The Use of the Modified Extended Hückel Method in the Dynamics of Molecules Containing Multiple Bonds

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(Z. Naturforsch. **26 a**, 947—952 [1971]; received 29 December 1970)

Using the acetylene, ethylene and ethane series, the applicability of the Modified Extended Hückel Method in the determination of the atomization energies as well as stable configurations of molecules has been demonstrated. It is believed, moreover, that within the procedual framework of our proposed technique the proportionality constants $F_\sigma(\mathrm{HH}) = 2.00$, $F_\sigma(\mathrm{CH}) = 1.75$, $F_\sigma(\mathrm{CC}) = 2.10$ and $F_\pi(\mathrm{CC}) = 1.45$ should prove adequate in the semi-empirical study of the atomization energies, stable configurations (and potential barriers) of all the hydrocarbons, be they aliphatic or aromatic.

Introduction

In the first two of this series of papers[1,2] concerning the use of the modified extended Hückel method in molecular dynamics, we showed that in molecules, which did not have nonbonding orbitals, the calculated total electronic energy[3] E_{MEH} simulated reasonably well the behavior of the actual molecular energy during the process of atomization. So much so that for MH_n type molecules, we suggested that the atomization energy Q_a be given by

$$Q_\mathrm{a}(\mathrm{calc}) = |E_{\mathrm{MEH}}(r_{\min}) - E_{\mathrm{MEH}}(\infty)| \approx n \cdot D(\mathrm{MH}_{n-1} - \mathrm{H}),$$

where $E_{\mathrm{MEH}}(r_{\min})$ and $E_{\mathrm{MEH}}(\infty)$ are the total electronic energies calculated respectively at the equilibrium and infinite $\mathrm{M}-\mathrm{H}$ separations, and where $D(\mathrm{MH}_{n-1}-\mathrm{H})$ is the $\mathrm{M}-\mathrm{H}$ bond dissociation energy in the given MH_n molecule.

It should be admitted, however, that, although general statements were made to the effect that the proposed technique was applicable to any type of bonding, its validity was demonstrated only in the case of σ-bonded molecules. In the present paper, we extend our previous work and demonstrate that the technique is equally applicable to molecules containing one or more π bonds.

The most obvious candidate for such a study was the $\mathrm{HC{\equiv}CH}$, $\mathrm{H_2C{=}CH_2}$, and $\mathrm{H_3C{-}CH_3}$ series. This series incorporates a variety of multiple bonds, widely varied CC bond dissociation energies, different geometries, and the three distinctive "hybridizations" of carbon orbitals (see Table 1). It also includes four types of atom-atom interactions and consequently requires the determination of *only* four proportionality constants. Fortunately, two of the latter, $F_\sigma(\mathrm{HH})$ and $F_\sigma(\mathrm{CH})$, were transferrable from our previous work on $\mathrm{CH_4}$, while the remaining two, $F_\sigma(\mathrm{CC})$ and $F_\pi(\mathrm{CC})$, were determinable, at least in principle, from any member of the series, for example, from $\mathrm{C_2H_2}$. Moreover, since $F_\sigma(\mathrm{HH})$, $F_\sigma(\mathrm{CH})$, $F_\sigma(\mathrm{CC})$ and $F_\pi(\mathrm{CC})$ exhausted all types

Table 1. Experimental parameters used in the present study.

(i)	The force constants[4] (md/Å).	
	$f_{\mathrm{C\equiv C}} = 15.6$,	$f_{\mathrm{CH}}(\mathrm{sp}) = 6.0$,
	$f_{\mathrm{C=C}} = 9.7$,	$f_{\mathrm{CH}}(\mathrm{sp}^2) = 5.1$,
	$f_{\mathrm{C-C}} = 4.5$,	$f_{\mathrm{CH}}(\mathrm{sp}^3) = 4.8$.
(ii)	The bond dissociation energies[5] (eV).	
	$D(\mathrm{HC-CH}) = 9.9$,	$D(\mathrm{C_2H-H}) = 4.9$,
	$D(\mathrm{H_2C-CH_2}) = 7.3$,	$D(\mathrm{C_2H_3-H}) = 4.3$,
	$D(\mathrm{H_3C-CH_3}) = 3.6$,	$D(\mathrm{C_2H_5-H}) = 4.2$.
(iii)	The equilibrium internuclear distances[5] (Å).	
	$r_{\mathrm{C\equiv C}} = 1.20$,	$r_{\mathrm{C-C}} = 1{,}54$,
	$r_{\mathrm{C=C}} = 1.34$,	$r_{\mathrm{C-H}} = 1.1$.
(iv)	The atomic orbital energies[6] h_{ii} (eV).	
	$H_{1\mathrm{sH}} = -13.6$,	$H_{2\mathrm{pC}} = -11.7$.
	$H_{2\mathrm{sC}} = -19.3$,	

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[1] W. A. YERANOS, Theor. Chem. Acta **13**, 346 [1969].

[2] W. A. YERANOS, Z. Naturforsch., in press.

[3] Here, and elsewhere, "the calculated total electronic energy" means the sum of the one-electron M.O. energies multiplied by their respective electron occupancies. MEH stands for modified extended Hückel method.

[4] G. HERZBERG, Molecular Spectra and Molecular Structure, Vol. II, D. Van Nostrand Co., Inc., New York 1966.

[5] G. HERZBERG, Molecular Spectra and Molecular Structure, Vol. III, D. Van Nostrand Co., Inc., New York 1966. The value of $D(\mathrm{C_2H_3-H})$ was interpolated from the values of $D(\mathrm{C_2H-H})$ and $D(\mathrm{C_2H_5-H})$.

[6] E. CLEMENTI, IBM J. Res. Develop. **9**, 2 [1965].

of atom-atom interactions in the said series, one was in a position to verify the general applicability of the technique by using these constants in the determination of the atomization energies and geometries of C_2H_4 and C_2H_6.

In the following pages we report the results of our study.

Theoretical Considerations

The atomization of a molecule is visualized as the stretching of all the bonds from their equilibrium values to infinity without changing the original shape of the molecule [7].

In the case of molecules with equivalent bonds, where all the bonds stretch at the same rate, the construction of such an atomization model is rather straighforward. Unfortunately, however, in molecules with non-equivalent bonds one *cannot* assume an identical rate of stretch for the different bonds during the process of atomization.

After considering several alternatives, we concluded that the simplest way to circumvent this difficulty was to assume that an acceptable expression relating the stretch of any two bonds could be obtained from Hook's Law. That is, in our case where only CH and CC bonds were present, we assumed that

$$r_{\rm CC} = \overset{\circ}{r}_{\rm CH} + (f_{\rm CH}/f_{\rm CC})^{1/2}\,(r_{\rm CH} - \overset{\circ}{r}_{\rm CH}),$$

where the f's are the simple valence field force constants, while the r^0's and r's are, respectively, the equilibrium and instantaneous lengths of the considered bonds.

The basis for our choice was the fact that our methodology of calculating the atomization energy of a molecule depended on the energy difference $E_{\rm MEH}(r_{\rm min}) - E_{\rm MEH}(\infty)$.

Since the molecular potential energy, whose behavior our calculated $E_{\rm MEH}$ was considered to be simulating, was taken to reflect harmonic nuclear motions about the equilibrium internuclear distances and since $E_{\rm MEH}(\infty)$ was a molecular constant, independent of the rates of stretch, the Hook's Law approximation seemed justifiable. There remained, of course, the behavior at the rest of the internuclear distances. As shall be seen later, our results seem to justify the use of the approximation at those distances as well.

Determination of the Atomization Energies

As was mentioned in the Introduction, we endeavored to determine the proportionality constants $F_\sigma(\rm CC)$ and $F_\pi(\rm CC)$ from the acetylene molecule because of its computational simplicity. The geometry as well as the atomic coordinate systems used in our generalized C_2H_2 molecule are given in Fig. 1.

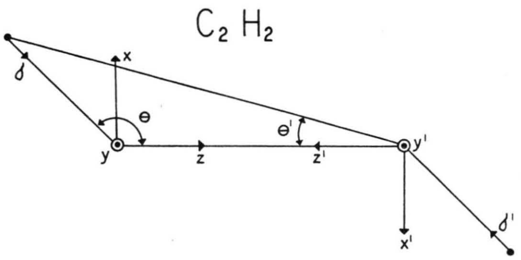

Fig. 1. Geometry and nuclear coordinate systems of C_2H_2 in C_{2h} symmetry.

Using $\Theta = 180°$ and different values of $F_\sigma(\rm CC)$ and $F_\pi(\rm CC)$, the total electronic energy $E_{\rm MEH}$ of C_2H_2 was calculated at C – H distances ranging from 0.1 to 5.0 Å. It was decided that the combination of $F_\sigma(\rm CC)$ and $F_\pi(\rm CC)$ which would be chosen for the series, and indeed for *all* the hydrocarbons, would best satisfy, in order of decreasing importance, the following criteria:

(i) $Q_{\rm a}(\text{calc}) \cong D(\text{HC}-\text{CH}) + 2\,D(\text{C}_2\text{H}-\text{H}) = 19.7$ eV.

(ii) The degenerate $\pi_{\rm u}$ orbitals would be the highest filled molecular orbitals.

(iii) The calculated $r_{\rm min}(\rm CH)$ should be as close as possible to the experimental value of 1.06 Å.

(iv) The calculated ionization potential would be within 2 eV from the experimental value of 11.4 eV [5, 8].

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[7] T. L. Cottrell, The Strength of Chemical Bonds, Butterworths, London 1958.

[8] Our previous work as well as Hoffmann's [9] indicated that the calculated values of the ionization potentials are about 2 eV greater than the observed. Our results for CH_4 and SiH_4 were respectively 15.18 and 13.9 eV as compared to the experimental values [10] of 12.99 ± 0.01 and 12.2 ± 0.01 eV.

[9] R. Hoffmann, J. Chem. Phys. **39**, 1397 [1963].

[10] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, Bond Energies, Ionization Potentials, and Electron Affinities, St. Martin's Press, New York 1966.

These constraints simplified considerably our search for the proper combination of the sought constants whose best values were found to be

$$F_\sigma(\mathrm{CC}) = 2.10 \quad \text{and} \quad F_\pi(\mathrm{CC}) = 1.45\,.$$

Figure 2 gives the E_{MEH} of C_2H_2 as a function of the C − H internuclear distance, while Table 2 gives the "derived" as well as experimental values of the parameters used in the above criteria. It should be noted that if, as we suggested, our technique was applicable to the C_2H_2, C_2H_4 and the C_2H_6 series, no further adjustments of the aforementioned constants would have been necessary.

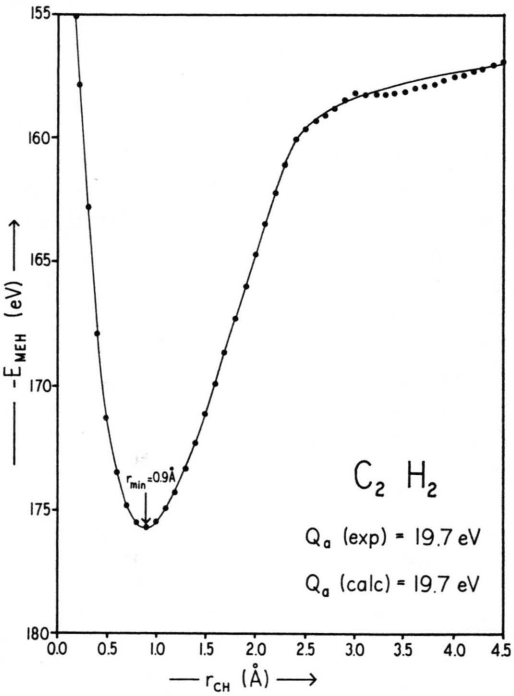

Fig. 2. E_{MEH} of C_2H_2 in $D_{\infty h}$ symmetry versus r(CH).

Table 2. Experimental and calculated values of some molecular parameters of C_2H_2 and C_2H_4.

	C_2H_2 ($D_{\infty h}$)	C_2H_4 (D_{2h})
(i) Atomization energies (eV).		
Exp.	19.7	24.5
Calc.	19.7	22.6
(ii) Energies of occupied M.O. levels* at $r_{\min}$(CH).		
	−13.389 (2)	−13.050
	−15.007	−13.821
	−18.851	−15.474
	−27.216	−16.277
		−19.433
		−26.933
(iii) Equilibrium internuclear distances† (Å).		
Exp.	1.06 (1.20)	1.1 (1.54)
Calc.	0.9 (1.1)	1.2 (1.65)
(iv) Ionization potentials (eV).		
Exp.	11.4	10.5
Calc.	13.4	13.1

* The parenthetic value represents the degeneracy.
† The parenthetic values represent $r_{\min}$(CC).

The geometry as well as the nuclear coordinate systems used in our generalized C_2H_4 molecule are given in Fig. 3. Using $\Phi = 180°$ (planar), $\Theta = 120°$, as well as the previously determined value of F_σ(HH), F_σ(CH), F_σ(CC) and F_π(CC), the total electronic energy E_{MEH} of C_2H_4 was calculated at C − H se-

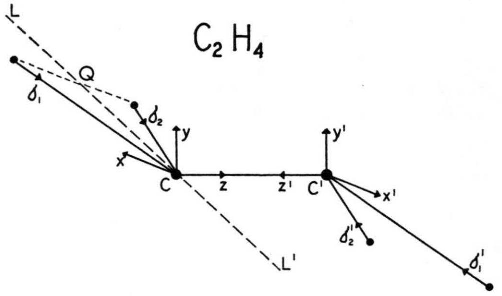

Fig. 3. Geometry and nuclear coordinate systems of C_2H_2 in C_{2h} symmetry *.

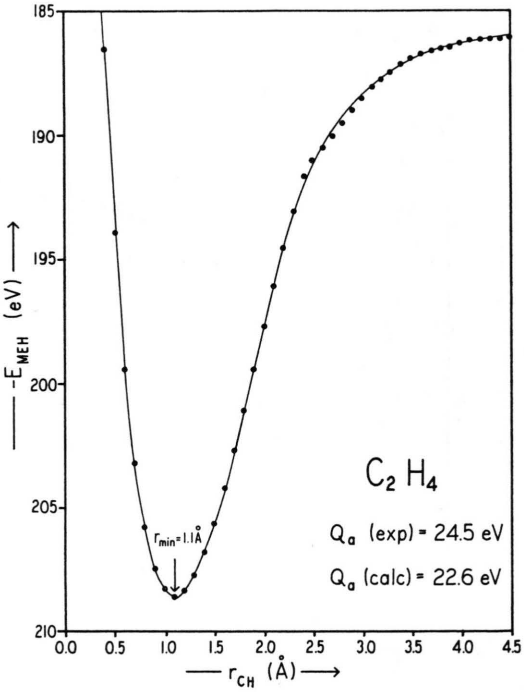

Fig. 4. E_{MEH} of C_2H_4 in D_{2h} symmetry versus r(CH)

* $\theta = \sphericalangle \sigma_1 CC'$ at $\Phi = \pi$ radians, $\Phi = \sphericalangle QCC'$, $\theta'' = \sphericalangle QC'\sigma_1$, and $\Phi' = \sphericalangle CC'Q$.

parations ranging from 0.1 Å to 5.0 Å. The results of our calculations are graphically portrayed in Fig. 4, while the "derived" as well as experimental values of some of the relevant parameters of C_2H_4 are given in Table 2. It is interesting to note that the error of the atomization energy of C_2H_4 is slightly less than 8%, and that, even in this crude approximation, one is able to discern a decrease in the ionization potential of the π electron when one goes from the acetylene to ethylene.

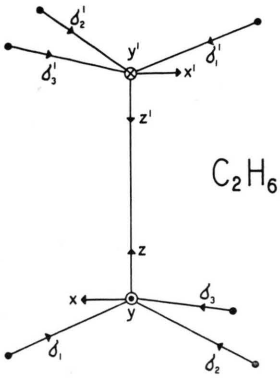

Fig. 5. Geometry and nuclear coordinate systems of C_2H_6 in D3d symmetry †.

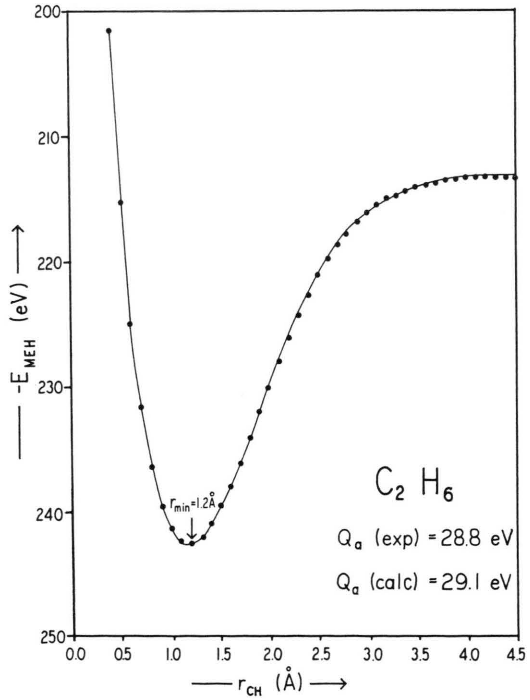

Fig. 6. E_{MEH} of C_2H_6 in D3d symmetry versus r(CH).

Finally, we considered the generalized C_2H_6 molecule (see Fig. 5). Using $\Theta = 109.5°$, the total electron energy E_{MEH} of C_2H_6 was calculated at C – H distances ranging from 0.1 Å to 5.0 Å. The results of our calculations are given in Fig. 6. Here again, considering the crudeness of the approximation, the agreement between the calculated and experimental values of the atomization energy seems to be phenomenal.

Determination of the Geometries

Next, in our study was, of course, the computation of the stable configurations of the studied molecules. It would be well to remember that the so-called equilibrium internuclear distances r_{min}(CH) and/or r_{min}(CC) as well as the atomization energies considered were actually determined assuming idealized geometries. Thus, using the experimental values of the equilibrium internuclear distances of the involved bonds, the angular dependence of the total electronic energy of C_2H_2, C_2H_4 and C_2H_6 were determined. The results of our calculations are given in Figs. 7, 8 a, 8 b, and 9. Table 3 lists the geometries of the above mentioned series and CH_4 as determined by our technique (Y), by the ordinary ex-

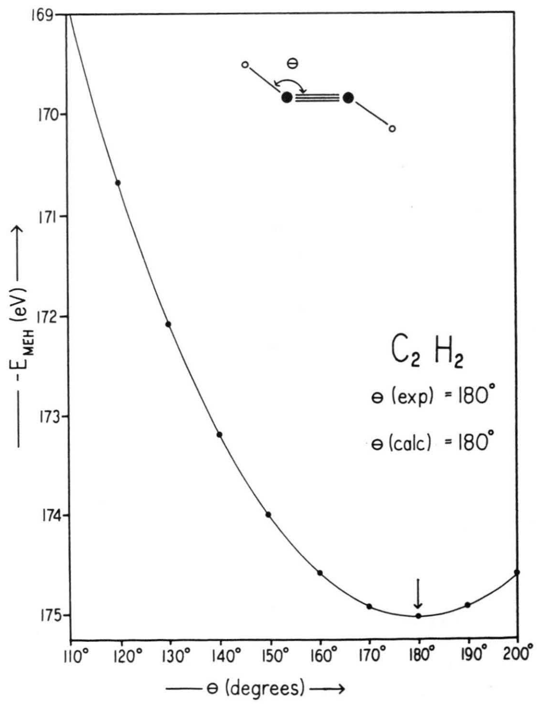

Fig. 7. Angular dependence of E_{MEH} in C_2H_2.

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† $\theta = \sphericalangle$ HCC′, and $\theta' = \sphericalangle$ C′CH.

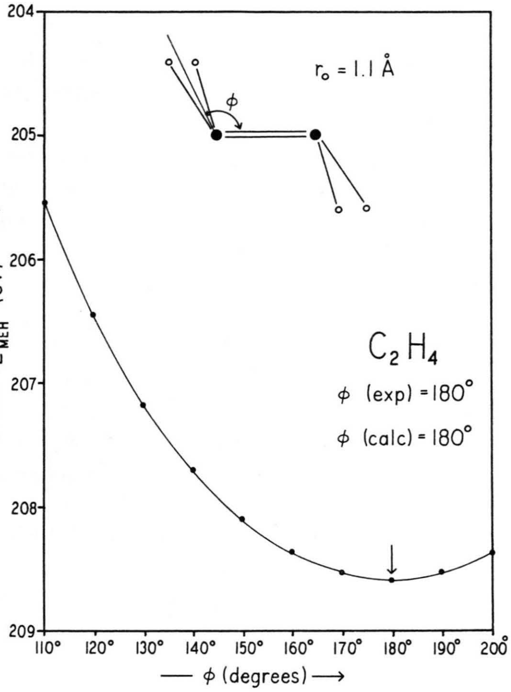

Fig. 8 a. Out-of-plane angular dependence of E_{MEH} in C_2H_4.

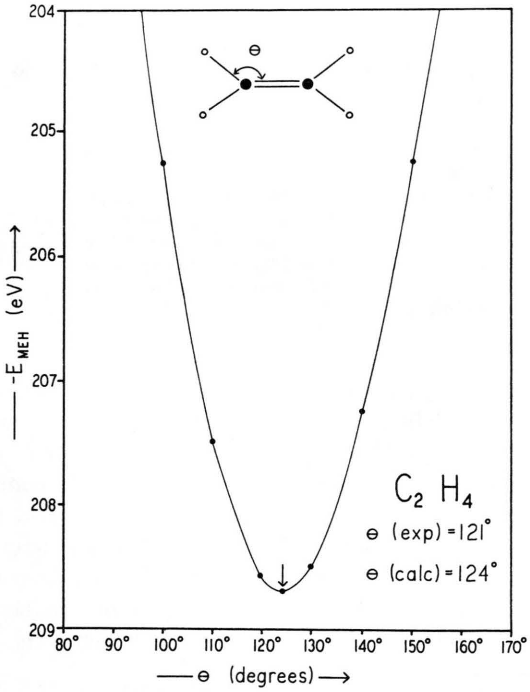

Fig. 8 b. In-plane angular dependence of E_{MEH} in C_2H_4.

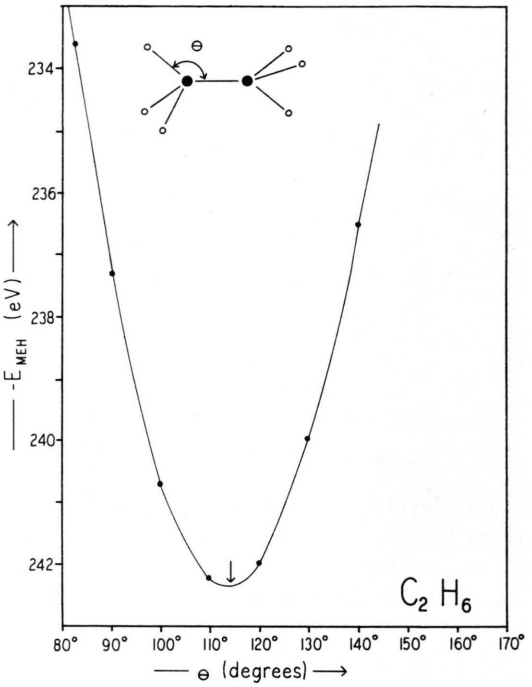

Fig. 9. Angular dependence of E_{MEH} in C_2H_6.

Table 3. Calculated and observed values of geometries under study. θ represent the HCH angles, with the exception of C_2H_2 in which case it represents the HCC angle.

		θ (degrees)	r_{CH} (Å)	r_{CC} (Å)
CH_4	H	109.5	1.02	—
	Y	109.5	1.10	—
	E	109.5	1.09	—
C_2H_2	H	180	0.85	1.0
	Y	180	0.90	1.1
	E	180	1.06	1.2
C_2H_4	H	125	0.95	1.47
	Y	112	1.10	1.34
	E	118	1.09	1.34
C_2H_6	H	109.5 (assumed)	1.0	1.92
	Y	105	1.2	1.65
	E	108	1.1	1.54

tended HÜCKEL[9] (H), and by experiment[5] (E). It is rewarding to find that our modification to the extended Hückel method not only gives reasonable values for the atomization energies but that, in general, it gives better approximations to the geometries as well. In fact, it even gives a better value for the potential barrier of the transition between the staggered and eclipsed form of ethane (see Fig. 10).

Discussion of Results

In the preceeding pages, we endeavored to show that our modification to the extended Hückel method was not only applicable to molecules involving σ but

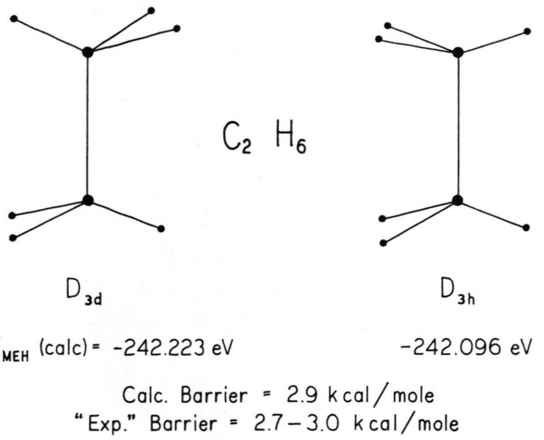

Fig. 10. The potential barrier in C_2H_6.

to those involving π bonds as well. It is our contention that the constants determined and used in this investigation are universal to all the hydrocarbons, be they aliphatic or aromatic. Furthermore, we believe that the technique as used in the determination of the atomization energies and stable configurations stands unique in its class of semi-empirical calculations.

Be that as it may, lest we mislead the reader with over-enthusiasm, we would like to stress that our methodology of estimating dissociation energies from the calculated atomization energies is not expected, because of its crude approximations, to be universally applicable. There is reason to believe, however, that the methodology has a greater chance of applicability whenever the ordinary extended Hückel calculation suggests a stable configuration and whenever nonbonding orbitals are not involved.

We certainly agree that many of our assumptions will not, and indeed cannot, pass the test of rigor. But then, why should one expect more rigor from the variants of the Hückel method when such rigor is not found in the Hückel method itself?

On the Senftleben-Beenakker Electric Effect in Gaseous Ammonia

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(Z. Naturforsch. **26 a**, 952—964 [1971]; received 1 December 1970)

The viscosity of gaseous ammonia in the presence of a static homogeneous electric field is calculated using the Waldmann-Snider equation. Special attention is paid to the field dependence of the effect which is strongly influenced by molecular inversion. The latter causes a coupling of tensors of different rank in $\boldsymbol{J}$ in the expansion of the distribution matrix, thereby leading to an infinite set of equations which is solved numerically by a limiting procedure. The effect has a complicated dependence on pressure p and field E but to a good approximation turns out to depend on E/p at pressures high with respect to an inversion pressure (about 5 atm for NH_3, 300 torr for ND_3) and, in agreement with the experiments, on E^2/p at low pressures.

Introduction

Recently, Senftleben-Beenakker (SB) effects[1] (i.e. changes in the transport coefficients due to the presence of external fields) have been measured in ammonia[2,3]. The viscosity of ammonia is remarkable in that it shows an *increase* in the presence of both a magnetic[2] and an electric field[3]. This is an exception, since the viscosity of all other gases measured so far decreases when a field is applied. Moreover, the viscosity of ammonia in an electric field is a function of E^2/p (where p is the pressure) to a good approximation, in contradistinction to all other gases of symmetric top molecules[4] whose viscosity is a universal function of E/p. The thermal conductivity shows a decrease, but the field dependence seems to be similar to that of viscosity[3]. A comparison between NH_3 and

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[1] J. J. M. Beenakker and F. R. McCourt, Ann. Rev. Phys. Chem. **21**, 47 [1970].

[2] J. Korving, Physica **46**, 619 [1970].

[3] F. Tommasini, A. C. Levi, and G. Scoles, Z. Naturforsch., to be published; J. J. de Groot, C. J. N. van den Meijdenberg, and J. J. M. Beenakker, to be published.

[4] F. Tommasini, A. C. Levi, G. Scoles, J. J. de Groot, J. W. van den Broeke, C. J. N. van den Meijdenberg, and J. J. M. Beenakker, Physica **49**, 299 [1970].