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MOLECULAR ORBITAL CALCULATIONS ON ORGANIC MOLECULES—I

CNDO SOLUTIONS FOR PARAFFIN HYDROCARBONS AND CARBONIUM IONS

N. S. ISAACS

Department of Chemistry, University of Reading, Whiteknights Park, Reading, England

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Abstract—Energies and charge distributions have been calculated by the CNDO method for the non-cyclic C_1–C_5 alkanes and the carbonium ions derived therefrom. Calculated energies are proportional to experimental values and stabilities of isomers are reproduced satisfactorily. The homoallyl cation is predicted to be most stable when the π- and vacant orbitals are directed towards each other.

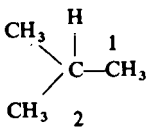
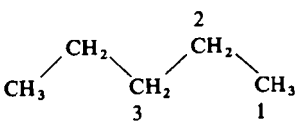
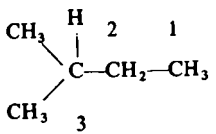
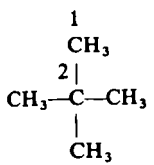
THE CNDO (Complete Neglect of Differential Overlap) technique developed by Pople *et al.*[1] is an approximately self-consistent method for the computation of molecular orbitals of closed-shell molecules containing first-row elements, in any prescribed geometry. The basis functions are 1s, 2s and 2p atomic orbitals and the Hückel-type secular determinant is constructed with appropriate ionization potentials as diagonal elements and semi-empirical resonance integrals, proportional to the overlap between atomic orbitals, as off-diagonal elements. The only information to be specified is the identity and co-ordinates for each atom in the molecule and the net charge.

The CNDO technique has been used on relatively simple molecules[2–4] and has been found to give satisfactory charge distributions and bond parameters, although

TABLE 1. CALCULATED BINDING ENERGIES (kcals.mole^{-1})

	Hydrocarbons			Cations	
1	Methane	874	9	Methyl	370
2	Ethane	1659	10	Ethyl	1218
3	Propane	2441	11	1-Propyl	1775
4	n-Butane	3223	12	2-Propyl	2045
5	Isobutane	3222	13	1-Butyl	2654
6	n-Pentane	4004	14	2-Butyl	2815
7	Isopentane	4002	15	Isobutyl	2798
8	Neopentane	4000	16	t-Butyl	2862
			17	1-Pentyl	3222
			18	2-Pentyl	3619
			19	3-Pentyl	3623
			20	3-Methyl-1-butyl	3577
			21	3-Methyl-2-butyl	3619
			22	2-Methyl-1-butyl	3583
			23	t-Amyl	3641
			24	Neopentyl	3587
			25	Allyl	1740

TABLE 2. CHARGE DENSITIES (10^3 ELECTRONIC UNITS)

	C_1	C_2	C_3	C_4	C_5	H_1	H_2	H_3	H_4	H_5
CH_4	−50·3					+12·5				
$CH_3—CH_3$	−7·7					+2·5				
$CH_3—\overset{2}{C}H_2—\overset{1}{C}H_3$	−8·8	+23·6				+0·9	−5·0			
$CH_3\overset{2}{C}H_2\overset{1}{C}H_2CH_3$	−11·6	+20·3				+4·6	−2·0			
	−9·1	+46·0				−0·8	−11·0			
	−11·3	+17·4	+17·1			−0·2	−0·5	−4·0		
	−13·2	+19·7	+42·7	−11·0		+1·0	−7·2	−10·9	−0·8	
	−8·7	+61·5				−2·2				

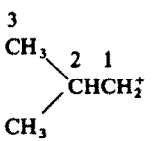
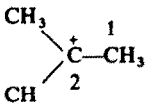
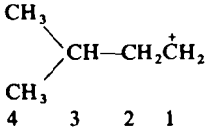
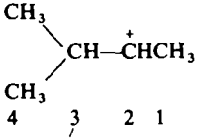
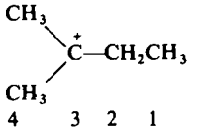
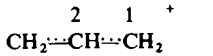
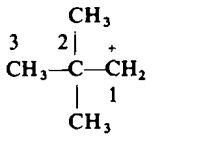
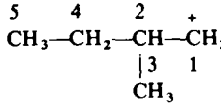
CH_3^+	+428					+191				
$\overset{2}{CH_3}\overset{1}{CH_2^+}$	+370	−89				+104	+181			
$\overset{3}{CH_3}\overset{2}{CH_2}\overset{1}{CH_2^+}$	+365	−180	−135			+187·7	+155	+91·8		
$CH_3\overset{2_+}{C}H\overset{1}{C}H_3$	−86·9	+352				+190·0	+102			
$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2_+}{C}H\overset{1}{C}H_3$	−74·4	+324	−10·5	+7·8		+115	+92	+79	+53	
$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1_+}{CH_2}$	+336	−10	+60	−28		+125	+20	+52	+40	
	+326	+37	+6·9			+121	+60	+45		
	−83·3	+340				+112				
$\overset{5}{CH_3}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{+}{\underset{1}{C}}H_2$	+340	+134	−111	−30	+16	+146	+89	+78	+154	−7
$\overset{5}{CH_3}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{\overset{+}{C}}H\overset{1}{C}H_3$	−83·4	+327	−26	+51	−19	+112	+94	+84	+22	+36
$\overset{3}{CH_3}\overset{2}{CH_2}\overset{+}{\underset{1}{C}}H\overset{1}{C}H_3$	+5·3	−21·0	+322			+47	+84	+91		

TABLE 2—*continued*

	C_1	C_2	C_3	C_4	C_5	H_1	H_2	H_3	H_4	H_5
	+327	−19	+83	−25		+122	+88	+24	+33	
	−84	+323	+24	+2·8		+112	+91	+49	+43	
	−23·3	−43·9	+328	−81·6		+36	+103		+99	
	+272	−39				+90	+101			
	+316·4	+57	−6·1			+113	+41			
	+323	+30	+6·7	+43	−25	+118	+56	+52	+41	+31

absolute molecular bonding energies were not well reproduced. Because of the convenience of application of this method and the potential uses it could have in predicting and explaining stabilities and possibly reactivities of organic molecules, we are seeking to establish the limits of reliability of these calculations and here report results for some saturated hydrocarbons and carbonium ions derived from them.

RESULTS AND DISCUSSION

Total bond energies calculated for the systems studied are given in Table 1 and charge distributions in Table 2.

I II

TABLE 3. CONFORMATIONAL EFFECTS UPON ENERGIES

	Kcal.
Staggered ethane	−1659
Eclipsed ethane	−1660
1-Butyl cation (*trans*)	−2698
1-Butyl cation (*gauche*)	−2654
n-Butane (*trans*, average bond lengths)	−3223
n-Butane (*trans*, accurate bond lengths)	−3229
n-Butane (*gauche*, accurate bond lengths)	−3228
Planar ethylene	−1319
Twisted ethylene	−1225

TABLE 4. EIGENVALUES (ATOMIC UNITS) AND EIGENVECTORS FOR THE METHYL CATION

Orbital	ψ_1	ψ_2	ψ_3	ψ_4
Eigenvalue	−1·6283	−1·2126	−1·2126	−0·4092
Eigenvectors				
C2s	0·7936	0	0	0
$C2p_x$	0	−0·3860	0·6551	0
$C2p_y$	0	0	0	−1·000
$C2p_z$	0	0·6551	0·3860	0
$H_1 1s$	0·3513	0·4569	0·2692	0
$H_2 1s$	0·3513	—0·4616	0·2611	0
$H_3 1s$	0·3513	0·0047	−0·5303	0

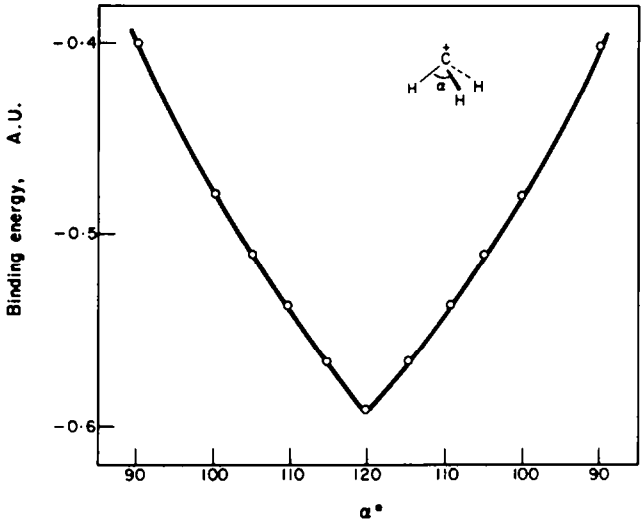


FIG. 1a. Bond angle dependence of the binding energy of the methyl cation.

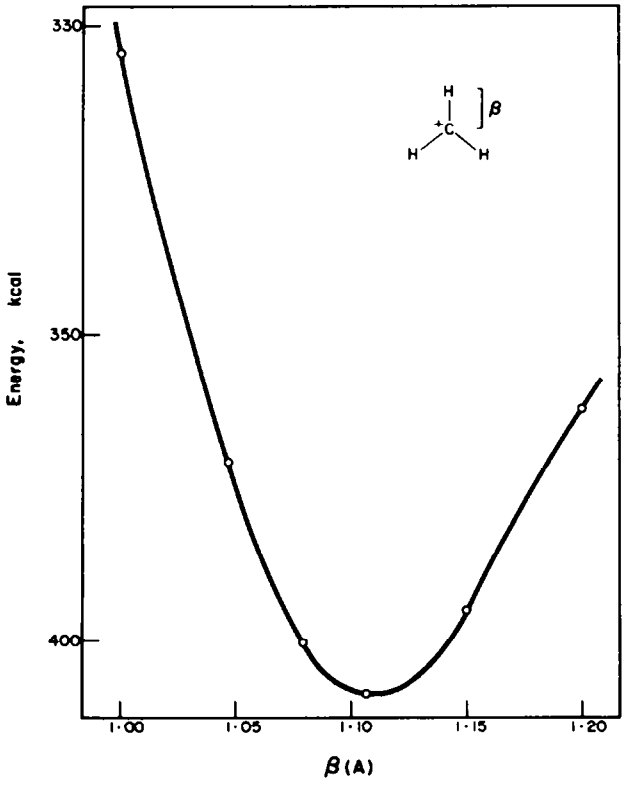


FIG. 1b. Bond length dependence of the binding energy of the methyl cation.

Molecular geometry. The bond lengths and angles used were average values recommended by Pople and Gordon.[2] The conformations found to yield minimum energies were the staggered, *anti* conformation of the hydrocarbons (I) and the "eclipsed" conformation, II, of the carbonium ions (Table 3). Thus, a small barrier of rotation about single bonds was observed, and quite a large one for rotation about the ethylenic double bond. A more detailed study of the methyl cation was made, a minimum energy for the system being obtained with a bond angle of 120°, i.e. a planar ion, with bond length of 1·10 Å (Fig. 1). These findings are in agreement with the experimental data which indicate a planar geometry for free carbonium ions[5,6] and predict somewhat loosened C—H bonds. The eigen values and vectors for the four lowest orbitals are shown in Table 4. The three occupied orbitals (excluding C_{2_s}) employ overlap of $2p_x$(C) and 2s(C) and of a $C2p_x$–$C2p_z$ combination with hydrogen while the lowest vacant orbital is pure $C2p_y$. Substitution of more accurate bond lengths and angles for butane[7] made a rather small improvement to the energy values (Table 3).

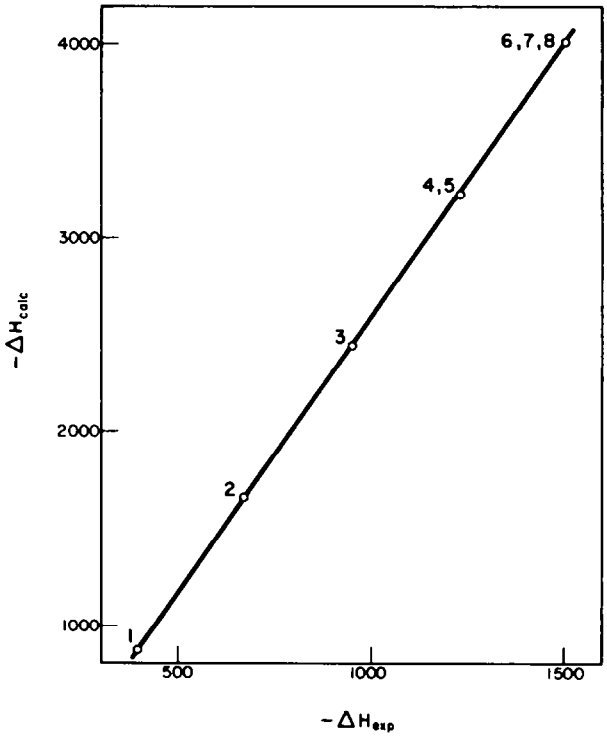


FIG. 2. Correlation between calculated and experimental atomization energies for hydrocarbons. (Numbers refer to species in Table 1).

The calculated binding energies of both hydrocarbons and cations are considerably larger in absolute magnitude than those determined from combustion data.[8,9] There is, however, a good linear correlation between these two quantities (Fig. 2) having the slope, 2·84. One can therefore treat the calculated binding energies as semi-empirical parameters in calculating new values. Less satisfactory is the small

differentiation in energy of the straight- and branched-chain hydrocarbons. Small dipole moments were obtained for the non-centrosymmetric molecules, which were generally in accord with the rather variable data available on these compounds.[10]

In a similar way a linear correlation was found between experimental gas phase ionisation energies for the reaction $RH \rightarrow R^+ + H^-$[11] and the values calculated as the difference in binding energy between hydrocarbon and carbonium ion (Fig. 3).

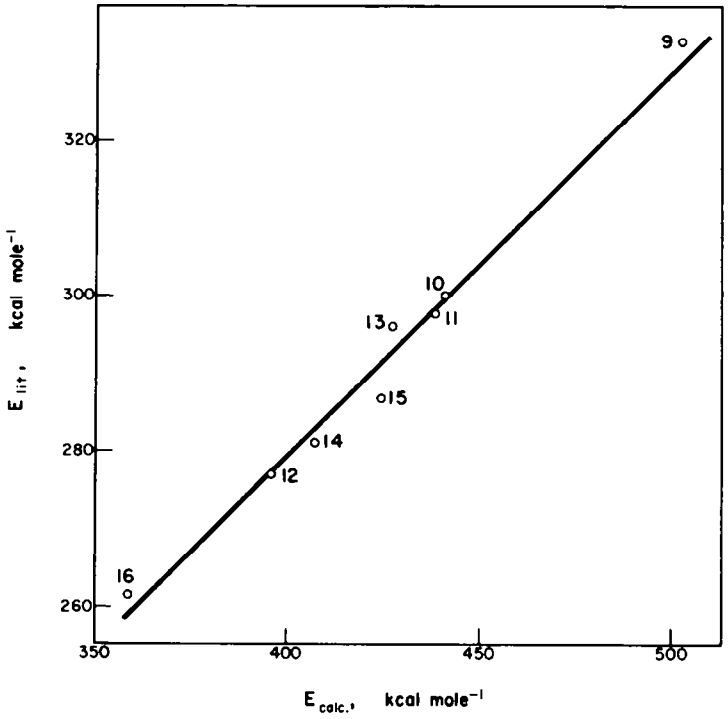
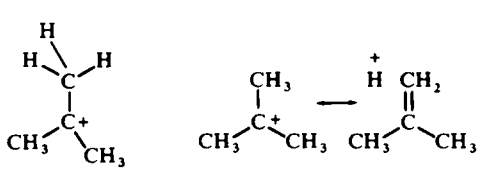


FIG. 3. Correlation between calculated and experimental energies of heterolysis for hydrocarbons. (Numbers refer to Table 1).

In this case, the slope has the value 2·03. The theory correctly predicts the relative stabilities of the isomeric carbonium ions, e.g. t-butyl > 2-butyl > n-butyl.

Calculated charge distributions in the hydrocarbons indicate a consistent gradation of electron density at carbon of $CH_3 > CH_2 > CH$ while the opposite order obtains on hydrogen. The charge on carbon in straight-chain cations appears to diminish smoothly down the chain but with little attenuation after the first bond. The charge on hydrogen shows a strong tendency to alternate, a trend also noticed by Pople and Gordon.[2] The carbonium carbon takes some 30–40% of the positive charge,



IIIa IIIb

the remainder appearing mainly on the hydrogen atoms as a result of electronegativity differences between these elements; for example the values for t-butyl (IIIa) accord with the intuitive picture of electron densities as a result of hyperconjugative stabilization (IIIb).

In general a "three-layer" structure of carbonium ions is predicted, the highly positive carbonium carbon being surrounded by a shell of rather negatively-charged carbon atoms which in turn are surrounded by positive hydrogens. The effectiveness of electron-release of alkyl groups is seen by comparing the charge-densities on the positive carbon in the series CH_3^+, $CH_3CH_2^+$, $(CH_3)_2CH^+$, $(CH_3)_3C^+$ which accords qualitatively with experimental stabilities and electron-release order [12, 14] as measured by σ^* (Fig. 4).

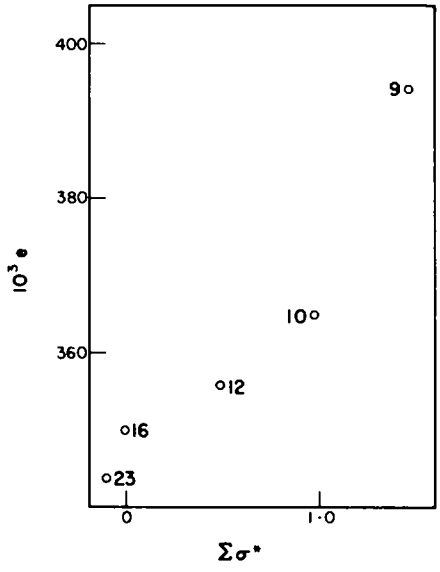
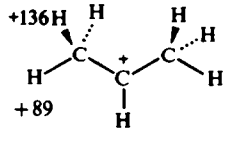


FIG. 4. Relation between residual charge on the carbonium carbon and donor character of substituents.

A number of tertiary carbonium ions have been preserved in solution in antimony pentafluoride[5, 13] and their proton NMR spectra recorded. The chemical shifts of protons (attached to carbon in the same hybridization state) should give a measure of their electron densities and offer a test for the calculated values. A moderate correlation between chemical shift and electron density is obtained for the limited amount of data available (Fig. 5). However, the calculated values are very sensitive to the conformation of the compound used in the calculations. For example, in the static conformation IV of the isopropyl cation two distinct types of methyl hydrogen



IV

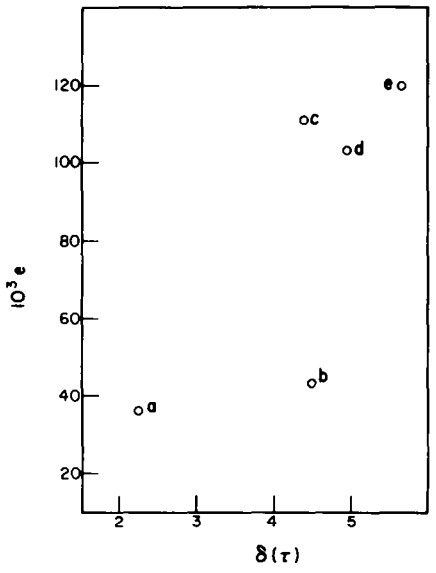


FIG. 5. Relation between excess charges on protons and their ^1H chemical shift.

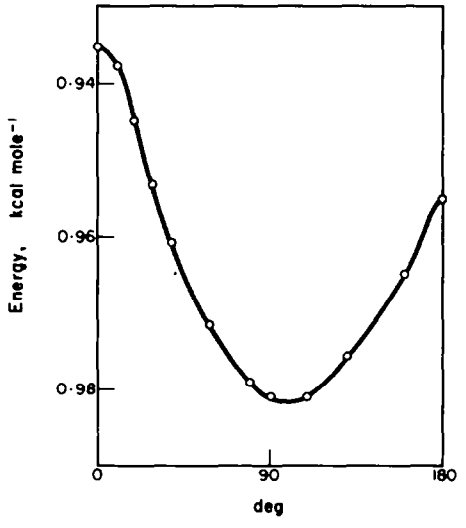
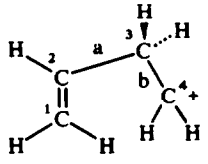


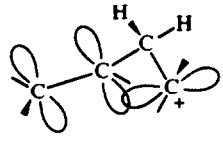
FIG. 6. Angular dependence of the energy of the homoallyl cation.

are apparent for which different charge densities are calculated. The values quoted in Table 2 are average values but it is possible in the real molecule that different weighting of conformers as well as solvent interactions will complicate the situation. A more satisfactory test of the theory would be provided by ^{13}C-shift data on these cations.

The field of "non-classical" carbonium ions offers possibilities of examination by the CNDO method. We have calculated the interaction between the positive centre and the double bond in the homoallyl cation, V: Fig. 6 shows the variation of binding energy with geometry, the simultaneous and equal rotation about the two bonds a and b. It is seen that the energy minimises in the conformation VI at a twist angle of



V



VI

90–110° from the planar ion, V, Fig. 6. As the π-orbital and vacant orbital on C_4 are twisted towards each other electronic charge is calculated to pass from the former to the latter as shown by charge density changes on the carbon atoms (Fig. 7).

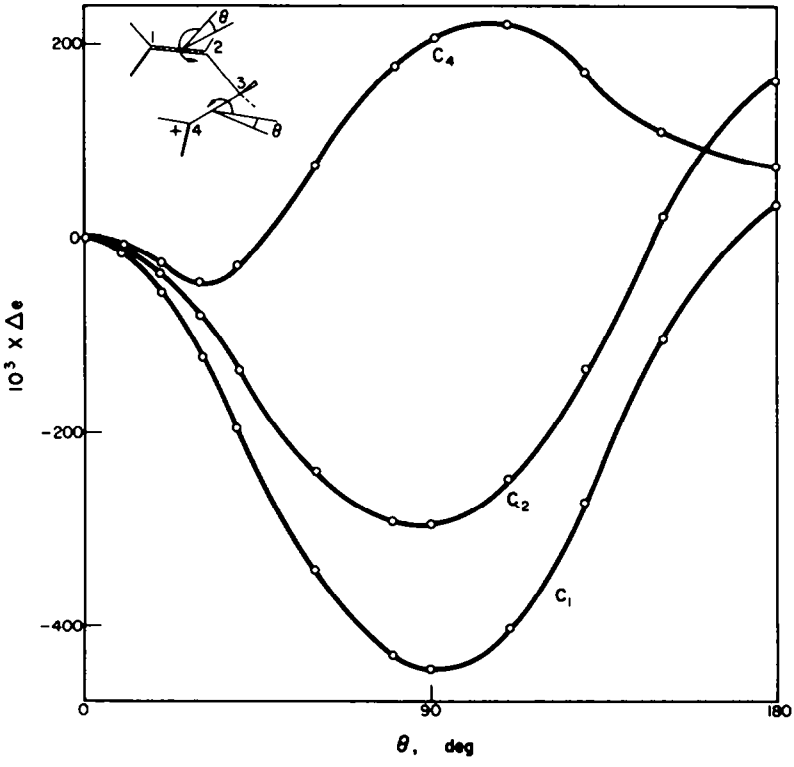


FIG. 7. Charge distribution in the homoallyl cation as a function of geometry.

This angular dependence of homoallylic participation is amenable to experimentation and is at present under study in this laboratory.

Acknowledgements—We thank the Science Research Council for computing facilities at the Atlas Computer Laboratory and Dr. K. Miller for supplying the CNDO programme.

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