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THE INTERNAL MOLECULAR POTENTIAL BETWEEN THE SUBSTITUENT GROUPS IN A BENZENE RING AS DERIVED FROM THE HEATS OF COMBUSTION*

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Abstract

It is shown that differences in the observed heats of combustion of isomeric benzene derivatives can be interpreted as the internal molecular potential existing between their substituent groups. A like interpretation can be given for the differences between the values observed for the heats of combustion of certain nonisomeric benzene derivatives and those calculated by the rule of additivity. This internal potential, to which the attractive and repulsive forces between the groups are due, results from the electrostatic potential of the group moments (dipole effect), the polarization of the substituents and of the ring (induction effect), the dispersion effect, and from steric hindrance. We have, therefore, a new and direct method of measuring the internal potential, which determines both the internal motion of groups within an organic molecule and its most stable configuration. The values thus measured are in good agreement with values theoretically evaluated from the above intermolecular (van der Waals) forces. From the data derived by this method we conclude in the case of o-xylene that valence angles of 120° between the C–CH_3 bond and the aromatic C–C bonds are extremely stable, for the energy required to distort these angles through 10° is greater than 2 K cal/mole. We find, also, very restricted rotation for the butane molecule, from which it follows that saturated aliphatic hydrocarbons in the gaseous state tend to form zigzag chains. Such restricted rotation is found for the ether molecule as well.

Introduction

ONE of the most interesting structure problems at present is the question as to the rotation of groups around a bond and to their most stable orientation within an organic molecule. This rotational motion of course is governed by the forces acting between the different groups, that is, by the internal molecular potential between them. It is necessary, therefore, to study by means of theory the nature and distance of action of these forces, and to develop experimental methods for determining the mutual influence and the potential energy of the neighboring groups.

As to the nature and classification of these forces we will make the following assumptions, which agree nicely with our empirical knowledge. The forces leading to a chemical bond between two atoms are given principally by the interchange binding forces and can be calculated only by the methods of quantum mechanics. The forces between two neighboring atoms, not too close together, are the van der Waals forces. These intermolecular forces can be

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treated by classical and wave mechanics methods. If two atoms not connected by a chemical bond approach each other too closely, there are produced strong repulsive forces, which have not yet been treated theoretically, and which we will classify generally as caused by steric hindrance. We shall use this scheme in interpreting the results derived in this paper from the heat of combustion as it is all we have at present. It may be pointed out, however, that most of our conclusions are independent of the nature of the assumed forces. The sphere of action is determined by the surface at which we have equilibrium between repulsive and attractive forces, i.e. a minimum of potential energy.

Of the different methods which permit us to study the rotation within, and the most stable configuration of a molecule, we may mention measurements and discussions of electric moments,[2] investigations of the Kerr effect,[3] x-ray[4] and electron beam[5] interferences. The interference methods yield direct information concerning the distance between the atoms in a molecule. By the use of all these methods we may determine whether repulsive or attractive forces act between these atoms. But none of these methods gives us the internal potential energy between the atoms and atom groups, by which the internal motion of groups and the configuration of the molecule are determined.

It is therefore justifiable and useful to look for other methods, which may allow us to measure directly the internal potential and settle these questions of structure.

Such a method is given by the discussion of the heats of combustion, especially of isomeric compounds. It will be shown here that the differences in the energies of the molecules can be easily interpreted as the differences in the internal potential of the substituent groups, which is due to the attractive and repulsive forces acting between them.

As is well known, simple addition of the different bond energies concerned yields a value, correct to within a few percent, for the heat of formation of an organic molecule. This value is approximate because the value of any bond energy may depend in some measure upon the nature of the other bonds acting on the same atom[6] since such bonds often influence each other. If we take isomeric compounds such as isomeric benzene derivatives, however, where the same bonds act on the corresponding atoms, we expect constant heats of formation and therefore also constant heats of combustion so long as there is no marked difference in the internal potential energy between the sub-

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[2] See for instance H. Sack, Erg. d. exakt. Naturw. **8,** 307 (1929) and H. A. Stuart, Phys. Zeits. **31,** 80 (1930); L. Meyer, Zeits. f. physik. Chem. **B, 8,** 27 (1930).

[3] H. A. Stuart, Zeits. f. Physik **63,** 533 (1930) and H. A. Stuart, Erg. d. exakt. Naturw. **10** (1931) in press.

[4] P. Debye, Phys. Zeits. **30,** 84, 524 (1929); **31,** 142 (1930). L. Bevilogna, ibid. **32,** 265 (1931).

[5] H. Mark and R. Wierl, Zeits. f. Physik **60,** 741 (1930); R. Wierl, Phys. Zeits. **31,** 366, 1028 (1930) and Leipziger Vorträge 1930, (1930).

[6] So we generally find differences in the aromatic and aliphatic bond energies, see H. Grimm and H. Wolff, Handbuch d. Physik **24,** 526 (1926).

stituents. We further expect that, on substituting in a benzene ring several groups, one after the other, the energy which is necessary for the successive groups will be independent of the presence of other substituents, so long as the internal potential between the substituents may be neglected. In this case the heat of combustion of the compound ought to be equal to the heat of combustion of benzene plus the amounts of energy characteristic of each substituent. The deviations from this additivity rule ought to increase with the potential energy between the substituents.

We shall first show that these ideas are in agreement with experimental data, and that deviations of the observed heats of combustion from the additivity rule can be interpreted quantitatively as potential energies between the substituent groups.

Experimental Data

In Table I, column 3, are summarized the observed heats of combustion of benzene and some simple derivatives in K cal/mole. As we have to compare the heats of combustion of the free molecules, or the heats of combustion for the gas at room temperature, we have to add to these observed values the heats of vaporization and in the case of solids also the heat of fusion, which are tabulated in columns 4 and 5. For our purpose it is sufficient to use the heats of fusion and of vaporization for the melting and the boiling point respectively. Where the heats of vaporization are not known, they are calculated by means of the Trouton rule, heat of vaporization $=20\times T_{\mathrm{abs}}$ cal/mole. The heats of fusion, when not measured, are interpolated and extrapolated. All values for the heat of fusion and heat of vaporization, which are not known by direct measurements, are put in parantheses in this and the following tables. The values corrected for the gaseous state are tabulated in column 6 and in the last column we find the differences between the heats of combustion of benzene and the different derivatives, that is the energy Q_{subst} characteristic of the substitution for the different groups.

TABLE I. *Thermal data and amounts of energy characteristic of each substituent for various benzene derivatives.*

Substance	Formula	H. Comb[7] obs. K cal/mole	H. Fusion K cal/mole	H. Vap. K cal/mole	H. Comb gas obs. K cal/mole	Q_{subst}
Benzene	C_6H_6	783.4		7.4	790.8	
Toluene	$C_6H_5\cdot CH_3$	936		8	944	+153.2
Phenol	$C_6H_5\cdot OH$	732	2.8	9	743.8	−47.0
Benzoic Acid	$C_6H_5\cdot COOH$	771.2	(5)	(10.5)	786.7	−4.1
Aniline	$C_6H_5\cdot NH_2$	812		9	821	+30.2
Nitrobenzene	$C_6H_5\cdot NO_2$	739		10	749	−41.8
Fluorobenzene	$C_6H_5\cdot F$	747.2		7.6	754.8	−36.0

In order to show how far the energy necessary to substitute a certain group is independent of the presence of other substituents, we give, in Table II, the observed heats of combustion of some p-derivatives which are cor-

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[7] All data of heats of combustion are taken from the Intern. Crit. Tables, which are based on the critical compilation by M. S. Kharasch, Bureau of Standards, J. of Research, *2*, 359 (1929).

rected to the gaseous state. In column 4 we find the heats of combustion calculated by adding the Q_{subst} values (Table I, last column) to the heat of combustion of the benzene. The energy differences ΔU between the observed and calculated values are given in column 5. The plus sign shows that the observed value is greater than the calculated one. In the next column, 6, are tabulated the electric moments of the substituents together with their direction. A minus sign means that the group is negative with respect to the carbon atom of the ring. We recognize that the energy differences ΔU or the deviations of the additivity rule are increasing with the electric moment of the substituents, i.e., with the electrostatic potential of the groups. The differences for the first four compounds are within the limits of experimental error. We further find a negative deviation where the electric moments have different signs and therefore attract each other. This is to be expected since a negative difference must be interpreted as attraction.

TABLE II. *Comparison of observed and calculated heats of combustion of various p-derivatives.*

Substance	Substituents	H. Comb.[8] (gas obs.) K cal/mole	H. Comb. (calc.) K cal/mole	Energy difference ΔU K cal/mole	Elec. moments $\mu \times 10^{18}$
p-Xylene	CH_3; CH_3	1097.7	1097.2	+0.5	+0.4; +0.4
p-Nitrotoluene	NO_2; CH_3	903	902.2	+0.8	−3.8; +0.4
p-Fluoronitrobenzene	NO_2; F	714	713	+1.0	−3.8; −1.3
p-Nitrophenols	NO_2; OH	701[9]	702	−1.0	−3.8; +1.6
p-Nitrobenzoic Acids	NO_2; COOH	747.8	744.9	+2.9	−3.8; (2.7 and 1.6)[10]
p-Nitranilines	NO_2; NH_2	777[9]	779.2	−2.2	−3.8; (+1.5)
p-Dinitrobenzenes	NO_2; NO_2	712.5	707.2	+5.3	−3.8; −3.8

In Table III are shown as a further example of the connection between the deviation from the additivity rule and the internal potential of the groups the heats of combustion of some isomeric di- and tri-substituted benzene derivatives. We always find that these energy differences ΔU given in the last column increase in the order para, meta and ortho positions. That is to be expected, since the potential between the groups, which is for these compounds, excepting for p- and m-nitraniline always repulsive, increases in the same direction. Besides the electrostatic potential and the polarization of the benzene ring we have in the case of the o-compounds always steric hindrance, that means strong repulsion.

CALCULATION OF THE INTERNAL MOLECULAR POTENTIAL BETWEEN THE SUBSTITUENT GROUPS

The question arises now, how far can these deviations from the additivity rule be interpreted as the internal potential of the substituents and how far

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[8] The observed data for the liquid state and the heats of fusion and vaporization are tabulated in Table III.

[9] Heat of Comb. observed = 686; H. Fusion (5.5); H. Vap. (9.5) gives for H. Comb. for the gas 701; K cal; for p-nitraniline the values are 761; 5; (11), respectively, which gives 777 K cal for the gas.

[10] The moment of the COOH group consists of three bond moments: $\mu_{c=0} = 2.3.10^{-18}$; $\mu_{0-H} = 1.6.10^{-18}$ and $\mu_{c-0} = 0.7.10^{-18}$

TABLE III. *Observed and calculated heats of combustion of some di- and tri-substituted benzene derivatives.*

Substance	Heat Comb. observed K cal/mole			H. Fusion K cal/mole			H. Vap. K cal/mole			H. Comb. gas K cal/mole observed			calc.	Energy Differences ΔU K cal/mole		
	p	m	o	p	m	o	p	m	o	p	m	o		p	m	o
Fluoronitrobenzene	703_s	706	707	(21)				9.5		714.5	715.5	716.5	713	+1.5	+2.5	+ 3.5
Nitrotoluene	889_s	893	897	(3)				(10)		902	903	907	902.2	−0.2	+0.8	+ 4.8
Nitrobenzoic Acid	728_s	729_s	735_s	8.8	4.6	6.7		(11)		747.8	744.6	752.7	744.9	+2.9	−0.3	+ 7.8
Dinitrobenzene	695_s	697_s	703.2_s	6.5	4.2	5.3	(11)	(11.5)	(11.5)	712.5	712.7	720	707.2	+5.3	+5.5	+12.8
Xylene	1089.1	1089.6	1092[11]				8.6	8.6	8.7	1097.7	1098.2	1100.7	1097.2	+0.5	+1.0	+ 3.5
	sym. 1, 3, 5	asym. 1, 2, 4		sym.	asym.		sym.	asym.		sym.	asym.			sym.	asym.	
Trinitrobenzene	664	674		(5.5)	3		(13)	(13)		682.5	690		665.4	+17.1	+24.6	

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[11] Instead of 1093 K cal as given in the Int. Crit. Tables, we use 1092 K cal, as Richards and Barry, J. Amer. Chem. Soc. **37**, 993 (1915) find for the difference between p- and o- xylene 2.6 K cal.

can they be explained by the well-known forces acting between different molecules, i.e., the van der Waals forces.

There are three effects which contribute to the potential of molecules or in our case to the potential of the substituent groups. First of all the electrostatic potential of the permanent electric moments associated with the substituent groups, the dipole effect, secondly the induction effect (Debye effect) caused by the polarization of the molecule by the electric field of the moments of the substituents.[12] In this connection we must consider not only the mutual polarization of the substituents but also the polarization of the benzene ring, which contributes large amounts to the potential energy. The third effect is the so called dispersion effect, which has been introduced by London[13] into the theory of molecular forces. This effect consists in the mutual perturbation of the rapid internal motion of the electrons and always gives attraction.[14]

The energy of the dispersion effect can be approximately calculated, according to London, by the following relation.

$$E_{\text{disp.}} = -\frac{3}{4}\frac{h\nu_0 \cdot \gamma^2}{r^6}$$

γ is the polarizability, that is the electric moment, induced by the unit of electric intensity, r the distance of the groups; for $h\nu_0$ the ionization potential may be used. This effect is in meta- and para-position always negligible (50 to 100 cal/mole), in ortho-position greater, for instance for two NO_2 groups 1500 cal/mole. But as we usually have steric hinderance in ortho-position, i.e., strong repulsion, the dispersion effect will be overcompensated.

The dipole effect may be neglected for para- and meta-positions, excepting in the case of two NO_2 groups. The electrostatic potential of two dipoles whose vectors lie in a plane can be calculated by means of the following expression

$$E_{\text{dipole}} = -\frac{\mu_1 \cdot \mu_2}{r^3}\left[2 \cos \alpha_1 \cos \alpha_2 - \sin \alpha_1 \sin \alpha_2\right].$$

α_1 and α_2 are the angles between the direction of the electric moments 1 and 2 and the line connecting both dipoles.

The energy contribution of the induction effect is given by the formula

$$E_{\text{ind.}} = -\tfrac{1}{2}\gamma F^2.$$

F is the electric intensity of the dipole moments. This energy may be neglected as far as the mutual induction of the substituents is concerned, excepting for a very strong group moment, such as the moment of NO_2 with $\mu = 3.8 \times 10^{-18}$. Considering the polarization of the benzene ring we find that

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[12] In this case the groups and molecules behave as systems with static charge distribution, dipoles, quadrupoles and so on, which polarize each other.

[13] F. London, Zeits. f. Physik **63,** 245 (1930); Zeits. f. physik. Chem. **B, 11,** 222 (1930).

[14] The van der Waals forces of the noble gases and of nonpolar molecules can be explained only by this effect.

this effect involves very large energies. If we substitute, for instance, one NO_2 group in the benzene ring the field of the group moment will polarize the rest of the molecule, first of all the six aromatic C–C bonds, 1, 2, 3 . . . 6, see Fig. 1. The energy of this polarization effect for the bonds 1 and 6 amounts to 3650 cal for each bond. For the 2 and 5 bonds we find 250 cal and for the 3 and 4 bonds 50 cal each. The total energy is therefore 7900 cal/mole.[15]

If we substitute two or more groups, we have to calculate the resulting field of all group moments acting on the different C–C bonds. It turns out that the energy contributed from the induction by one group depends on the presence of the other ones and that the total energy of the induction effect is not the sum of the energies characteristic of the single groups, whereas the potentials of the dipole and the dispersion effect are always additive and independent of the benzene ring. As long as the groups have electric moments with the same direction with respect to the ring, the fields of the single moments weaken each other in most cases so that we get less energy for the induction effect. This corresponds to an increase in the total potential energy or in the heat of combustion.

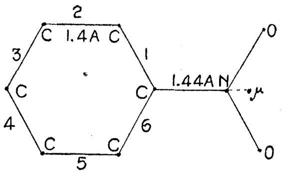

Fig. 1.

In Table IV are given some of these calculated energies which arise from the polarization of the ring. In column 1 we find the number and nature of the substituents and in column 2 the energies of the induction effect. Column 3 shows the deviations from the energies we should find if each substituent would polarize the ring independently. These deviations, as mentioned above,

TABLE IV. *Calculated energies which arise from a polarization of the ring.*

Substituent	Induction effect calc. K cal/mole	Deviation from additivity K cal/mole
1 NO_2	−7.9	
2×NO_2 p	−12.7	+3.1
m	−11.3	+4.5
o	−15.9	+0.7
3×NO_2 sym.	−10.9	+12.8
asym.	−15.1	+8.6
1 F	−1.5	
1 F and 1 NO_2 p	−8.2	+1.2
m	−7.5	+1.9
o	−8.5	+0.9
1 NH_2	−1.9	
1 NH_2 and 1 NO_2 p	−10.6	−0.8
1 CH_3	0	
1 CH_3 and 1 NO_2 p	−7.9	0

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[15] The fact that all aromatic bond energies are larger than the aliphatic ones may be to some extent due to this induction effect.

in so far as they are positive, increase the total potential and this corresponds to repulsion or higher heat of combustion.

In the calculations the following distances and assumptions are used. The distances of the atoms are known from x-ray diffraction data, which give us for $C–C_{ar}$ 1.4, for $C–C_{al}$ 1.5, and for C–N 1.44A; the distance C–F is about 1.6A. The electric moment of the NO_2 group is localized at a point 0.4A behind the N-atom. The distance between this moment and the C-atom of the ring is therefore 1.84A and the distance between the moment of the C — F bond and the C atom is 1.4A.[16] The refraction R of the six aromatic C–C bonds is equal to the molecular refraction of benzene minus the refraction of the six C–H bonds, i.e., $26.18-6\times1.7=16$. The polarizability, $\gamma=3R/4\pi N$, of one C–C bond amounts therefore to $10.6.10^{-25}$. The C–C bonds are treated as polarizable spheres located in the middle of the bond.

After we have determined in this way the energy amounts caused by the induction of the C–C bonds, we can calculate the total internal potential of the substituent groups for some simple derivatives. In Table V, columns 2 to 5, are given the energy amounts of the dipole and dispersion effects as well as of both induction effects. In column 6 and 7 we find the sum, i.e., the total potential energy together with the observed energy differences ΔU taken from Table III, last column.

TABLE V.

Substance[17]	Dipole effect $K\frac{cal}{mole}$	Disp. effect $K\frac{cal}{mole}$	Induct. of subst. $K\frac{cal}{mole}$	Induct. of ring $K\frac{cal}{mole}$	Total int. potential calc. $K\frac{cal}{mole}$	Energy diff. ΔU obs. $K\frac{cal}{mole}$	Potential of steric hindrance $K\frac{cal}{mole}$
p-dinitrobenzene	+1.6	0	0	+3.1	+4.7	+5.3	0
m- "	+1.8	0	0	+4.5	+6.3	+5.5	0
o- "	+7.7	−1.9	−1.0	+0.7	+5.5	+12.8	+7.3
1, 3, 5, trinitrobenzene	+5.3	0	0	+12.8	+18.1	+17.1	0
1, 2, 4 "	+10.8	−1.9	−1.0	+8.6	+16.5	+24.6 (20.8)	+8.1
p-fluoronitrobenzene	+0.5	0	0	+1.2	+1.7	+1.5	0
m- "	+0.8	0	0	+1.9	+2.7	+2.5	0
o- "	+3.2	−1.7	−0.2	+0.9	+3.2	+3.5	+0.3
p-nitrotoluene	−0.1	0	0	0	−0.1	−0.2	0
m- "	−0.1	0	0	0	−0.1	+0.8	0
o- "	−0.8	−1.6	−0.4	0	−2.8	+4.8	+7.6
p-nitraniline	−0.6	0	0	−0.8	−1.4	−2.2	0
p-xylene	0	0	0	0	0	+0.5	0
m- "	0	0	0	0	0	+1.0	0
o- "	0	−1.0	0	0	−1.0	+3.5	+4.5

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[16] The distances N–O and O–O are 1.13 and 2.09A respectively. Using the fact that for the N = O bond the center of the positive charges is located at 1/4th of the distance N = O near the oxygen atom, we can localize the moment of the NO_2 group (see L. Meyer, Zeits. f. physik. Chem. **B, 8,** 27 (1930)).

[17] The values for m- and o-nitraniline, the nitrobenzoic acids, and the nitrophenols are not given, as we do not know enough about the situation, the orientation, and the amount of the moments associated with these groups, which are not in the plane of the ring.

[18] For these calculations the following data are used. The polarizabilities are for NO_2 32.2×10^{-25}, for CH_3 24.9×10^{-25} and for F about 7×10^{-25}, the ionization potentials are for Cl 13 volts, for F 16.9, for NO_2 estimated to 13 volts and for CH_3 estimated to 10 volts.

There is an excellent agreement between the observed and calculated values, excepting for the ortho- compounds where we have steric hindrance. The agreement is surprisingly good considering the simplifying assumptions, which are the dipole moments are localized at a point and that the polarizable C–C bonds are substituted by polarizable spheres in the middle of the bonds. In the case of p-nitraniline we find in agreement with the observation an attractive potential and for p- and m-xylene within the limits of experimental error no internal potential at all. We are therefore justified in interpretating an observed energy difference ΔU as the internal potential between the substituent groups.

In the case of the ortho-compounds and of 1, 2, 4 trinitrobenzene the observed energy differences are always much greater than anticipated. The calculation of the electrostatic potential is in these cases somewhat uncertain because the distances of the group moments are comparable with the real dimensions of the dipoles. However we can best explain these deviations as caused principally by steric hindrance, which produces strong repulsive forces. These potentials of steric hindrance or these deviations are tabulated in the last column of Table V. We expect an increase in these deviations with an increase in the diameter of the substituent groups, as is observed. Fluoronitrobenzene has the smallest repulsion potential 0.3 K cal, o-xylene 4.5 K cal, nitrotoluene 7.6 K cal, dinitrobenzene 7.3 K cal and 1, 2, 4 trinitrobenzene 8.1 K cal. The two last compounds have, as is to be expected within the limits of experimental error, the same repulsive potential.

The total internal potential of o-xylene, which is given by the energy difference of the para- or meta- and ortho-compound, as there is no internal potential in p- and m-position, amounts to about 3 K cal.[19] In order to find the internal potential for the higher CH_3 derivatives we have tabulated in Table VI the heat of combustion for each of these compounds together with the values calculated according to the additivity rule. The last column gives us the energy difference ΔU or the internal potential. We recognize that these energies are increasing with the number of the substituents as is to be expected. We see furthermore that these potentials are within the limits of

TABLE VI.

Substance	H. Comb. obs. $K\frac{\text{cal}}{\text{mole}}$	H. Fusion $K\frac{\text{cal}}{\text{mole}}$	H. Vap. $K\frac{\text{cal}}{\text{mole}}$	H. Comb. gas obs.	K cal/mole calc.	Internal potential $K\frac{\text{cal}}{\text{mole}}$
1,2,4 Trimethylbenzene (Pseudocumene)	1241.7		9	1250.7	1250.4	+0.3
1,2,4,5 Tetramethylbenzene $(\text{Durol})_s$	1393.6	(5)	9.5	1408.1	1403.6	+4.5
$\text{Pentamethylbenzene}_s$	1554	(4)	(10)	1568.0	1556.8	+11.2
$\text{Hexamethylbenzene}_s$	1711.9	(6)	10.5	1728.4	1710.0	+18.4

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[19] This value depends only on the relative accuracy of the measurements of the heats of combustion of the three xylenes and is therefore more reliable than the difference of 3.5 K cal between the observed and calculated heat of combustion of o-xylene.

error, 6×3, 4×3, and 2×3 K cal, for hexamethylbenzene, pentamethylbenzene and tetramethylbenzene respectively.[20] Because the CH_3 groups have no induction effect where the energy is not additive, and because the p- and m-compounds have no marked internal potential, the total internal potential for hexamethylbenzene is six times as large as the single potentials between two neighboring CH_3 groups. Thus we find that two neighboring groups in hexamethylbenzene have practically the same repulsive potential as in o-xylene. This result is not obvious. Using it we can draw some conclusions regarding the stability of the valence angles between the $C-CH_3$ and the C–C bonds.

Conclusions

It is known from Lonsdale's x-ray[21] investigations of the crystal structure of $C_6(CH_3)_6$ that the carbon atoms of the CH_3 groups are situated in the plane of the ring, in spite of the repulsive forces (this already shows the stability of the valence angles). We have therefore valence angles of 120° between $C-CH_3$ bonds and the aromatic C–C bonds. In the case of o-xylene both groups may yield to the repulsive forces but remain in the plane of the ring so that we get a deviation of these valence angles. The angles will not be distorted more than 10° each, as this change is already sufficient to increase the distance between the carbon atoms of the two CH_3 groups from 2.9 to 3.4A where we certainly have equilibrium or even attraction of the two groups.

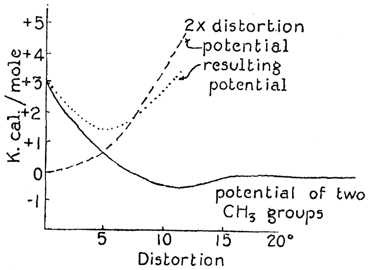

Fig. 2.

As we find for the o-position in xylene the same potential energy of 3 K cal as for the ideal 120° position in hexamethylbenzene, the decrease of the repulsive potential caused by the increasing C–C distance in case of o-xylene must be compensated by the energy, which is necessary to distort both valence angles. Such a compensation is only possible if the energy which is necessary to bend the angles so far that the two CH_3 groups are in the equilibrium position, is greater than the energy difference between the ideal 120° position, and this equilibrium position.[22]

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[20] The values for hexa-and pentamethylbenzene are very reliable as here experimental errors do not effect the value for the internal potential energy very much. This is not true for trimethylbenzene where the observed heat of combustion is certainly too small.

[21] K. Lonsdale, Proc. Roy. Soc. (London), **A123,** 494 (1929).

[22] If the distortion potential for this equilibrium angle is equal or smaller than 4.5 K cal, the resulting potential, see Fig. 2, has a minimum and therefore the total potential for o-xylene would be less than 1/6 of the potential of hexamethylbenzene, therefore the distortion energy must be greater than about 2 K cal for each angle.

This energy difference is about 4 K cal since the minimum potential due to the dispersion attraction is about 1 K cal, and the energy required to distort the valence angles between a C–CH_3 and C–C bonds in a benzene ring through 10° is therefore greater than 2 K cal. Thus we see how stable the valence angles are. It may be mentioned that this result is in agreement with values which the author[23] has calculated for the stability of the valence angles of some molecules such as HCN, C_2H_2, CO_2, CS_2, where the fundamental frequencies are known. The distortion energies for these molecules vary between 700 and 4000 cal/mole for a deviation of 10°.

From the heats of combustion for the xylenes we found that two CH_3 groups have a repulsion potential of about 3 K cal/mole. On the other hand the very exact measurements of the heats of combustion of the nine isomeric heptanes established by the Bureau of Standards give nearly constant energies. There are some small deviations which might indicate a slight attraction between two CH_3 groups bound to the same carbon atom, but not a repulsion,[24] although the carbon atoms are only 2.5A distant. From this result we recognize very distinctly that the potential of two CH_3 groups depends, as is to be expected, not only on their distance, but also on their orientation. Therefore the diameter of the sphere of action of a CH_3 group is not the same in all directions. The shape will be very irregular, but will have approximately rotational symmetry around the direction of the C–CH_3 bond. The following form of the sphere of action, see Fig. 3a and b, may explain that we have no marked repulsion for two CH_3 groups bound on the same carbon atom, but a strong one in o-xylene. The greatest diameter perpendicular to the direction of the fourth valence may be taken from Lonsdale's data for the crystal structure of hexamethylbenzene. She finds for the closest distance, to which two CH_3 groups in different molecules can approach each

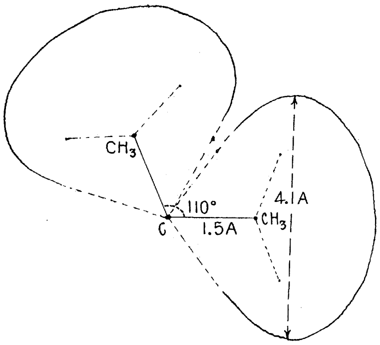

Fig. 3a.

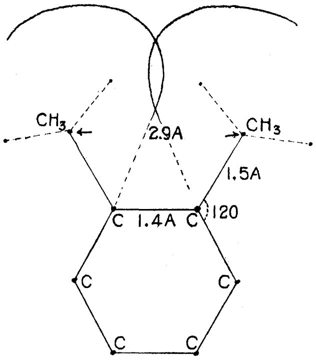

Fig. 3b.

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[23] H. A. Stuart, Phys. Zeits. **32** (1931) in press.

[24] As an alternative to the assumption of zero repulsion, we should have to assume that any possible changes in the internal potentials of adjacent CH_3 groups are just compensated by bond energy changes resulting from the replacement of C-H by C-C bonds. That such compensation exists in all nine isomers with their different configurations is, of course, highly improbable.

other, 4.1A.[25] The greatest radius of the group taken from the C-atom as the center will probably be in the direction of the C–H bonds. We see that for o-xylene the spheres of action overlap each other.

Finally we will discuss the most stable positions of saturated hydrocarbons and of the ether molecule, using the fact that two CH_3 groups in o-xylene have a repulsive potential of about 3 K cal. In the butane molecule where the valence angles are 110° (tetrahedron angle of the quadrivalent carbon atom), we have rotation of the last CH_3 group around the C–C bond. In position II the distance of the two carbon atoms is only 2.6A, so we must have a greater repulsive potential than that in o-xylene, where the distance is 2.9A, or more, and the potential amounts to 3 K cal. As this energy is much greater than the energy of the temperature motion, *KT* about 600 cal at room temperature, it follows that position II is impossible.[26] In position I (180°) we certainly have no repulsion, perhaps a little attraction, so we probably have at room temperature torsional vibrations with great amplitudes around position I. We may therefore expect for the saturated hydrocarbons also in the gaseous state a tendency towards zigzag chains, as they are observed in liquids and crystals. Nevertheless it is possible that we will find for long chains something like a closed form which, of course, is oriented very far from a planar configuration, especially if the chain has large dipoles on its ends.

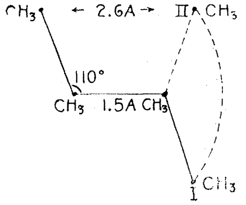

Fig. 4.

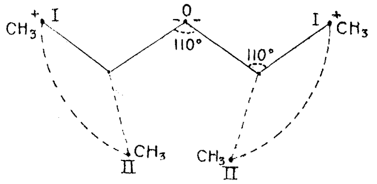

Fig. 5.

Let us consider now the ether molecule, see Fig. 5. We assume as usual 110° for the valence angle of the oxygen atom. We recognize then that position II is absolutely impossible as we have here an enormous steric hindrance, the distance of the carbon atoms of the CH_3 groups being only 1.7A. If at the same time we turn both CH_3 groups through 90°, the distance is still 3.2

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[25] This diameter is very reasonable, as with a smaller one, about 3.4A, we could not understand the repulsion in o-xylene

[26] A rotation through 90° to 120° from position II will be sufficient to avoid the repulsive forces as the distance is 3.0A for 60° and 3.5A for 120°.

to 3.3 and becomes, at about 110°, 3.5A, where the repulsion disappears. A configuration with one group in II, the other in I, also seems to be impossible as we have then a repulsive potential similar to that in butane (distance C–C 2.5A). On the other hand, position I is, on account of the dipole attraction, energy approximately equal to $\frac{1}{2}KT$, the most stable one, so that we have in the ether molecule rotation vibrations of about 70° around position I. This is in excellent agreement with results derived by the author from discussions of electric moments in homologous series[27] and from observations of the Kerr constant[28] of the ether molecule, which show directly that position I is the most stable one.

If we had more and, what is of even greater importance, more exact data for the heats of combustion of other isomeric compounds, such as the CH_3 and Cl derivatives of methane, ethane, ethylene, benzene, etc., we should be able to draw very precise conclusions regarding the internal potential of the substituent groups as a function of the distance and the orientation and also as to the mutual influence of the bond energies. This paper may be considered as a first attempt to employ heats of combustion in answering questions as to the free rotation and the stable configuration of groups in an organic molecule.

In conclusion the author wishes to express his thanks to Professor Lewis for his hospitality, and to Professor Pauling, and the other members of the University of California with whom he has had the privilege of discussing this problem.

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[27] H. A. Stuart, Phys. Zeits. **31,** 81 (1930).

[28] H. A. Stuart, Zeits. f. Physik **63,** 533 (1930).