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Energy Partitioning with the CNDO Method

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The partitioning of the total energy from CNDO computations into mono and bicentric terms and into physical components is examined. It is noted that the two-center terms are a measure of the strength of the chemical bond. This relationship is illustrated in the case of a nonclassical bond in a carbonium ion. The consideration of the interaction between vicinal H atoms leads to the discovery of a trans effect which is important in the interpretation of torsional barriers in hydrocarbons. The investigation of the structure of C – C bonds and the analysis of the derivatives of the total energy with respect to a bond length gives hints which are important for the parametrization of a semiempirical theory.

Die Aufteilung der nach einem CNDO-Verfahren berechneten Gesamtenergie eines Moleküls auf mono- und bizentrische Anteile und deren Zerlegung in physikalische Komponenten wird untersucht. Es wird festgestellt, daß ein bizentrischer Anteil der Gesamtenergie ein Maß für die Stärke einer chemischen Bindung ist. Dies wird am Beispiel einer nichtklassischen Bindung in einem Carboniumion erläutert. Die Betrachtung der Wechselwirkungen zwischen nichtgebundenen H-Atomen führt zur Aufdeckung eines Trans-Effektes, der eine Rolle bei der Interpretation von Torsionsbarrieren in Kohlenwasserstoffen spielt. Die Untersuchung der Struktur von C – C-Bindungen und die Analyse der Ableitungen der Gesamtenergie nach einer Bindungslänge gibt wichtige Hinweise zur Parametrisierung einer semiempirischen Theorie.

Etude de la partition de l'énergie totale dans un calclul CNDO en termes mono et bicentriques et en composantes physiques. On remarque que les termes bicentriques donnent une mesure de la force de la liason chimique. Cette relation est illustrée dans le cas d'une liason non classique dans un ion carbonium. Introduisant l'interaction entre atomes H voisins on met en évidence un effet trans important pour l'interprétation des barrières de torsion dans les hydrocarbures. L'étude de la structure des liaisons C–C et l'analyse des dérivées de l'énergie totale par rapport aux longueurs de liason fournit des suggestions importantes pour la paramétrisation d'une théorie semi-empirique.

1. Introduction

The use of SCF-MO methods in the calculation of the energies and structures of chemical compounds is becoming more and more common. However, the explanation of the special bond relationships in reaction intermediates and transition states requires a mode of analysis that results in information which is also meaningful to the chemist.

The partitioning of the SCF total energy into physical components and bond components seems to hold promise as a solution of the problem. Ruedenberg [1] pointed out the advantage of such a partitioning and carried out an exact analysis of the energy with the help of density matrices. Moffat and Pophie [2] performed numerically such an analysis on small systems. Clementi [3] proposed that a connection exists between the two-center energy components and the concept of the chemical bond. A rough separation of the total energy of an *ab initio* SCF calculation according to physical aspects was presented by Fink and Allen [4]. However, attempts to apply this method in the interpretation of the rotational barrier in ethane [4, 5] and of the inversion barrier in ammonia [6] were not very satisfactory. Pople [7] first noted the possibility of partitioning the total molecular energy E obtained with the semiempirical CNDO theory into one and two-center terms:

$$E = \sum_{\mathrm{A}} E_{\mathrm{A}} + \sum_{\mathrm{A>B}}\sum E_{\mathrm{AB}}. \tag{1}$$

A more detailed analysis of the two-center terms was used very recently by Gordon [8] to explain torsional barriers.

In this work the partitioning of the energy terms E_{A} and E_{AB} into their physical components is demonstrated. The analysis was performed for C–C bonds with the use of our modified CNDO method [9]. The partitioning leads to new insights into the structure of the chemical bond, and should be very helpful in the parametrization of the semiempirical theory through comparison with the corresponding *ab initio* results.

Three criteria are used to determine if the E_{AB} in Eq. (1) can be interpreted as a measure of the strength of the A–B bond. Such a measure would be most useful in the study of nonclassical bonds.The case of the cyclobutenyl cation [10] will be discussed as an example.

The E_{AB} values and their physical components between nonbonded H atoms in hydrocarbons are studied in another section. It is shown that there is always an attraction between H atoms which are trans to each other on neighbouring C atoms. The interaction comes from the $p_\pi - p_\pi$ term in the energy of the C–C bond. The case of ethane shows the importance of this trans-effect in the explanation of rotational barriers.

The first and second derivatives of the total energy with respect to a bond length have also been partitioned. The analysis of these derivatives is especially important for the optimal parametrization of the CNDO method.

2. Partitioning of the Energy

The total energy of a molecular system according to SCF MO theory is given by [11] [1]

$$E = 2\sum_i H_i + 2\sum_i\sum_j J_{ij} - \sum_i\sum_j K_{ij} + \sum_{\mathrm{A<B}}\sum \frac{Z_{\mathrm{A}} Z_{\mathrm{B}}}{R_{\mathrm{AB}}}. \tag{2}$$

The first term contains the expectation values of the one-electron operator $\boldsymbol{H}$, which describes the kinetic and potential energies of the electrons in the field of the nuclei. The second term describes the electronic repulsion and the third contains the electronic exchange interaction. Finally, the last term gives the nuclear repulsion potentials. Following the proposal of Ruedenberg [1] the electronic exchange is considered to include the diagonal elements K_{ii} in order to preserve the invariance of the sum to unitary transformation of the occupied orbitals.

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[1] Our notation is the same as in Refs. [7, 9, 11]

In the ZDO approximation [7] (χ_μ and χ_ν are AO basis vectors)

$$\langle \chi_\mu, \chi_\nu \rangle = \delta_{\mu\nu}, \tag{3a}$$

$$(\mu\varrho|\nu\sigma) = \delta_{\mu\varrho}\delta_{\nu\sigma}\gamma_{\mu\nu} \tag{3b}$$

the energy of the system is given by Eq. (1). The E^{A} and E^{AB} can be forther partitioned into physical components, which are derived from the various terms of Eq. (2). We have carried out this partitioning for the CNDO method, in which the following approximations are used [7]:

$$\gamma_{\mu\nu} = \gamma_{\mathrm{AB}} \quad ; \quad \mu \in \mathrm{A}, \nu \in \mathrm{B}, \tag{4a}$$

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{\mathrm{B} \neq \mathrm{A}} V_{\mathrm{AB}} \quad ; \quad \mu \in \mathrm{A}, \tag{4b}$$

$$H_{\mu\nu} = \beta_{\mu\nu} \cdot S_{\mu\nu} \quad ; \quad \mu \neq \nu. \tag{4c}$$

γ_{AB} is the electronic repulsion between an electron on atom A and an electron on atom B; $H_{\mu\nu}$ is a matrix element of $\boldsymbol{H}$ in the AO basis; $U_{\mu\mu}$ is the one-electron energy of an electron in AO μ in the isolated atom; V_{AB} is the potential energy of an electron on atom A in the field of nucleus B; $S_{\mu\nu}$ is the overlap of the STO's (Slater type orbitals) μ and ν; and $\beta_{\mu\nu}$ is a parameter which is dependent on the types of orbitals μ and ν.

E_{A} and E_{AB} of Eq. (1) can now be written in the form:

$$E_{\mathrm{A}} = E_{\mathrm{A}}^U + E_{\mathrm{A}}^J + E_{\mathrm{A}}^K, \tag{5a}$$

$$E_{\mathrm{AB}} = E_{\mathrm{AB}}^R + E_{\mathrm{AB}}^V + E_{\mathrm{AB}}^J + E_{\mathrm{AB}}^K + E_{\mathrm{AB}}^N. \tag{5b}$$

The superscripts characterize the physical nature of the energy terms. Using the definition

$$P_{\mathrm{A}} = \sum_{\mu \in \mathrm{A}} P_{\mu\mu} \tag{6}$$

where $P_{\mu\mu}$ are elements of the bond order matrix, the terms are given by the following equations:

a) The One-Electron Energies

$$E_{\mathrm{A}}^U = \sum_{\mu \in \mathrm{A}} P_{\mu\mu} U_{\mu\mu}; \tag{7}$$

E_{A}^U is the total (one center) one-electron AO energy of the electrons on atom A.

$$E_{\mathrm{AB}}^V = -P_{\mathrm{A}} \cdot V_{\mathrm{AB}} - P_{\mathrm{B}} V_{\mathrm{BA}}; \tag{8}$$

E_{AB}^V is the potential energy of the electrons on atom A in the field of nucleus B plus that of the electrons on atom B in the field of nucleus A.

$$E_{\mathrm{AB}}^R = 2 \sum_{\mu \in \mathrm{A}} \sum_{\nu \in \mathrm{B}} P_{\mu\nu} \beta_{\mu\nu} S_{\mu\nu}; \tag{9}$$

E_{AB}^R is the contribution of the resonance integrals to the energy of the A–B bond and is the main feature of the covalent bond. The $P_{\mu\nu} \cdot S_{\mu\nu}$ are components of the overlap population [12]. Thus an analysis of E_{A}^U and E_{AB}^R is equivalent to a population analysis wherein the individual terms are weighted with an energy factor $\beta_{\mu\nu}$.

b) *The Electronic Interaction Energies*

$$E_{\mathrm{A}}^{J}=\tfrac{1}{2}P_{\mathrm{A}}^{2}\gamma_{\mathrm{AA}}\,;\quad E_{\mathrm{AB}}^{J}=P_{\mathrm{A}}P_{\mathrm{B}}\gamma_{\mathrm{AB}}\,;\tag{10}$$

E_{A}^{J} is the electronic repulsion of the electrons on atom A and E_{AB}^{J} is the repulsion of the electrons on the atoms A and B.

$$E_{\mathrm{A}}^{K}=-\tfrac{1}{4}\gamma_{\mathrm{AA}}\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{A}}P_{\mu\nu}^{2}\,;\quad E_{\mathrm{AB}}^{K}=-\tfrac{1}{2}\gamma_{\mathrm{AB}}\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{B}}P_{\mu\nu}^{2}\,;\tag{11}$$

E_{A}^{K} and E_{AB}^{K} are the corresponding terms of the electronic exchange interactions.

c) *The Nuclear Repulsion Energies*

$$E_{\mathrm{AB}}^{N}=\frac{z_{\mathrm{A}}z_{\mathrm{B}}}{R_{\mathrm{AB}}}\,;\tag{12}$$

E_{AB}^{N} represents the nuclear repulsion energy of the nuclei A and B.

The numerical analyses in the following sections were performed with the modified CNDO method which was proposed by us in a previous paper [9]. The evaluation of $\beta_{\mu\nu}$ and V_{AB} of Eq. (4) is carried out in the following manner:

$$V_{\mathrm{AB}}=z_{\mathrm{B}}\left[(1-\alpha)\cdot\gamma_{\mathrm{AB}}+\alpha\sqrt{R_{\mathrm{AB}}^{2}+1/\mu_{\mathrm{A}}^{2}}\right];\quad \alpha=0.22\,,\tag{13a}$$

$$\beta_{\mu\nu}=\tfrac{1}{2}(k_{\mathrm{A}}\cdot I_{\mu}+k_{\mathrm{B}}\cdot I_{\nu})\,.\tag{13b}$$

Eq. (13) reduces to the original CNDO/2 approximation with

$$I_{\mu}=I_{\nu}\quad\text{and}\quad\alpha=0\,.\tag{14}$$

All numerical values in the following sections were obtained with the calculated equilibrium geometries of the molecules.

3. The Structure of C—C Bonds

Table 1 presents a detailed examination of the C—C bonds of acetylene, ethylene and ethane using the energy partitioning of Eqs. (7)—(12). For this purpose, the resonance energy E_{CC}^{R} was further partitioned into the terms which the various AO's contribute to the C—C bond.

It is worthy of notice that E_{CC}, the total energy of the C—C bond, is relatively high in comparison with the heat of atomization of the corresponding compound. These high energies are due to the fact that the electronic configuration of the atoms in the molecule is much less favorable than in the isolated atoms. The energy difference is made up of the promotion energy (0.37 a. u. for carbon) and the electronic repulsion, which is greater in molecules by 0.25 γ_{AA} per AO with a assumed population of one (a total of 0.59 a. u. for carbon).

It can be seen from Table 1 that E_{CC} correlates closely with the corresponding E_{CC}^{R} values. The electrostatic interactions ($E_{\mathrm{CC}}^{V}+E_{\mathrm{CC}}^{J}+E_{\mathrm{CC}}^{N}$) become more repulsive with the shortening of the bond length in the series of the three hydrocarbons,

Table 1. *The structure of the C−C bonds in acetylene, ethylene and ethane*[a] *(all values in a.u.)*

	C_2H_2	C_2H_4	C_2H_6	isolated C atom
E_{CC}	− 1.576	− 1.128	− 0.690	
E^N_{CC}	6.980	6.309	5.570	
E^J_{CC}	6.636	6.122	5.553	
E^K_{CC}	− 0.586	− 0.371	− 0.171	
E^V_{CC}	−13.142	−12.120	−10.948	
E^R_{CC}	− 1.465	− 1.067	− 0.694	
$2s-2s$	− 0.357	− 0.224	− 0.122	
$2s-2p_z$	− 0.540	− 0.476	− 0.363	
$2p_z-2p_z$	− 0.088	− 0.140	− 0.176	
$2p_x-2p_x$	− 0.240	− 0.032	− 0.017	
$2p_y-2p_y$	− 0.240	− 0.195	− 0.017	
σ total	− 0.985	− 0.840	− 0.660	
$p_\pi-p_\pi$ total	− 0.480	− 0.227	− 0.034	
E_C	− 4.873	− 4.855	− 4.838	− 5.747
E^U_C	− 9.206	− 9.141	− 9.119	− 9.289
E^J_C	4.960	4.904	4.895	3.542
E^K_C	− 0.628	− 0.617	− 0.614	

[a] In all calculations, the C−C bond is along the z axis and at least one proton is in the xz plane

but this effect is overcompensated by the electronic exchange energy. For this reason, the absolute value of E^R_{CC} in acetylene is about 0.11 a. u. ($\approx 7\%$) smaller than the total energy of the bond, whereas the difference in ethane is only about one-half per cent.

The partitioning of the E^R_{CC} among the AO's forming the C–C bond of acetylene leads to the result that each of the π-bonds ($2p_x-2p_x$ and $2p_y-2p_y$) contribute 0.24 a. u. to the bond energy. Thus about one third of the resonance energy of this bond is due to the π-orbitals. The π-bond of ethylene is not as strong (0.195 a.u.). Ethylene has another π-system perpendicular to the first, but this system is made up mainly of σ−C−H bonds and contributes only 0.032 a. u. to the C−C bond through "hyperconjugation". In ethane, the $2p_x$ and $2p_y$ orbitals are used almost exclusively in the formation of the C−H bonds, but, in this case as well, these orbitals contribute a small amount (0.034 a. u.) to the C−C bond, a contribution which has a causal relationship to the torsional barrier in ethane (see Sect. 5).

The strong increase of the σ-bond component of the resonance energy when going from the C−C single bond (0.66 a. u. in ethane) through the double bond (0.84 a. u. in ethylene) to the triple bond (0.98 a. u. in acetylene) is notable. This increase is mainly due to the increase of the s-character of the bond, which is, in turn, caused by the changing hybridization at the C atoms. The steepness of the increase is therefore a result of Eq. (13b) because $I_{2s}/I_{2p} > 1$. However, it should be noted that the ratio of the E_{CC} value of ethane to that of ethylene and acetylene is nearly independent [13] of the factor I_{2s}/I_{2p}, which is equal to 2 in the modified and 1 in the original CNDO theory.

A similar energy analysis of *ab initio* results for C−C bonds would be very helpful in the parametrization of the CNDO theory. Unfortunately, no such results are available to this date. Investigations in this direction are planned.

4. The Properties of E_{AB}

This section will examine the question of the suitability of the total bond energies E_{AB} and the resonance energies E^R_{AB}, which correlate with the E_{AB} for covalent bonds, as measures of the strength of chemical bonds. The decision will be based on three criteria: transferability, monotony and the smallness of terms between nonbonded atoms.

a) Transferability. Similar bonds in different molecules should have similar E_{AB} values. As shown in Table 2 for several C–H and C–C bonds, the criterion is fully satisfied.

b) Monotony. The stronger a bond is according to chemical experience the larger should be the absolute value of E_{AB}. It should be noted that E_{AB} is a static property of the A–B bond and cannot be directly compared with experimental dissociation energies. Some elaboration is needed for the examples included in Table 2: The C–H bonds become stronger with change of hybridisation from sp^3 to sp. The high s character of the C–H bonds in cyclopropane is correctly predicted by the computation, which shows them to be almost as strong as those in ethylene. On the basis of E_{CH} values the stability of C–H bonds of sp^3 hybridized

Table 2. *E_{AB} and E^R_{AB} values of some* C–C *and* C–H *bonds (values in a.u.)*

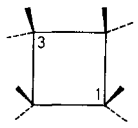
Type of the bond A–B	compound	$-E_{AB}$	$-E^R_{AB}$
$C_{sp^3}-H$	methane	0.593	0.539
	ethane	0.586	0.532
	propane (prim.)	0.586	0.532
	propane (sec.)	0.579	0.528
	i-butane (tert.)	0.580	0.530
	propene	0.586	0.531
	propyne	0.582	0.530
	cyclopropane	0.597	0.548
$C_{sp^2}-H$	benzene	0.597	0.552
	ethylene	0.598	0.551
	propene	0.601	0.553
	allene	0.599	0.554
$C_{sp}-H$	acetylene	0.630	0.594
	propyne	0.633	0.594
C–C	cyclopropane	0.617	0.634
	cyclobutane	0.642	0.644
	ethane	0.690	0.694
	propane	0.679	0.678
	propene	0.710	0.720
	butadiene	0.728	0.740
	propyne	0.758	0.788
$C-C_{arom.}$	benzene	0.913	0.904
C=C	ethylene	1.128	1.067
	propene	1.115	1.054
	butadiene	1.109	1.051
	allene	1.141	1.097
	butatriene 1–2	1.133	1.100
	butatriene 2–3	1.184	1.161
C≡C	acetylene	1.576	1.465
	propyne	1.558	1.448

Table 3. *Interactions between nonbonded atoms in ethylene (energy values in* 10^{-4} *a. u.; distances in* Å*)*

A – B	E_{AB}	E^R_{AB}	E^K_{AB}	$E^V_{AB}+E^J_{AB}+E^N_{AB}$	bond order	distance A – B
$H-H_{gem.}$	133	87	– 9	55	–0.079	1.84
$H-H_{cis}$	35	21	– 3	17	–0.056	2.56
$H-H_{trans}$	– 16	–15	–10	9	0.110	3.15
$C-H_{vic.}$	161	82	– 4	82	–	2.16

Table 4. 1 – 3 *interactions in the cyclobutenyl Cation and in Cyclobutane (energy values in a. u.; distances in* Å*)*

	E_{13}	E^R_{13}	R_{13}
Cyclobutenyl cation	–0.248	0.301	1.65
Cyclobutane	0.001	–0.025	2.17



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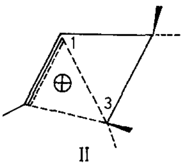

II

atoms decreases when going from compounds such as methane and ethane to more highly substituted carbon atoms (as in propane or *i*-butane), as would be expected from experimental data [14]. The E_{CC} values of the C – C bonds in ethane, ethylene and acetylene are in the ratio 1 : 1.6 : 2.3, in good agreement with the ratio 1 : 1.7 : 2.4 of experimental bond energies [15]. Considering the C – C single bonds, it can be seen that the E_{CC} values of the strained bonds in cyclobutane and cyclopropane are much smaller than in ethane. On the other hand, the values for conjugated single bonds and those for bonds between *sp* and sp^3 hybridized carbon atoms are considerably higher than in ethane. Conjugated double bonds are somewhat weaker than the C – C bond in ethylene, whereas the cumulated bonds are somewhat stronger. In agreement with the trend of the experimental bond lengths [16] the outer bonds in butatriene are calculated to be weaker than the central bond. Thus the second criterion is fulfilled in all cases studied.

c) The example of ethylene is used in Table 3 to demonstrate that the E_{AB} between atoms which are not bound to each other amount to only a few per cent of the corresponding values for single bonds. However, these small terms can be important for the relative energies of conformers, as will be shown in Sect. 5.

Thus the E_{AB} values and the correlated E^R_{AB} are indeed suited to characterize the strength of chemical bonds. It is especially important to have an MO theoretical criterium for the strength of a chemical bond in those cases where it is not possible to identify bonds unequivocally by their length alone (e. g. non-classical bonds). An example is the cyclic vinyl cation II [10]. The comparison of E_{13} or E^R_{13} (Table 4) with the corresponding values in cyclobutane shows clearly the presence of a non-classical bond between C_1 and C_3 in II and proves the existence of a non-classical cyclopropenyl cation system in compound II.

5. Interactions between Non-Bonded Hydrogen Atoms; Trans Effect

It can be seen in Table 3 that the small interactions between non-bonded H atoms in ethylene have different signs. A more exact study of the table brings to light the following trends: One of the components of the interaction is a relatively small electronic repulsion, which is dependent upon the interatomic distance and results from the partial positive charge on the hydrogen atoms [9]. More important are the contributions of the resonance energy term E^R_{HH} and the electronic exchange term E^K_{HH}. E^R_{HH} is antibonding for geminal and for cis vicinal protons and bonding for trans protons. Because this trans effect is a quite general phenomenon, as has been verified by the study of computations of many hydrocarbons [13], a study of the causes is presented here.

The reasons for the different signs of the E^R_{HH} values is the varying sign of the H–H bond order (Eq. 9; S_{HH} is always positive), which was first noted by Pople [18]. The bond orders are included in Table 3. As will be shown, the signs of the bond orders are not a result of the particular parametrization of the theory, but are caused by the structure of the MO's. It can easily be proven that the symmetry requirements of the MO's in ethylene result in a negative geminal H–H bond order when the population of the p_x orbital (orientation as in Table 1) on the C atom is less than one and the partial charge on hydrogen is not negative. This incomplete hybridization of the C atom is always to be expected when $U_{2s2s} < U_{2p2p}$ in Eq. (4b).

In ethylene there are two occupied MO's (Fig. 1) which lead to different signs of the cis and trans H–H bond orders. One (B_{3u}) is symmetrical to the symmetry plane perpendicular to the C–C bond, whereas the other (B_{2g}) is antisymmetrical to the same plane. The second MO, which gives the positive contribution to the trans H–H bond order, has larger coefficients on the H atoms, because the node between the $2p_x$ orbitals has an antibonding effect on the C–C bond. Therefore, the trans H–H bond order must be greater than the cis H–H bond order. Because the contributions of the other orbitals to the H–H bond order almost completely compensate each other, the cis bond order is negative and the trans bond order is positive. The corresponding difference in the absolute values of the $2p_x$ coefficients of the two MO's gives an exact measure of the contribution of the p_x orbitals to the energy of the C–C bond of ethylene (see Table 1).

The trans effect described above is not only observed for ethylene and for other C–C double bonds, but is a direct consequence of the $p_\pi - p_\pi$ contribution to the C–C single bond and is also found for H atoms bound to sp^3 hybridized carbon. The analysis of the H–H interaction in ethane as a function of the

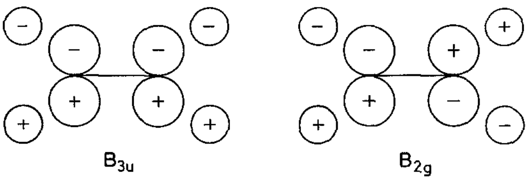

Fig. 1

Table 5. H – H *interactions in ethane (values in* 10^{-4} *a. u.)*

∢H–C–C–H conformer[a]	0 *e*	30 *g*	60 *s*	90 *g*	120 *e*	150 *g*	180 *s*
E_{HH}	51	43	27	11	0	− 8	−10
E^R_{HH}	34	26	11	− 2	− 9	−12	−13
E^K_{HH}	− 4	− 3	− 1	0	− 2	− 5	− 6
$E^V_{\mathrm{HH}}+E^J_{\mathrm{HH}}+E^N_{\mathrm{HH}}$	21	20	17	13	11	9	9

[a] *e* = eclipsed; *g* = gauche; *s* = staggered.

Table 6. *The rotational barrier in ethane and the* H – H *interactions (values in* 10^{-4} *a. u.)*

Conformer	$E-E^{0\mathrm{a}}$	$\sum E_{\mathrm{HH}}$	$\sum E^R_{\mathrm{HH}}$
eclipsed	24	153	48
staggered	0	132	27
difference	24	21	21

[a] E^0 is the total energy of staggered ethane. In this table the bond lengths of eclipsed ethane were assumed to be the same as in the staggered conformation.

H – C – C – H dihedral angle in the various conformers is given in Table 5. Along with the electrostatic repulsion, one notes a positive E^R_{HH} in cis interactions, a vanishing E^R_{HH} near 90°, and a negative value in trans interactions. The exchange energy E^K_{HH} is not quite as strongly dependent on the dihedral angle: it is always bonding, but less so for cis than for trans.

These various H – H interactions are responsible for the torsional barrier of ethane, as demonstrated by Gordon [8]. The results of our modified CNDO calculations are given in Table 6. However, this analysis also proves that these interactions have a causal relationship with the $p_\pi - p_\pi$ contributions, which make the C – C bond noncylindrical [19].

In this paper we have considered only interactions between vicinal and geminal hydrogen atoms. Other relationships are found for larger separations of hydrogen atoms, cf. [20].

The trans effect described here should be taken into account in analysis of the stability relationships of conformers. Moreover, it is possible that the trans effect is also important for reaction intermediates of elimination and addition reactions, and may account for the stereo selective course of many such reactions. Investigations in this field are in progress.

6. The Partitioning of the Derivates of the Total Energy

The summation of Eq. (5) over the atoms and bonds gives a partitioning of the total energy into physical components which one can write in the following way:

$$E = E^U + E^R + E^V + E^J + E^K + E^N . \tag{15}$$

The superscripts indicate the physical nature of the energy values in the same manner as in Eq. (5).

The derivatives of the total energy with respect to a geometric parameter, *e. g.* a bond length, can be partitioned into terms for bonds, atoms and physical components as in Eqs. (1) and (5).

The first derivative of the total energy with respect to the bond length R_{AB} determines the equilibrium distance R^0_{AB} by

$$\frac{\partial E}{\partial R_{AB}}(R^0_{AB}) = 0\,. \tag{16}$$

The second derivative is the force constant k_{AB} of the bond A–B:

$$\frac{\partial^2 E}{\partial R^2_{AB}}(R^0_{AB}) = k_{AB}\,. \tag{17}$$

Table 7 gives the numerical results of the partitioning of the total energy and its derivatives with respect to the C–C bond lengths for the CNDO/2 and

Table 7. *Components of the total energy and their derivatives in respect to the* C–C *bond length (all values in a. u.)*

	CNDO/2			mod. CNDO		
	energy	1st deriv.	2nd deriv.	energy	1st deriv.	2nd deriv.
Acetylene						
ΔH^a	−1.737			−0.653		
E	−15.344	0	2.302	−13.147	0	1.425
$E^{E\,a}$	−28.296	3.577	−0.669	−26.046	3.496	−1.436
E^V	−23.615	4.577	−1.078	−23.737	4.931	−1.823
E^U	−20.336	−0.249	0.179	−19.312	−0.072	−0.294
E^R	−3.940	1.228	−0.104	−2.617	0.766	−0.045
E^J	22.171	−2.152	0.370	22.178	−2.294	0.759
E^K	−2.576	0.173	−0.034	−2.557	0.165	−0.025
E^N	12.951	−3.577	2.971	12.898	−3.496	2.859
Ethylene						
ΔH^a	−2.188			−0.895		
E	−17.732	0	1.613	−14.389	0	0.935
E^E	−36.420	3.622	−0.888	−33.606	3.491	−1.411
E^V	−36.201	5.471	−1.599	−36.100	5.584	−2.086
E^U	−21.438	−0.282	0.252	−20.206	0.005	−0.308
E^R	−4.727	0.892	−0.078	−3.221	0.566	−0.062
E^J	29.095	−2.559	0.563	29.038	−2.758	1.064
E^K	−3.149	0.101	−0.028	−3.117	0.094	−0.014
E^N	19.346	−3.622	2.498	19.216	−3.491	2.347
Ethane						
ΔH	−2.663			−1.136		
E	−18.826	0	1.039	−15.630	0	0.535
E^E	−45.425	3.693	−1.050	−41.911	3.481	−1.358
E^V	−50.402	6.302	−2.039	−49.862	6.169	−2.274
E^U	−22.596	−0.301	0.336	−21.166	−0.023	−0.188
E^R	−5.549	0.596	−0.050	−3.832	0.380	−0.073
E^J	36.868	−2.943	0.708	36.648	−3.082	1.182
E^K	−3.746	0.039	−0.006	−3.698	0.037	
E^N	26.600	−3.693	2.083	26.281	−3.481	1.893

[a] ΔH = heat of atomization; E^E = electronic energy.

modified CNDO calculations of ethane, ethylene and acetylene. It can be seen that the physical components make different contributions to the total energy and to the first and second derivatives:

a) The partitioning of the total energy of the molecule is similar to that discussed in section 2 for E_{AB}.

b) The electrostatic terms and also the resonance energy E^R are important in the first derivative. On the other hand, the influence of E^U is small.

c) The second derivatives are made up almost entirely of electrostatic terms. The resonance energy contributes very little, although it, like the force constant, is a measure of the strength of a bond. It is now understandable why the EHT method [17], in which only E^R and E^U are calculated, is often successful in predicting the differences in total energy of different molecules but is little suited to calculating bond lengths and force constants [21].

These considerations formed the basis for the modification of the CNDO method [9]. The problem was to reduce the value of the zero order and second derivatives of the total energy while holding the first derivative as constant as possible, as the equilibrium distances calculated with the CNDO/2 method are satisfactory. The second derivative of E^V is very sensitive to changes in α in Eq. (13a), the absolute value increasing with increasing α. One can compensate the small influence of α upon the first derivative by reducing k_A in Eq. (13b). At the same time, the absolute value of the total energy can be reduced to a value which is close to the experimentally observed value [9]. This state of affairs is illustrated in Table 7 with a comparison of results from CNDO/2 and from the modified CNDO.

A partitioning of the derivatives of the total energy analogous to that of the total energy itself in Eq. (1) enables one to determine how much influence E_{AB} has on the equilibrium bond length and the force constant of the A−B bond. The examination in the case of acetylene gives the following results (Table 8): The first derivative of E_{CC} is not equal to zero at the equilibrium distance R^0_{CC}. The condition

$$\frac{\partial E_{CC}}{\partial R_{CC}}(R^0_{CC}) = 0$$

Table 8. *Partitioning of the derivatives of the total energy of acetylene with respect to the C–C bond length into mono and bicentric terms. (values in a. u.)*

	$H_3-C_1\equiv C_2-H_4$		
	energy	1st deriv.	2nd deriv.
E	−15.344	0.000	1.43
E_{12}	− 1.576	0.163	1.35
E_{13}	− 0.630	−0.017	0.06
E_{14}	0.020	−0.010	0.00
E_{34}	0.000	0.002	−0.04
E_1	− 4.873	−0.054	0.00
E_1^U	− 9.206	−0.033	−0.17
$E_1^J + E_1^K$	4.332	−0.021	0.17
E_3	− 0.303	−0.001	0.00

would lead to an equilibrium distance about 0.06 Å shorter than that found by Eq. (10). Thus the equilibrium bond length is influenced by the one-center energy terms of the bonded atoms and by non bonded interactions. The second derivative of the E_{CC} of acetylene with respect to the C–C bond length accounts for about 95% of the second derivative of the total energy. The monocentric terms compensate each other (see also Table 7), and the contribution of the nonbonded interactions to the force constant is small. These results also support the definition of E_{AB} as a measure of the strengths of chemical bonds.

The calculations were performed on a CDC 3300 computer using a Fortran program based on Pople and Segal's CNDO/2 program. Our program includes a section which calculates the "energy matrices" containing the terms of the energy partitioning. A subroutine varies the bond lengths and bond angles to obtain equilibrium geometries and force constants.

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