

# THE INTERACTION CURVE OF NON-BONDED CARBON AND HYDROGEN ATOMS AND ITS APPLICATION

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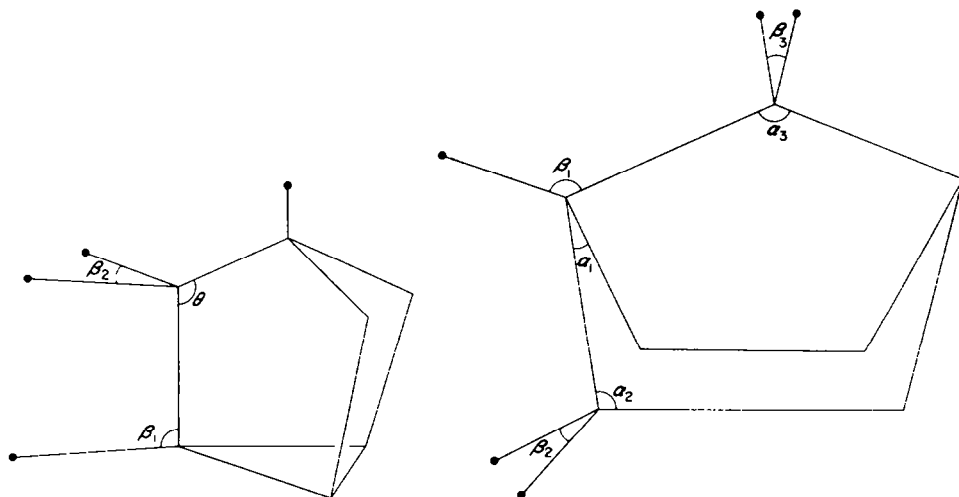
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(Received 25 November 1960)

**Abstract**—A universal interaction curve of non-bonded carbon and hydrogen atoms has been proposed. This curve has been successfully applied to determine numerous properties of various saturated and unsaturated hydrocarbons such as the equilibrium of molecular conformation, the strain energy of molecules, the sublimation heat of organic crystals and so on.

## 1. INTRODUCTION

In dealing with problems of physical chemistry it is advantageous to consider the molecule as a system of interacting atoms. The approximate additivity of molecular properties, the low interdependence of valence angles and bonds during the vibration of the molecule as well as many other arguments permits the separation of the inner potential molecular energy into three parts: the bond energy, the interaction energy of non-bonded atoms and the energy of deviation of angles from their ideal value. The energy of atomic interaction within the molecule must therefore involve the sum of energies from all atom pairs and that of directed valency must be taken as the sum of  $\frac{1}{2}C\alpha^2$  stress in all valency angles of the molecule.



As to the molecular interaction energy (for a substance in a condensed state) it must be estimated as the overall interaction energy of all atomic pairs of different

\* Translated by A. L. Pumpiansky, Moscow.

molecules. We shall henceforth assume no difference between the interaction curves of non-bonded 'neutral' atoms belonging to the same or different molecules.

For this theory to be applicable to various problems of reactivity, kinetics, adsorption, thermal chemistry, and others, it is necessary to have data for the curves of interaction energy of non-bonded atoms.

The most precise X-ray studies of the electronic density distribution in crystals show that within the precision of 0.1 to 0.2 electrons, the electronic density of chemically bonded atoms can be represented by a spherically symmetric function. This can be considered as some justification for regarding a molecule as a system of interacting atoms.

If the atoms of the molecule are electrically charged then the expression of the energy should also include the electrostatic interactions. Mostly, however, the electric interactions are of no importance. Thus, for example, in the interaction energy of molecules in a crystal the dipole interaction does not exceed a few per cent. As the electric potential varies slowly it will not play any important part in the study of conformation. There is also a large class of molecules whose atomic charges are practically equal to zero. We are essentially concerned with the interaction curve of 'neutral' non-bonded atoms.

In terms of the well known theoretical derivation of the interaction energies at great distances the interaction energy may be written as  $A r^{-6} - B r^{-n}$  or  $A r^{-6} - B \exp\left(-\frac{r}{\rho}\right)$  these expressions being often used for various calculations.

The interaction energy of non-bonded atoms affects a large number of different phenomena. Its magnitude determines partly the heat of combustion, it is essentially responsible for the stereochemical configuration of the molecules, its magnitude fully accounts for the intermolecular interaction which defines the values of heats of sublimation and adsorption, equilibrium distances in crystals, etc.

In organic chemistry different combinations of few atoms give rise to very many compounds. The question is whether there are universal constants  $A$ ,  $B$ ,  $\rho$ , that can be used to account for the interaction of 'neutral' atoms independent of the molecules to which they belong.

We found that with some reduced coordinates one can propose a universal curve involving the interaction  $C \dots C$ ,  $H \dots H$ , and  $C \dots H$  that holds true both for saturated and unsaturated hydrocarbons.

## 2. THE UNIVERSAL INTERACTION CURVE OF CARBON AND HYDROGEN ATOMS

The experimentally best known parameters of the interaction curves are the intermolecular distances in the crystal. These undoubtedly hold (at least with an accuracy of 5 per cent) for all hydrocarbons and in general for all organic substances independent of their chemical nature. Taking into consideration that on entering the crystal the molecules are being slightly 'pressed', we shall assume the equilibrium distances of 'isolated' atoms to be  $C \dots C$  3.8 Å,  $C \dots H$  3.15 Å and  $H \dots H$  2.6 Å. These figures indicate the equilibrium intermolecular distances in crystal  $C \dots C$  3.6 Å and  $H \dots H$  2.35 Å, that is, to mean experimental values.<sup>1</sup>

<sup>1</sup> A. I. Kitaygorodsky, *Organic Crystal Chemistry*. Moscow (1955).

Let us denote by  $z = \frac{r}{r_0}$  the relation of the distance between the atoms to their equilibrium distance and rewrite the expression of 6-exp potential  $-\frac{A}{r^6} - B \exp\left(-\frac{r}{\rho}\right)$  into

$$V = V_{2/3} \frac{\frac{1}{z^6} - \frac{6}{\alpha} e^{\alpha} e^{-\alpha z}}{11.4 - \frac{6}{\alpha} e^{2/3}}$$

where  $V_{2/3}$  is the energy value at  $r = \frac{2}{3}r_0$  ( $\frac{2}{3}r_0$  is a typical contraction met with in organic molecules. Thus, in aliphatic chains carbon atoms bonded to the same atom are at a distance about  $\frac{2}{3}r_0$ ).

Parameter  $\alpha = \frac{r_0}{\rho}$ , of  $V_{2/3} = -\frac{A}{r_0^6} \left(11.4 - \frac{6}{\alpha} e^{-\alpha/3}\right)$ , parameter B is excluded, as usually, in terms of the equilibrium condition  $B = \frac{6A}{\alpha r_0^6} e^{\alpha}$ .

The above transformation substantially facilitates the search for unknown parameters and makes the problem much clearer. It is seen that  $V/V_{2/3}$  is the function of only one parameter. The second parameter can be easily picked out as a scale value. It is self evident that  $V_{2/3}$  is the value of the order of a few kcal/mole. It is rather

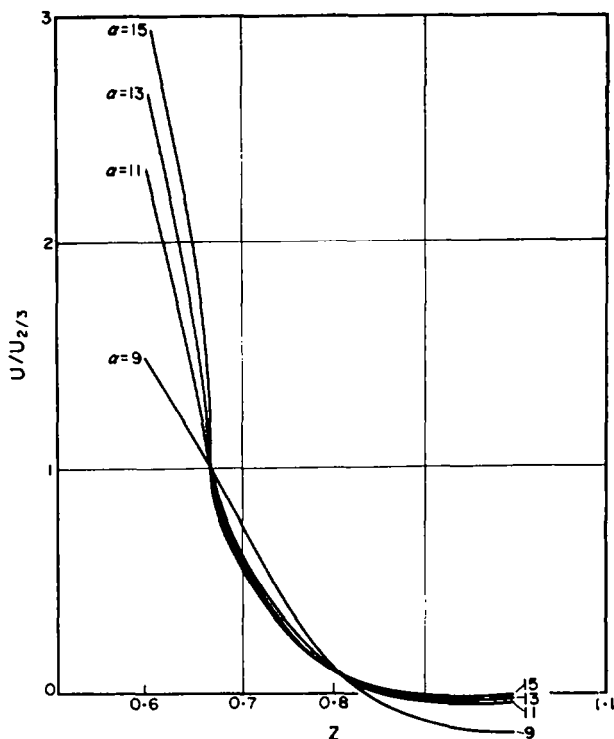


FIG. 1.

important that a reasonable range of values for  $\alpha$  is also self evident. Indeed, calculating  $V/V_{2/3}$  for  $z = 1$  it is at once obvious that the interaction energy values at equilibrium (mainly determining the sublimation heat) will be reasonable only for  $\alpha$ , that are within the 11 to 18 range. Thus the advantage of the new form of 6-exp. potential lies in the small scattering of possible values for two parameters (the third one  $r_0$  has already been introduced into the formula).

As is seen from Fig. 1, the curve  $V/V_{2/3}$  is fixed in point  $z = \frac{2}{3}$ , and its minimum abscissa is constant (at  $z = 1$ ). As the value of  $V/V_{2/3}$  in the minimum is very small actually the curve is fixed in two points so that the variation of  $\alpha$  is of no special importance, the curve being hardly sensible to the parameter  $\alpha$ . This is quite distinctly seen from the pattern.

The parameters  $\alpha$  and  $V_{2/3}$  for hydrocarbons were chosen so as to meet in the best way the existing manifold experiment.

It is of interest that the values of  $\alpha$  and  $V_{2/3}$  for all interactions seem to be very close to each other. At this initial stage of the investigation we believe it possible to make use of the universal expression (in reduced coordinates) as follows:

$$V = 3.5 \left( -\frac{0.04}{z^6} - 8.6 \cdot 10^3 \cdot e^{-13z} \right) \quad (1)$$

The choice of  $\alpha = 13$  determines the values of two coefficients given in brackets. The value for  $V_{2/3} = 3.5$  kcal/mole is chosen independently.

The constants A, B and  $\rho$  for C...C, C...H, and H...H interactions are

	A $\frac{\text{kcal}}{\text{mole}} \text{ \AA}^6$	B $\frac{\text{kcal}}{\text{mole}}$	$\rho \text{ \AA}$
C...C	420	$3 \cdot 10^4$	0.29
C...H	140	$3 \cdot 10^4$	0.24
H...H	43	$3 \cdot 10^4$	0.20

Thus in respect to our previous work<sup>2</sup> we have advanced a step forward. Previously we suggested a universal expression  $V' \left( \frac{\Delta r}{r} \right)$ .

The present investigation indicates the possibility of applying the universal curve not only for the derivation of the energy but for the energy itself.

The previous expression  $\frac{V'}{C}$  is in good agreement with the expression used in this work.

### 3. MOLECULAR INTERACTIONS

Our future communications will deal with the precision of the formula, elucidation of the limits of its applicability and the search for similar expressions for other atoms. Here we are concerned with the main results of the manifold application of the proposed potential.

In Fig. 2 is plotted the energy of the crystalline methane lattice calculated in terms of the formula (1). The values shown correspond to those obtained experimentally 2.6 kcal/mole for the lattice constant (5.8 Å) and the lattice energy (the experimental

<sup>2</sup> A. I. Kitaygorodsky, *Tetrahedron* 9, 183 (1960).

value, calculated from the sublimation heat is equal to 2.6 kcal/mole). The asymmetry of the curve leads also to a reasonable course of the lattice parameter with changing temperature. The energy of methane in a gas-crystalline (rotation-crystalline) state, or such a state of the substance when the molecular centres form a regular lattice and the azimuths of the molecules are random toward the crystallographic axes, is the same up to 0.2 kcal/mole.

The calculated energy of the quasicrystalline aggregation of molecules and molecules arranged in the nearest order does not markedly differ from that of the crystal.

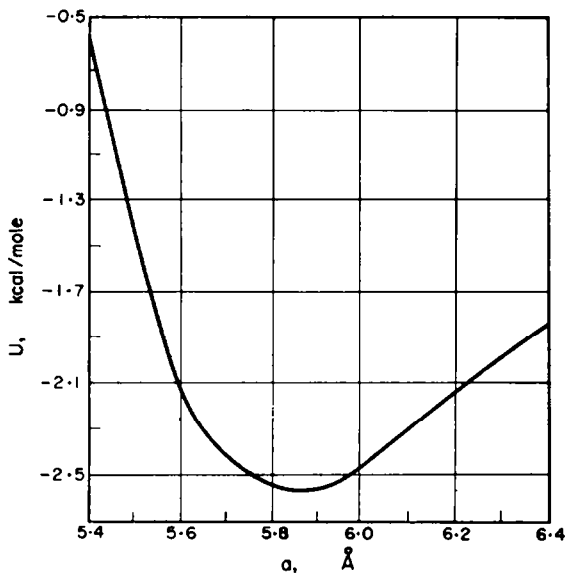


FIG. 2.

This is already seen from the fact that it changes very little with changing lattice parameter from 0°K to the melting point.

The equilibrium values of the lattice energy were calculated for other substances as well. Thus, for the gas-crystalline state of cyclopentane the calculation resulted in 7 kcal/mole rather than 8 kcal/mole obtained from the experimental value of the sublimation heat. It will be noted that for gas-crystalline cyclohexane the calculated and experimental values are markedly different, being 3 and 9.6 kcal/mole, respectively. This difference is interpreted as follows. The calculation was made allowing for a complete randomness in the molecular azimuths. But the molecule of cyclohexane is essentially different in its form from a sphere. The availability of a nearest order excludes such an arrangement of neighbours when the largest diameters of the molecules overlap. The overestimation in the calculation of "overcrowded" positions leads of course to the rise in repulsion and hence, to the rise in energy (decrease in absolute value).

The calculation of the energy in the benzene lattice is rather tedious. We have calculated<sup>3</sup> the contribution to the energy of the interaction of a molecule with its twelve nearest neighbours making up the first co-ordination sphere. This resulted in 6.5 kcal/mole.

<sup>3</sup> A. I. Kitaygorodsky and K. V. Myrskaya *Crystallographia URSS* In press.

On the basis of less cumbersome calculations carried out for gas-crystalline substances we found that the contribution to the energy of the first co-ordination sphere is 85–90 per cent. As the experimental value of the energy for the benzene lattice is 9–10 kcal/mole, the calculated and experimental values are seen to be in excellent agreement.

Our curve of the energy for atom interaction practically coincides with that of carbon atom interaction found by Crowell<sup>4</sup> when analysing the properties of graphite. Our curve also points to the observed decrease in the distances between the aromatic molecules when the latter increase in size. The investigation of the properties of lattices of organic crystals is the main means of obtaining the interaction curve of neutral atoms more precisely.

Besides estimating the energy and the equilibrium distance, interaction curves can also be used to obtain compressibility values. The calculation of compressibility for methane resulted in 0.16 kcal/mole Å against the experimental value 0.18.

#### 4. INTRAMOLECULAR INTERACTIONS

To evaluate the strain energy of the molecule

$$W = \frac{1}{2} \sum C \alpha_i^2 + \sum V_{ik}$$

it is necessary to obtain the elasticity coefficient of the ideal angle  $C$  of the molecule.

It is possible to choose the value  $C$  for the carbon atom by making use of the data for the optical force constant. By definition  $\gamma = \left[ \frac{\partial^2 W}{\partial \alpha^2} \right]_{\alpha=\alpha_0}$ , where  $\alpha_0$  is the equilibrium value, a  $W$  is the elasticity energy of the ideal angle plus the interaction energy of non-bonded atoms. To recalculate the values  $C$  corresponding to values of  $\gamma$  one must know the shape of the interaction curve since

$$\gamma = \frac{\partial^2 W}{\partial \alpha^2} = C + V'(r) \frac{\partial^2 r}{\partial \alpha^2} + V''(r) \left( \frac{\partial r}{\partial \alpha} \right)^2$$

The value  $C = 35$  kcal/mole in combination with the expression for our potential leads to the figures  $\gamma_{\text{OCC}} = 95$  kcal/mole,  $\gamma_{\text{HCH}} = 79$  kcal/mole, in full accord with optical data.

Using this value of  $C$  we have calculated the values of the strain energy as well as the optimal conformations for a number of hydrocarbon molecules, the experimental and theoretical data being listed in Table 1.

The conformation data are in close agreement with those of our previous work. A new approach allowed us to estimate in addition the magnitudes of the strain energy.

As will be seen from Table 1 the main contribution to the strain energy results from the repulsion of the non-bonded atoms rather than from the deviation of the angle from its tetrahedral value. Thus, even with cyclobutane  $\frac{1}{2}C\alpha^2 = 2$  kcal/mole whereas the strain energy per one  $\text{CH}_2$  group is 21 kcal/mole. This of course should be considered as resulting from a different, and presumably more correct, definition of strain energy. In classical works strain energy is referred to as the strain energy in excess of that of alkanes. This excess strain energy is accounted for by 2/3 by the

<sup>4</sup> A. D. Crowell, *J. Chem. Phys.* 29, 446 (1958).

TABLE I

Molecule	Angles	Values of angles (deg)			Strain energy per CH <sub>2</sub> group kcal/mole	Excess strain energy as compared to that of alkanes	
		theoretical		Experimental		Theor.	Experim.
		present work	Ref. 2				
Ethane	HCH	109.4	—	109.3	—	—	
Alkanes	CCC	112	111.5	112	18	—	
	HCH	110	108	—			
Cyclopropane	HCH	116.5	118	118.2	23	5	10
Cyclobutane	HCH	113	112	114	21	3	7
Cycloheptane	HCH	110.5	109	—	18.5	0.5	1
Cyclohexane	CCC	112.5	112	—			
	HCH	110	108	—	18	0	0
Nortricyclene	$\theta$	98.5	96	96.5	—	—	
	$\beta_1$	122	121	—			
	$\beta_2$	113	112	—			
Norcamphane	$\alpha_1$	114	109.5	—			
	$\alpha_2$	103	103*	—			
	$\alpha_3$	91	92	—			
	$\beta_1$	106	108.5	—			
	$\beta_2$	112	107.5*	—			
	$\beta_3$	114	113*	—			

\* Values of angles  $\alpha_2$ ,  $\beta_2$ ,  $\beta_3$  in ref. 2 were erroneous

energy due to the distortion of tetrahedral angles. It will be noted that the calculated values of the excess strain energy are substantially lower than the experimental (calorimetric) ones. It follows that half of the strain is due to the change in the magnitude of the interaction energy of bonded atoms (bond strain).

The above examples show that the applied universal potential leads to reasonable results in the evaluation of many properties of compounds. Further study will enable us to make the interaction curves more precise. It seems, however, that this method of calculation to a precision substantially better than that of one order of magnitude is already worth considering.