four next-to-outer electrons. Each ϵ represents the *orbital* energy of one of the two outer electrons; ϵ_3^0 is the energy of the $1b_{3u}$ planar ethylene C—C bonding orbital of form $\xi + \xi'$, ϵ_4^0 is the energy of the corresponding C—C antibonding orbital $1b_{2g}$ of form $\xi - \xi'$, and ϵ_3^p is the energy of the nearly non-bonding $2e$ orbital of perpendicular ethylene. *It is I and the ϵ's which we have computed, as a function of the angle of twist ϕ.*

TABLE 1

Energy relations

PLANAR ETHYLENE	PERPENDICULAR ETHYLENE
Theoretical relations: $N: E = A^0 + I^0 + 2\epsilon_3^0 + J_{33}^0 - \gamma K_{34}^0$ $T: \quad + \epsilon_3^0 + \epsilon_4^0 + J_{34}^0 - K_{34}^0$ $V: \quad + \epsilon_3^0 + \epsilon_4^0 + J_{34}^0 + K_{34}^0$ $Z: \quad + 2\epsilon_4^0 + J_{44}^0 + \gamma K_{34}^0$ $I: \quad + \epsilon_3^0$ $\gamma \approx K_{34}^0/(E_Z - E_N)$	*Theoretical relations:* $T: E = A^p + I^p + 2\epsilon_3^p + J_{34}^p - K_{34}^p$ $N': \quad + 2\epsilon_3^p + J_{33}^p - K_{34}^p$ $V: \quad + 2\epsilon_3^p + J_{34}^p + K_{34}^p$ $Z': \quad + 2\epsilon_3^p + J_{33}^p + K_{34}^p$ $I: \quad + \epsilon_3^p$ $J_{33}^p > J_{34}^p$
Estimated: (a) $\gamma \approx 0.1$ (b) $J_{33}^0 + \gamma K_{34}^0 = J_{34}^0$ *Observational data (see reference 6):* (a) $E_V - E_N = 7.6$ ev. (b) $E_V - E_T \approx 2.2$ ev. (?)	*Estimated:* (a) $J_{33}^p - J_{34}^p = 0.6$ ev. (b) $K_{34}^p = 0.75$ ev. (c) No appreciable energy change due to stretching of carbon-carbon distance (d) (*Assumed*) $A^0 + J_{33}^0 - \gamma K_{34}^0 = A^p + J_{33}^0$
Deduced from theoretical relations and these data: (a) $K_{34}^0 = 1.1$ ev. (b) $\epsilon_4^0 - \epsilon_3^0 = 6.5$ ev. (c) $\beta_{spec} = -3.0$ ev.	*Deduced from theoretical relations and above estimates and assumptions:* (a) $Q \equiv E_{N'}^p - E_N^0$ $= (I^p + 2\epsilon_3^p) - (I^0 + 2\epsilon_3^0) - K_{34}^p$ $= (I^p + 2\epsilon_3^p) - (I^0 + 2\epsilon_3^0) - 0.75$ ev. (b) $Q_T \equiv E_T^p - E_N^0 = Q - (J_{33}^p - J_{34}^p)$ $= (I^p + 2\epsilon_3^p) - (I^0 + 2\epsilon_3^0) - 1.35$ ev.

The values of the J's and K's, or of their variations with ϕ, have been estimated (see table 1) with the help of detailed theoretical formulas, or partly from experimental data, and also partly from theoretically computed integrals[6] available in the literature. The Coulomb integrals J and the exchange integral K_{34} are defined by

$$J_{ij} \equiv \int \phi_i^2(\mu)(e^2/r_{\mu\nu})\phi_j^2(\nu)\, dv_\mu dv_\nu$$

$$K_{34} \equiv \int \phi_3(\mu)\phi_4(\mu)(e^2/r_{\mu\nu})\phi_3(\nu)\phi_4(\nu)\, dv_\mu dv_\nu$$

where ϕ_3 refers to the $1b_{3u}$ MO of planar ethylene or to the corresponding twisted

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[6] Mainly from the computations of Goeppert-Mayer and Sklar on benzene (1), as extended by Griffing (1a). Reference 1 gives values of the necessary integrals for a C—C distance of 1.39 A. only, while reference 1a gives them for a range of distances, including the value 1.35 A. needed for ethylene.

MO, ϕ_4 refers to $1b_{2g}$ or the corresponding twisted MO, and μ and ν refer to two electrons at a distance $r_{\mu\nu}$ apart. The J's are known, from computations[6] by the approximate-theoretical LCAO MO method, to have values in the range 8–15 ev. The value of K^0_{34} is 1.1 ev. from experiment. Its value according to the theoretical method is[6] 4.0 ev.; the large discrepancy is an argument in favor of the present semiempirical method.

Details in partial justification of the estimated and assumed relations, involving A and the J's and K's and given in the lower part of table 1, will appear in the complete paper. These relations constitute the most doubtful part of the present work, but we feel moderately hopeful that we are approximately right in our estimates and assumptions about them, or at least that we are right in our conclusion that the variation of A and the J's and K's with ϕ is subordinate in importance to our computed variation of I and the ϵ's with ϕ. In any event, we believe that the present computations are instructive and suggestive.

V. THE SEMIEMPIRICAL LCAO MO COMPUTATIONS

We now outline the method used in computing I and the ϵ's as functions of ϕ. For the planar molecule, I^0 breaks up into the orbital energy of two electrons in the $1b_{2u}$ MO, plus that of two electrons in the $1b_{3g}$ MO. These and the orbital energies of the last two electrons, which occupy the $1b_{3u}$ or $1b_{2g}$ orbital (energies ϵ^0_3 or ϵ^0_4), can be computed separately, because in the planar model the MO's concerned all belong to different group-theory species.

The following equation (6, 9, 10) represents the orbital energies for the $1b_{3u}$ and $1b_{2g}$ MO's of planar ethylene in LCAO approximation (the upper sign gives ϵ^0_3, the lower ϵ^0_4):

$$\epsilon^0_{\substack{3\\4}} = \alpha \pm \beta/(1 \pm S) \tag{2}$$

where α is an atomic Coulomb integral giving the major part of the binding energy of the electron, β is the *bond integral* (9, 10), and S is the overlap integral $\int \xi\xi' dv$. The quantity α enters only as an additive constant, so that for our purposes it is unnecessary to determine its value. S is computed theoretically with sufficient accuracy, using approximate carbon atom $2p_x$ AO's (ξ means $2p_x$; see preceding paper (8) after equations 3).

Finally, β remains as one of our principal empirical parameters. An empirical value for β, which we call β_{spec}, is determined from observational spectroscopic data on ethylene in the manner indicated in the left-hand lower part of table 1. As shown there,

$$\epsilon^0_4 - \epsilon^0_3 = E_V - E_N - K_{34}$$

if we assume J^0_{33} approximately equal to J^0_{34}, as can be shown to be reasonable. K_{34} is approximately known empirically; then, from equation 2, we have

$$\epsilon^0_4 - \epsilon^0_3 = -2\beta/(1 - S^2)$$

from which is obtained our empirical $\beta_{spec} = -3.0$ ev. This empirical value is not necessarily the best, but its approximate correctness is indicated by the results of its use in other computations (6, 9, 10). It is to be hoped that an improved value will come out of a trial-and-error process of using it in various computations and checking the results against experiment.

When the molecule is twisted, the MO's occupied by the six outer electrons partially lose their symmetry, and now fall into just two group-theory species: namely, b_2 and b_3 (see scheme 1). The occupied MO's for the general case of an intermediate angle of twist are $1b_2$, $1b_3$, and $2b_3$, while $2b_2$ is also important for the excited states; for $\phi = 90°$, $1b_2$ joins $1b_3$ in belonging to $1e$ and $2b_2$ joins $2b_3$ in belonging to $2e$ (*cf.* scheme 1). It can be shown that $1b_2$, $2b_2$, and a third highly excited MO $3b_2$ are solutions of a cubic secular equation, while $1b_3$, $2b_3$, and a highly excited MO $3b_3$ are solutions of a second cubic secular equation.[3] The secular equation for the three b_2 MO's is given here in order to illustrate the empirical parameters involved; full details will be given in the complete paper. It is as follows. The secular equation for the b_3 MO's is similar, and involves the same parameters:

$$\begin{vmatrix} X - \delta & [\cos\tfrac{1}{2}\phi/(1+S)^{\frac{1}{2}}][S^*X - \beta^*] & [-\sin\tfrac{1}{2}\phi/(1-S)^{\frac{1}{2}}][S^*X - \beta^*] \\ [\cos\tfrac{1}{2}\phi/(1+S)^{\frac{1}{2}}][S^*X - \beta^*] & X - \beta/(1+S) & 0 \\ [-\sin\tfrac{1}{2}\phi/(1-S)^{\frac{1}{2}}][S^*X - \beta^*] & 0 & X + \beta/(1-S) \end{vmatrix} = 0 \quad (3)$$

Here X is an abbreviation for $\epsilon_i - \alpha$, and the three solutions of the equation give ϵ_2 (for $1b_3$), ϵ_3 (for $2b_3$), ϵ_6 (for $3b_3$) for any angle ϕ; ϵ_1, ϵ_4, ϵ_5 come from the other secular equation. The quantity S^* is an overlap integral which can be computed theoretically.

The quantities β, β^*, and δ are the *three empirical parameters* which are involved in our computation. The parameter β has already been discussed. The parameter β^* is a C—H *bond integral* associated with the interaction between an η carbon AO and an ss composite hydrogen orbital (see equations 3 of previous paper (8) and following text). *Both β and β^* are negative.* The parameter δ is a *relative electronegativity parameter.* Specifically, δ is the difference in Coulomb energy $\alpha_H - \alpha_C^{2p}$ between a $1s$ hydrogen AO and a $2p$ carbon AO, the latter being what is involved here (η is $2p_y$). It is expected to be *negative*, since hydrogen is *more* electronegative than carbon $2p$, even though it is *less* electronegative than an average (sp^3 hybrid) carbon AO.

In solving the secular equations, we have taken β as the unit of energy (10). The solutions depend only on β^*/β and δ/β. The value of β obviously enters only in determining the absolute values of the MO energies ϵ_i.

We have solved the secular equations for several values of ϕ ranging from 0° to 90°, for each of several sets of the adjustable parameters β^*/β and δ/β, as follows:

(A) β^*/β very large (*case of no hyperconjugation*)
(B) $\beta^* = 2\beta, \delta = 0$
(C) $\beta^* = 2\beta, \delta = \beta$ (4)
(D) $\beta^* = 1.5\beta, \delta = 0$
(E) $\beta^* = 1.5, \delta = \beta$

The various ϵ_i's were obtained, in units of β, for each parameter-set and for various angles. Adding up the ϵ_i's, each times the number of electrons in the corresponding MO, for each of the various states N, T, V, Z, I (see equations 1), and multiplying by $\beta = -3.0$ ev. in all cases, the total orbital energy of each state (aside from an additive unchanging constant) was obtained and plotted as ordinate against ϕ as abscissa.

Finally, these curves were corrected for the specific interelectronic interactions of the last two electrons. This was done by using certain relations, given in the second column of table 1 under the heading "Estimates", to determine the *differential* contributions, at 90° as compared with 0°, of these interelectronic interactions to the total energy. Having corrected the relative ordinates of the energy curves at 0° and 90° by this means (the corrections are a semi-order-of-magnitude smaller than the difference in ordinate between 0° and 90° based on the orbital energies alone), the final curves were drawn by assuming their ordinates to be everywhere proportional to those for the curves of orbital energy alone. We feel that this somewhat arbitrary procedure should not lead to any serious error for the conclusions drawn below.[7]

VI. THE POTENTIAL CURVE FOR TWISTING

Let us denote by $U(\phi)$ the curve of total energy E of state N as a function of ϕ. $U(\phi)$ is the potential-energy function for the twisting vibration ν_4 (Herzberg's notation) of ethylene. If we define

$$k \equiv (d^2U/d\phi^2)_{\phi=0}$$

then

$$\nu_4(\text{in cm.}^{-1}) = (1/2\pi c)(k/m_{\text{H}}\rho^2)^{\frac{1}{2}} \tag{5}$$

as is easily shown, where c is the speed of light, m_{H} is the mass of a hydrogen atom, and ρ is half of the hydrogen–hydrogen distance in a CH_2 group. Let us adjust the additive constant in $U(\phi)$ so that $U(0) = 0$.

On plotting our $U(\phi)$ curves we find, *for all the different sets of parameters tried*, that all may be represented by expressions of the form

$$U(\phi) = \tfrac{1}{2}k\phi^2 + a\phi^4 + \cdots \tag{6}$$

with a small positive a. That is, $U(\phi)$ is *nearly parabolic but has a small positive anharmonicity*.

Of course equation 6 fails to hold close to $\phi = \pi/2$, where $U(\phi)$ has a maximum. Let us denote the barrier height, for a process of *cis–trans* isomerization by going over the maximum of $U(\phi)$, by Q; then

$$Q = U(\pi/2) \tag{7}$$

It is of interest to compare our computed Q values with those for a simple parabolic curve $U(\phi) = \frac{1}{2}k\phi^2$. For the latter, it is found that $Q = \pi^2k/8$. For

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[7] As to possible further lowering of the curves owing to increased C—C distance for perpendicular ethylene (causing, among other things, a decrease in β), preliminary consideration indicates that this would amount to only 0.2 ev.

all our computed curves, it is found that $Q > \pi^2 k/8$. This is qualitatively just as if equation 6 were valid all the way to $\phi = \pi/2$.

Our theoretically predicted positive anharmonicity is possibly of significance in connection with the fact that the weak but well-established infrared band at 800 cm.$^{-1}$ has been identified as ν_4, whereas in the Raman effect the frequency 1656 cm.$^{-1}$ has been identified as $2\nu_4$.[8] If both identifications are correct, they would correspond to a positive anharmonicity.

It is of considerable interest that our computed $U(\phi)$ curves are radically different from the potential curve of the cos 2ϕ form usually assumed (3). Again setting $U(0) = 0$, and defining k as above, the cos 2ϕ type of curve is given by

$$U(\phi) = \tfrac{1}{4}k(1 - \cos 2\phi) \tag{8}$$

For a given k—hence for a given ν_4—equation 8, which corresponds to a strong negative anharmonicity, gives a much smaller barrier height than a parabolic curve or, even more so, than our computed curves. The comparison is as follows:

$$\begin{gathered} \text{For equation 8: } Q = \tfrac{1}{2}k \\ \text{For } U = \tfrac{1}{2}k\phi^2\text{: } Q = (\pi^2/8)k \\ \text{For our } U \text{ curves: } Q > (\pi^2/8)k \end{gathered} \tag{9}$$

A word here about the potential curve for our case A of relations 4, the hypothetical case of *no hyperconjugation*. For this case, with $\beta^* >> \beta$, the orbital energies of $1b_2$ and $1b_3$ should be independent of ϕ, and (aside from electronic interaction corrections) $U(\phi)$ should be given by the orbital energy of an electron pair in $2b_3$, alone. Again taking $U(0) = 0$, this is easily shown to be

$$U(\phi) = -2\beta/(1 + S) + 2\beta|\cos\phi|/(1 + S|\cos\phi|) \tag{10}$$

from which

$$Q = -2\beta/(1 + S) = 4.7 \text{ ev.}$$

This $U(\phi)$ function gives $k = -2\beta/(1 + S)^2$, or

$$Q = k(1 + S)$$

in which S is about 0.25.

The $U(\phi)$ curves for our cases B to E of relations 4 are lower than for case A, and give Q values 1–2 ev. lower than for case A, because hyperconjugation stabilizes perpendicular ethylene more than it stabilizes planar ethylene. But as already noted, the $U(\phi)$ curves for all the cases A to E give positive anharmonicity, and give Q greater than for $U = \tfrac{1}{2}k\phi^2$. As already discussed above, the $U(\phi)$ curves and Q values in all cases are lowered somewhat by the specific

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[8] *Cf.* Herzberg (2). Although ν_4 (Herzberg's notation) is infrared forbidden, Herzberg suggests that Coriolis forces may explain its appearance; specific heats also indicate $\nu_4 \approx$ 800 cm.$^{-1}$ But see also Rasmussen and Brattain (14), who confirm the existence of the 800 cm.$^{-1}$ band but argue that 995 cm.$^{-1}$ may be ν_4.

electronic interaction terms, but there seems to be no reason why this should change their shapes.

However, as shown by Penney (12, 13), the AO approximation gives

$$U(\phi) = (3/4)I_2(1 - \cos 2\phi)$$

where I_2 is the major π electron exchange integral of the AO method. From this, he obtained also an expression for the twisting frequency ν_4, in terms of I_2 and the moment of inertia for twisting; and then from an empirical value $\nu_4 = 750$ cm.$^{-1}$ he obtained a value for I_2.

VII. THE TWISTING FREQUENCY

From plots of our final $U(\phi)$ curves corresponding to cases A to E of relations 4, the corresponding k and ν_4 values have been determined and are recorded in table 2. Similar plots have also been made for the ionized molecule in its normal state I (see table 1), and the corresponding ν_4 determined. In all cases we have taken $\beta = -3$ ev.

TABLE 2

Computed and observed twisting frequencies

	ν_4 (STATE N)	ν_4 (STATE I)
	cm.$^{-1}$	*cm.*$^{-1}$
Computed:		
Case A (no hyperconjugation)	892	660
Case B ($\beta^* = 2\beta$, $\delta = 0$)	836	Imaginary
Case C ($\beta^* = 2\beta$, $\delta = \beta$)	775	530
Case D ($\beta^* = 1.5\beta$, $\delta = 0$)	747	
Case E ($\beta^* = 1.5\beta$, $\delta = \beta$)	648	
Observed (2, 6, 14):		
Infrared, ν_4	800	
Specific heats	800	
Raman, from $2\nu_4$	828	
Ultraviolet, from possible $2\nu_4$		235 (145 for C_2D_4)

From other experience (6) we have reason to believe that the empirical parameters of case C are about right. However, there are some indications that the best values of $-\beta^*$ and $-\delta$ may *both* be a little smaller. This would not change the computed ν_4 very much. However, if $-\beta^*$ were *much* smaller, the energy order of $1b_{3g}$ and $1b_{3u}$ of planar ethylene would be reversed, in probable contradiction of the spectroscopic evidence.

The listed experimental ν_4 for state I is based on an ultraviolet frequency interval observed for a Rydberg state (6), which should be practically the same as the ionized state so far as the interatomic forces are concerned. The possibility of a very low computed ν_4 in agreement with that observed is shown by the fact that, in case B, ν_4 for state I is imaginary; that is, $U(\phi)$ has a maximum instead of a minimum at $\phi = 0$ (at larger ϕ it rises again). Thus it is reasonable to expect that for a suitable choice of the parameters β^* and δ, the experimental ν_4 could be matched. The observed isotope effect (C_2H_4 as against C_2D_4) for the ultraviolet frequency interpreted as ν_4 is *greater* than in the ratio $2^{\frac{1}{2}}$ predicted for ν_4. This could be explained by a very strong positive anharmonicity, a condition which also could probably be matched by suitable choices of the values of β^* and δ.

VIII. THE BARRIER HEIGHTS

The barrier height Q for *cis–trans* isomerization along the $U(\phi)$ curve for state N has already been defined; it is equal to $U(\pi/2)$. There is also another, lower, barrier height. It has been recognized for some time (5, 6) that state T should be somewhat lower in energy at $\phi = \pi/2$ than state N. We therefore define

TABLE 3

Computed and observed barrier heights in electron volts

	Q	Q_T
Computed:		
Case A	3.3	2.7
Case B	2.9	2.3
Case C	2.5	1.9
Case D	2.3	1.7
Case E	1.8	1.2
Experimental:		
Thermal reaction rates (4)	(1.9)*	0.9†
Spectroscopic (ν_4 = 800):		
Equations 8, 9	1.0	
Our $U(\phi)$ (equation 9)	2.5	

* Complicated molecules.

† 2-Butene (also complicated molecules).

$$Q_T \equiv E_T(\pi/2) - E_N(0)$$

According to table 1, we estimate that

$$Q_T = Q - 0.6 \text{ ev.}$$

Penney (13) gives $Q_T = Q - 0.2$ ev.

Magee, Shand, and Eyring (4) have analyzed data on the thermal *cis–trans* isomerization of various unsaturated compounds, which they interpret as giving in some cases Q, in others Q_T. Most of their data are on conjugated compounds, to which it is doubtful that the present computations would apply. In one case, however, that of 2-butene, a comparison of their empirical value of Q_T with ours should be in order. In table 3 our computed values for Q and Q_T for cases A to E are listed.

If Magee, Shand, and Eyring's Q and Q_T can be accepted for our case, they suggest that our estimated electronic interaction energy corrections, especially for state T, should be somewhat altered.

The "spectroscopic" Q's in table 3 depend on what form $U(\phi)$ is assumed to have. According to our computations, as well as the data of Magee, Shand, and Eyring, equation 8 gives much too low a Q. Penney (13), using equation 8 as given by the AO method, and using $\nu_4 = 750$ cm.$^{-1}$, got $Q = 1$ ev.

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