BOND ENERGIES AND BOND LENGTHS

ON March 9 the Royal Society, with the president, Sir Robert Robinson, in the chair, held a discussion on the subject of bond energies and bond lengths. The meeting was opened by Prof. M. G. Evans, and then followed ten papers on various aspects of the subject, both experimental and theoretical. The greater part of the day's discussion was devoted to the measurement and interpretation of bond dissociation energies and interatomic distances in molecules; but several points of interest also arose in connexion with dipole moments and force constants, which are intimately bound up with bond strengths in a manner not yet fully understood.

In his introductory remarks Prof. Evans suggested a classification of bond properties into those mainly associated with σ -electrons and those mainly associated with π -electrons. The first five contributions to the discussion were concerned principally with σ -bonds, and the last five with σ - π -bonds. The length of a bond is a quantity of unambiguous interpretation, but the concept of bond energy requires some clarification. The thermochemical heat of formation of a compound from the elements in standard states is a measurable quantity, and so is the heat of formation of a molecule or radical from its atoms in specified states; but as a rule the heat of formation cannot be partitioned among the various bonds in any unique manner. For example, the energy to be associated with the O—O bond in hydrogen peroxide is found to be 33 or 52 Cal./mole according as the O—H bond energy is calculated from the heat of formation of water or from that of the hydroxyl radical. Prof. Evans suggested that the dissociation energy of a bond—that is, the energy required to rupture the bond in a given molecule—was a more satisfactory concept because bond dissociation energies are directly measurable and can be expressed entirely in terms of the heats of formation of atoms, molecules and radicals. There is no reason why the dissociation energies of similar bonds in different molecules should be equal; indeed, differences in dissociation energy between bonds of the same kind in different molecules give valuable information about resonance energies and promotion energies in the various molecules or atoms concerned. With regard to promotion energies, Prof. Evans cited the fact that the energies required to remove successive methyl groups from mercury dimethyl are 50 and 8 Cal. respectively; the smallness of the latter figure is almost certainly due to the loss of energy by the resulting mercury atom as it falls from the divalent triplet-state to the normal ground-state. Coming to the more difficult question of the relation between bond strength and the atomic numbers of the atoms concerned, Prof. Evans outlined briefly the theory of ionic-homopolar resonance and described how it had been applied to the mechanical properties of bonds. He felt that, in spite of its comparative successes, the theory needed drastic revision, and said that this question would be dealt with more fully by later speakers. But the concepts of the theory have such a widespread application that it may be possible to re-interpret the theory in new and more fundamental terms.

The next speaker, Dr. M. Szwarc, described the experimental methods which have been used for

measuring bond dissociation energies and the heats of formation of radicals. It is possible in principle to measure either the energy of combination of two radicals to form a molecule, or the energy of the reverse reaction. The former method has been applied to the combination of hydrogen atoms and the combination of oxygen atoms, but is not generally a practicable method. However, the unimolecular dissociation of a molecule into two radicals can be conveniently studied by a number of methods, including electron bombardment, photodissociation and thermal decomposition. It can be shown that in cases of interest the activation energy for the thermal decomposition is identical with the dissociation energy of the ruptured bond, so that bond dissociation energies can be determined from the measured activation energies of unimolecular dissociations. The principal kinetic problem is to eliminate the radicals formed in the decomposition, since these may recombine or initiate chain reactions and thus make the overall kinetics of the reaction very difficult to unravel. This problem is solved by using toluene as a carrier gas; it is found that many radicals react instantly with toluene, according to the equation:

and the resulting benzyl radicals survive long enough to escape from the zone of reaction, eventually forming dibenzyl. Thus the rate of the unimolecular decomposition $\text{R}_1\text{R}_2 \rightarrow \text{R}_1\cdot + \text{R}_2\cdot$ can be measured by the rate of formation of either R_1H , R_2H or dibenzyl. This technique has been used for measuring the heats of the following bond dissociations:

- (1) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\cdot + \text{CH}_3\cdot$ (77.5 Cal./mole)
- (2) $\text{C}_6\text{H}_5\text{CH}_2\text{Br} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\cdot + \text{Br}\cdot$ (63 " " ")
- (3) $\text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\cdot + \text{H}\cdot$ (50.5 " " ")
- (4) $\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_2\cdot$ (60 " " ")

In the first three of these reactions the heats of formation of the species concerned, except the benzyl radical, are all known from other sources. Therefore, the heat of formation of the benzyl radical can be calculated from any one of the three bond dissociation energies, and the concordance of the results provides a valuable cross-check on the measured bond dissociation energies. Dr. Szwarc concluded by describing briefly a modification of the same method, by which it is possible to determine the influence of substituents on bond dissociation energies, for reactions in which the frequency factor has a constant value.

In reply to a question by Sir Robert Robinson, Dr. Szwarc described the precautions which had been taken in analysing the products, so that no important side-reactions should escape detection.

The next paper, entitled "Factors affecting Bond Strengths", was read by Dr. A. D. Walsh, who discussed the concept of electronegativity, its experimental definition and its theoretical significance. Intuitively speaking, electronegativity is a quantity which should decrease on passing down the Periodic Table, and increase with group number within any period of the Table. Pauling's definition of electronegativity, based on thermochemical relationships,

satisfies these requirements, but has little obvious connexion with electrical quantities; whereas Mulliken's definition of electronegativity, as the sum of the ionization potential I and electron-affinity E , is in many cases incapable of experimental utilization. Dr. Walsh suggested that the stretching-force constant of the $A-H$ bond might provide a suitable measure of the electronegativity of element A . Since the electronegativity is also related to the ionization potential, there should be a smooth relationship between $k(A-H)$ and $I(A)$, and indeed the relation $k(A-H) \propto I^2(A)$ is found to hold with fair accuracy for some thirty-five diatomic hydrides. For bonds of the type $A-B$, where neither A nor B is hydrogen, there is a linear dependence of $k(A-B)$ on $I(A)$ as A varies within a vertical group of the Periodic Table; but certain anomalies show that repulsion between lone pairs on A and B must have an important effect on the $A-B$ force constant. In polyatomic molecules the electronegativity of a multivalent atom must be dependent on its state of hybridization; and Dr. Walsh suggested that the small differences in $C-H$ force constant between methane, ethylene and acetylene were due to this effect. Summing up his remarks, Dr. Walsh said that any theory of the factors affecting bond strength must comprehend the striking relationships which are observed between force constants and ionization potentials, and that there seemed to be good experimental grounds for connecting the electronegativity of an element with the force constant of its bond to hydrogen.

Commenting on Dr. Walsh's paper, Dr. J. W. Linnett agreed to the value of any attempt at an improved definition of electronegativity. However, in correlating force constants with ionization potentials, the same difficulty arises as in applying Mulliken's definition of electronegativity, namely, that it is not possible to measure directly the ionization energy of the appropriate valence state; a correction should really be applied to take account of the change in multiplicity accompanying the ionization. Dr. Linnett went on to give an illuminating pictorial sketch of the way in which the valence state of a carbon atom will govern the strength or force constant of a $C-H$ bond.

Dr. H. A. Skinner asked whether the apparent anomalies observed by Dr. Walsh in bonds between atoms having unshared electron pairs are, in fact, real; such atoms would have comparatively large electron affinities, and the electron affinity would play as large a part as the ionization potential in determining the electronegativity, as indicated by Mulliken's definition. The anomalies might be largely due to neglect of these electron-affinity terms.

The next speaker, Dr. E. Warhurst, discussed ionic character in bonds and its relation to bond lengths and other properties. As he pointed out, the theory of ionic-covalent resonance in single bonds involves assumptions which are incapable of proof from first principles and rests largely on the successful interpretation of various experimental results. The phenomena to which the theory has been successfully applied include: ionic resonance energies, as discussed by Pauling in terms of the electronegativity concept; the dipole moments of simple halides and hydrides, studied by Wall, Baughan, Evans, Polanyi and Fairbrother; bond contractions relative to the covalent radius sum (Warhurst); and the dependence of force constants upon the dielectric constant of the environment. However, the assumptions involved

in the theory are in many cases open to severe objection; for example, it is necessary to assume that the deviations from charge symmetry in the bond arise entirely from the ionic part of the wave function, whereas contributions to the total bond-moment will, in fact, arise also from the covalent part of the wave function in a heteronuclear molecule. Further, there is considerable uncertainty in the matrix elements occurring in the secular equation and their variation with internuclear distance; and, although simple assumptions about these quantities lead to reasonable agreement with experiment, the theoretical basis of such assumptions is by no means clear. Dr. Warhurst ended with the hope that it would be possible to reformulate the theory of ionic-covalent resonance in such a way that its successes can be more easily understood in terms of fundamental physical principles.

Commenting on Dr. Warhurst's paper, Prof. E. B. Wilson stressed the grave difficulties accompanying the calculation of dipole moments from first principles; the homopolar (covalent) contribution to the dipole moment of a bond is an exceedingly sensitive function of the form of the atomic orbitals and the extent to which they are supposed to overlap. Indeed, it is surprising that any simple theory should give even a semi-quantitative account of observed bond-moments, and discrepancies should not be taken too seriously.

The next contribution was a paper, by T. L. Cottrell and Dr. L. E. Sutton, entitled "Covalency, Electrovalency and Electronegativity". Dr. Sutton described calculations that have been made on a number of idealized molecules, with the view of obtaining a clearer understanding of the dependence of bond strength on nuclear charge in diatomic molecules. The Heitler-London-Sugiura treatment has been extended to electron-pair bonds between nuclei the charges of which are greater or less than that of an electron and may or may not be equal. It is found that transfer of positive charge between initially equal nuclei leads to an increase in the purely covalent part of the binding energy, this effect being largely due to the decreased internuclear repulsion, and independent of any ionic character in the bond. These results make it possible to reconcile Pauling's adjacent charge rule with Gordy's rule connecting electronegativities and bond strength. They also clarify the basis of Pauling's electronegativity scale, and justify Walsh's views concerning polarity and bond strength. As Mr. Cottrell said in the succeeding discussion, "Perhaps the most interesting result of our calculations on model systems is that the covalent energy for heteronuclear molecules is much greater than that given by the geometric or arithmetic mean rule. This means that calculations on covalent-ionic resonance, assuming the geometric mean rule, may not be valid if it is considered that the covalent bond is described by a Heitler-London wave function."

The last paper in the 'mainly sigma' part of the discussion was read by Prof. C. A. Coulson, who gave a critical survey of the method of ionic-homopolar resonance and a statement of the present theoretical position. In order to use the method in a quantitative manner, it is necessary to know the energies to be associated with the covalent and ionic parts of the wave function and the covalent-ionic exchange integral. Three main difficulties of principle appear in the conventional treatment: first, there seems to be no clear justification for the use of a mean rule in calculating the covalent energy term; secondly, it is

uncertain whether the same atomic orbitals are appropriate both for the covalent and ionic parts of the wave function; and thirdly, whatever the best atomic orbitals may be, the bond properties will depend profoundly on the degree of hybridization of these orbitals. Hybridization determines the covalent radius of the atoms forming the bond, the covalent energy term and the charge distribution, especially that part of the dipole moment associated with atomic lone pairs. These difficulties are all repeated in polyatomic molecules, with the added complications of bond delocalization, an interdependence of the ionic character of adjacent bonds, and the possibility of 'bent bonds' being formed in certain cases. The case of water has been worked out in some detail (H. H. Greenwood and U. Danielsson). Working backwards from the observed valence angle and dipole moment, and allowing for a homopolar dipole due to the difference in size between a hydrogen atom and an oxygen, it is found that the individual hydroxyl bonds have dipole moments in the opposite sense from the molecular dipole moment, which arises almost entirely from the unshared electrons of the oxygen, and scarcely at all from any ionic character in the bonds themselves. Prof. Coulson suggested possible lines for future work, including the study of pairing schemes, the theoretical evaluation of covalent bond energies, the relation between hybridization and ionic resonance, the conditions favouring *p*- and *d*-hybridization, and a study of the repulsions between valence-shell and inner electrons, which often play an important part in determining bond lengths and force constants.

The second part of the discussion, on σ - π -bonds, was opened by Sir John Lennard-Jones. He traced the concept of the π -bond from the early days when it was introduced to account for the paramagnetism of the oxygen molecule and the torsional rigidity of the ethylene molecule, and reviewed briefly its application to unsaturated organic molecules. Within the framework of molecular orbital theory, the idea of delocalized π -electrons has been very fruitful; it has been possible to make extensive calculations of resonance energies and bond lengths, assuming that the so-called 'resonance integral' between adjacent atomic orbitals is a simple function of the distance between the atoms concerned. The strict calculation of bond lengths in unsaturated molecules involves the technique of successive approximations, since there is a cyclic dependence between energy, resonance integrals and bond lengths. However, Coulson's definition of bond order provides a very convenient technique for the calculation of equilibrium bond lengths, since to a good approximation there should be a smooth relation between bond order, as usually calculated, and bond length; and Coulson's bond-order/bond-length curve has been successfully used for predicting carbon-carbon bond lengths in many unsaturated hydrocarbon molecules. More recently the theory has been developed to deal with the chemical reactions of conjugated molecules, with promising results. In hydrocarbon ions such as the benzyl cation or anion, the electron defect or excess can be shown to be associated with alternate atoms in the system, in agreement with the qualitative resonance theory; and such results point the way to a simple semi-quantitative molecular orbital theory of organic reactivity. The implications of these ideas were still being worked out, and would be discussed in the last paper of the afternoon. In conclusion, Sir John expressed the view that we now

had an inherently sound theory of the various factors affecting bond lengths in conjugated hydrocarbons and reactivities in simple heteromolecules; but, as would emerge from the next few papers, there were still a few discrepancies which had not yet been resolved, and it remained to be seen how far the theory of bond lengths would be capable of extension to molecules other than aromatic hydrocarbons. In such molecules molecular orbital theory is no longer strictly self-consistent and may require modification in order to overcome this difficulty.

Prof. J. M. Robertson then read a paper on the X-ray measurement of bond lengths in planar aromatic hydrocarbons. Such hydrocarbons may be classified according to their crystal structures into two fairly distinct types. The first class includes pyrene $C_{16}H_{10}$, dibenzanthracene $C_{22}H_{14}$, coronene $C_{24}H_{12}$ and ovalene $C_{32}H_{14}$. These molecules tend to stack in columns, the molecules in each column lying at about 45° to the symmetry plane of the crystal; and their structures may be obtained with considerable accuracy by calculating electron-density projections on the symmetry plane. In Prof. Robertson's opinion, the measured bond lengths for pyrene are probably accurate to about 0.03 Å., the observed variations being from 1.39 to 1.45 Å. Comparison of the experimental lengths with those calculated by Coulson gives an average discrepancy of 0.022 Å., which is less than the estimated experimental error. For coronene and ovalene the resolution is better, and the estimated experimental error is only 0.01–0.02 Å. In both these cases the average discrepancy between theory and experiment is 0.013 Å., which is quite as satisfactory as can be expected. The second class of molecule studied includes naphthalene and anthracene, in which the molecules are more steeply inclined to the symmetry plane of the crystal. Here it is necessary to make a comprehensive three-dimensional analysis, which gives values for the bond lengths correct to 0.01 Å. or better. There are some discrepancies with theory which appear simply to involve an error of scale, but apart from these the central bond in naphthalene does appear to be appreciably longer than theoretical calculations suggest. Nevertheless, Prof. Robertson felt that, on the whole, the agreement between theory and experiment was extremely satisfactory and amply justified the large amount of work which had been expended on these structures.

The next contribution to the discussion was from Prof. E. G. Cox and Dr. G. A. Jeffrey, who discussed bond-order/bond-length relationships in conjugated heteronuclear molecules. The theoretical calculation of bond lengths in such molecules requires the knowledge of certain energy parameters the values of which would determine the bond orders; the bond length would then presumably be a smooth function of bond order, as in the unsaturated hydrocarbons. A most important step, therefore, in the theoretical interpretation of bond lengths is the construction of reliable bond-order/bond-length curves for as many atom pairs as possible. The minimum requirements for such a curve are (1) the length of a pure single bond, (2) the length of a pure double bond, and (3) the length and order of some intermediate bond. Prof. Cox considered in turn carbon-nitrogen, carbon-sulphur and carbon-oxygen bonds, for which most experimental data are available. The C–N single-bond length is known to be 1.47 Å., and 1.27 Å. is a plausible length for the C=N double bond. Pyrrole and pyridine provide intermediate points; and,

although they are not consistent, suggesting that the electron-diffraction data on pyrrole are unreliable, the general trend of the curve is reasonably certain. It is interesting that the carbon-nitrogen bond length is not as sensitive to hybridization as might have been expected, and also that a surprisingly large number of carbon-nitrogen bonds lie in a narrow range corresponding to bond orders of 1.5-1.8. Prof. Cox suggested that cyclic molecules such as melamine might well repay further theoretical study. Bonds between carbon and sulphur have been less completely studied. The single-bond length is 1.81 Å, but the double-bond length is much less certain (? 1.63 Å). The only satisfactory intermediate point is derived from recent experimental and theoretical studies on thiophene (Cox, Gillot and Jeffrey; Evans and de Heer; and Longuet-Higgins). The excellent agreement between theory and experiment for the carbon-carbon bonds in this molecule suggests that for the carbon-sulphur bonds the calculated orders and observed lengths probably provide the most reliable intermediate points available. The situation with regard to carbon-oxygen bonds is unsatisfactory, and urgently demands both experimental and theoretical attention. Dr. Jeffrey mentioned barbituric acid and diketopiperazine as worthy candidates for theoretical study in the future.

A general survey of bond length calculations in conjugated molecules was then given by Prof. Coulson. As he explained, in molecules containing σ - π -bonds it is always assumed that the σ - and π -electrons may be treated separately. The σ -electrons are supposed to be localized, and the energy and wave function of the π -electrons are then obtained either by the valence bond method or by the method of molecular orbitals, in terms of exchange or resonance integrals. Except for simple molecules, it is not practicable to calculate the equilibrium lengths by minimizing the energy with respect to variations in bond length, and one has to fall back on the concept of fractional bond order, which should be smoothly related to bond length. Robertson's accurate work on naphthalene and anthracene shows that this idea is sound, but there are small discrepancies which may be removed by further refinements in the theory. Such refinements present certain difficulties: for example, it is not known to what extent hybridization will affect bond lengths, and in hetero-molecules a self-consistent field approach may be necessary; but certain improvements can undoubtedly be made in bond-length calculations. These improvements include: making allowance for bond-length changes due to repulsion between neighbouring net charges and to mutual polarization of the atoms; allowing for variations in resonance integral due to inequalities of bond length, and obtaining a consistent set of such integrals by iteration; and investigating the effects of interaction between different electronic configurations. All these improvements have been applied to naphthalene and have corrected the simple calculations by about 0.005 Å. each. It would therefore be impossible at present, without very detailed study, to predict lengths to better than about 0.015 Å. in hydrocarbons or 0.03 Å. in other kinds of molecule.

The last paper in the discussion, read by Dr. H. C. Longuet-Higgins, was entitled "The Influence of Conjugation on Ionic Dissociation Energies". Dr. Longuet-Higgins considered the ionization of hetero-aromatic amines of the type of the amino-quinolines. By a combination of molecular orbital theory and

first-order perturbation theory, it can be shown that the ionization energy of such an amine is linearly related to the π -electron density at the appropriate position in the iso-electronic hydrocarbon. For amines of the type under consideration, the iso-electronic hydrocarbon would be a carbanion, with π -electron densities equal to $1 + c_r^2$, where c_1, c_2 , etc., are the atomic orbital coefficients in a non-bonding molecular orbital. The values of these coefficients can be written down by inspection, and so it is possible to find the required electron densities in a very simple manner. It is found that the charge excess in the carbanions is invariably distributed over alternate atoms only, so that the π -electron densities would be alternately greater than and equal to unity throughout the molecule. Although no direct experimental data are available on heats of ionization, an approximately linear relation is found to hold between the calculated electron densities and the measured free energy of ionization (Albert, Goldacre and Phillips) for forty-one amines belonging to thirteen different heteroaromatic systems. Among the available data a few anomalies are observed, but these are without exception molecules in which the amino group is ortho or peri with respect to the nuclear nitrogen atom. The agreement between theory and experiment is surprisingly good, considering the drastic assumptions of the theory and the fact that solvent and entropy effects are not allowed for. This agreement seems to substantiate the view that the π -electron system plays a predominant part in determining the tendency of such bases to accept a proton; and there is hope that similar elementary calculations will be successful also in other fields of physical organic chemistry.

Summing up the day's discussion, Prof. Evans said he felt that it had succeeded in bringing together many important lines of research into bond properties and their theoretical interpretation. The work of Szwarc and others showed more clearly than ever the importance of radical resonance energies and the valence-state energies of atoms in determining bond dissociation energies. The calculations of Cottrell and Sutton, and the empirical rules enunciated by Walsh, made it clear that the concept of electronegativity is still a fruitful one, although its precise significance is still open to discussion. Warhurst's work showed that the same is true of the theory of ionic-covalent resonance, although, as pointed out by Coulson, orbital hybridization might invalidate the approximations of the theory, especially as applied to dipole moment calculations. On the subject of bond lengths, Prof. Evans agreed with Sir John Lennard-Jones that we now seemed to have an essentially sound theory of the lengths of σ - π -bonds, at any rate in aromatic hydrocarbons. It was gratifying that Coulson's refined calculations on naphthalene justified so happily the neglect of configurational interaction in the more naive theory of bond order and bond length; very few people would complain of an inaccuracy of as little as 0.015 Å. in *a priori* bond-length calculations. As Prof. Coulson had explained, there might be particular difficulties associated with the calculation of bond lengths in molecules containing heteroatoms; but the success which had attended recent studies on thiophene seems to justify an attitude of cautious optimism. It seemed that we were gradually obtaining a quantitative theory of the chemistry of hetero-molecules, and might hope to achieve also before long a better understanding of their physical properties.

H. C. LONGUET-HIGGINS