# The Nature of the Chemical Bond. VI. The Calculation from Thermochemical Data of the Energy of Resonance of Molecules Among Several Electronic Structures[1]

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In the first part of this paper there is given a set of bond-energy values for single, double, and triple bonds between atoms, obtained from thermochemical data, such that the total energy of formation from separate atoms of a molecule containing given bonds is equal to the sum of the energies for those bonds. In the derivation of these values data were used only for molecules for which it is probable that one electronic structure, corresponding to one distribution of valence bonds, represents the normal state to a satisfactory degree of approximation. For other molecules more than one electronic structure of this type contributes essentially to the normal state, the energy of formation of the molecule then being larger than that for any one of the contributing structures. On comparing the energies of formation given by thermochemical data with the values calculated for various structures, it is verified that this difference is always positive or zero (to within the limits of error involved). The difference in energy is interpreted as the resonance energy of the molecule among several electronic structures, and its existence in a given case provides strong evidence that more than one structure is contributing to the normal state of the molecule, the number and importance of the contributing structures being indicated by the magnitude of the resonance energy. In this way the existence of resonance is shown for many molecules, and values found for the resonance energy are tabulated. The substances discussed include carbon dioxide, carbon disulfide, alkyl isocyanates, carboxylic acids and esters, aliphatic amines, carbonic esters, urea and related substances, benzene and benzene derivatives, naphthalene and other condensed ring systems, pyridine and related heterocyclic compounds, biphenyl, fluorene, phenylethylene, dihydronaphthalene, quinone, some ureides and purines, etc.

## INTRODUCTION

IT has been recently recognized that molecules can be divided roughly into two classes, the first comprising those for which the normal electronic state can be reasonably well approximated by an eigenfunction corresponding to a single electronic structure of the Lewis type; that is, to a single distribution of valence bonds, and the second those for which the normal electronic state can be satisfactorily represented only by a linear combination of several such eigenfunctions. A molecule belonging to this second class is said to resonate among the corresponding electronic structures. Information as to the classification of a given molecule may be obtained from the consideration of theoretical or empirical energy curves,[2] from the comparison of observed interatomic distances with the sum of atomic radii,[3] and in other ways. In particular the comparison of the energy of the molecule with the

values corresponding to various electronic structures should provide a valuable criterion, inasmuch as the energy of the normal molecule must be equal to or less than the energy for any electronic structure. If more than one of the reasonable electronic structures for a molecule correspond to nearly the same energy value, which is somewhat higher than the actual energy of the molecule, the difference in energy may be confidently interpreted as the resonance energy of the molecule among these electronic structures. Assuming that the total energy of formation of a nonresonating molecule from separated atoms may be represented as the sum of bond energies, we in this work have calculated values of the energies of various single, double, and triple bonds from thermochemical data. With the use of these we have then predicted energies for various electronic structures for other molecules, and have in this way shown the existence of resonance and have calculated values of the resonance energy for a large number of substances, including in particular carboxylic acids, amides, and other compounds with a resonating

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[1] The fifth paper of this series appeared in J. Chem. Phys. 1, 362 (1933).

[2] L. Pauling, J. Am. Chem. Soc. 54, 988 (1932).

[3] L. Pauling, Proc. Nat. Acad. Sci. 18, 293, 498 (1932).

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double bond, aromatic hydrocarbons and their derivatives, heterocyclic compounds, etc.

It has been pointed out[4] that bonds between non-identical atoms may be considered to resonate between a covalent and an ionic structure, the bond in this way having partially covalent and partially ionic character. The resonance energy of this effect, which is usually essentially the same for a given bond in different molecules, is included in the values given for the bond energies in the nonresonating molecules discussed.

Although much of the body of thermochemical data which we use has been available for a long time, and many attempts at interpreting it by the introduction of the concept of bond energies have been made, the derivation of a satisfactory set of essentially constant bond energies was not made earlier because the necessity of using a restricted class of molecules was not recognized. It remained for the quantum mechanics to indicate the possibility of resonance of some molecules among several structures corresponding to different distributions of valence bonds, with a consequent change in total energy, and to suggest the determination of bond energies by the consideration of only those molecules for which a single electronic structure can be written with considerable confidence.

## BOND ENERGIES IN MOLECULES REPRESENTED BY A SINGLE ELECTRONIC STRUCTURE

In formulating a set of bond-energy values we first calculated the energies of formation of molecules from experimental values of the heats of combustion of the compounds[5] and thermochemical data pertaining to the products of combustion—carbon dioxide, water, nitrogen, etc. The same values for the latter quantities were used as previously.[4]

Throughout this paper the unit of energy is the volt-electron (1 v.e. = 23.054 kcal.). The symbol A−B denotes a single bond between the atoms A and B, A=B a double bond, etc. The letter $E$ represents the heat of formation of the gaseous substance at 25°C from widely

separated atoms, the energy of the substance (except for small $pv$ terms) being equal to $-E$.

In a previous discussion[4] it was pointed out that there is some arbitrariness in the choice of bond energies, arising from uncertainty in the experimental data, lack of constancy of bond energies from compound to compound, and other causes. Because of differences in the data used and their treatment, the values given in that paper and the present one differ somewhat; the difference in no case exceeds 0.1 v.e., however, which is of the order of magnitude of the errors inherent in the data.

The bond-energy values obtained in this way[6] are given in Table I. It is noteworthy that the

TABLE I. *Bond energies.*

| Bond | Energy | Source |
|------|--------|--------|
| C−H | 4.323 v.e. | Methane |
| N−H | 3.895 | Ammonia |
| O−H | 4.747 | Water |
| C−C | 3.65 | Paraffins |
| C=C | 6.56 | Olefins and Cyclic Compounds |
| C≡C | 8.61 | Acetylene Hydrocarbons |
| N−N | 1.44 | Reference 4 |
| C−O | 3.47 | Aliphatic Primary Alcohols |
|  | 3.59 | Aliphatic Ethers |
| C=O | 7.20 | Formaldehyde |
|  | 7.56 | Other Aldehydes |
|  | 7.71 | Ketones |
| C−N | 2.95 | Amines |
| C=N | 5.75 | Estimated Value |
| C≡N | 8.75 | Hydrogen Cyanide |
|  | 9.07 | Aliphatic Cyanides |
| C−S | 2.92 | Mercaptans and Thio-ethers |
| C=S | 5.60 | Estimated Value |

energy of a given bond may in some cases change somewhat from one compound to another of different type; thus the C=O bond energy is considerably changed as hydrogen attached to the carbon atom under consideration is replaced by aliphatic radicals. This effect is probably due in the main to interactions of bonds from the same atom, inasmuch as it is especially pronounced for bonds (such as C−O, C=O, C≡N) with which large electric dipole moments are associated. In default of a thorough understanding of the phenomenon, we have contented ourselves with using for each substance values of bond energies obtained from substances resembling it.

[4] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[5] The heats of combustion used were taken from Kharasch's compilation (Bur. Standards J. Research **2**, 359 (1929)) or from Landolt-Börnstein Tables.

[6] The detailed discussion of the derivation of these values is omitted for the sake of brevity.

The surprisingly large value of the C=O bond is no doubt associated with the possibility of writing for $R_2CO$ the structure $R_2 = \overset{+}{C} : \overset{..}{O} : \overset{-}{}$ as

well as $R_2 = C :: \overset{..}{O} :$, the former "semipolar" structure contributing an appreciable resonance energy. The magnitude of this contribution might be especially easily influenced by adjacent groups, the presence of hydrogen attached to the carbon atom having a pronounced effect in inhibiting it.

## RESONANCE ENERGIES OF CARBON DIOXIDE, ALKYL ISOCYANATES, ETC.

In calculating the resonance energy of a molecule, we write for the molecule the electronic structure corresponding to the usually accepted distribution of valence bonds, and calculate the corresponding value of $E'$ by summing the bond energies, using values from similar compounds in case more than one bond energy is given in Table I. The difference between the experimental value of $E$ and the calculated value of $E'$ is interpreted as resonance energy resulting from contributions of other electronic structures to the normal state of the molecule. This treatment is applicable at present only to molecules for which stable structures can be written involving neutral atoms only; compounds such as $HN_3$, with the structure $H : \overset{..}{N} :: \overset{+}{N} :: \overset{..}{N} : \overset{-}{}$ making the largest contribution to the normal state, cannot be discussed until methods are developed for evaluating the energies of partially ionic bonds.

Evidence from interatomic distances[3] has shown the existence of resonance in CO, $CO_2$, $CS_2$, RNCO, and many other simple molecules. This is supported by the consideration of the energy of these molecules. The value of $E$ for CO is 11.30 v.e., 3.59 v.e. greater than the ketone value for C=O. This very large difference has already been accounted for[3] as resulting from the great stability of the structure $: \overset{-}{C} ::: \overset{+}{O} :$, whose contribution to the eigenfunction for the normal state is even larger than that of $: C :: \overset{..}{O} :$.

Carbon dioxide, with $E = 16.79$ v.e., has a resonance energy of 1.37 v.e. relative to the structure $: \overset{..}{O} = C = \overset{..}{O} :$, with the ketone C=O value. This large resonance energy is due to the structures $: \overset{+}{O} ::: C : \overset{..}{O} : \overset{-}{}$ and $: \overset{..}{O} : \overset{-}{C} ::: \overset{+}{O} :$, direct evidence for which is provided by the observed interatomic distances. The molecules SCO, with $E = 14.55$ v.e., and $CS_2$, with $E = 12.46$ v.e., have resonance energies of 0.84 v.e. and 0.46 v.e., respectively.

The values $E = 29.64$ v.e. for methyl isocyanate and $E = 41.99$ v.e. for ethyl isocyanate correspond to resonance energies of 0.26 v.e. and 0.31 v.e., respectively, relative to the structure $R : \overset{..}{N} = C = \overset{..}{O} :$. The other structures contributing to the normal state are no doubt the same as in $CO_2$. Methyl isothiocyanate, $CH_3NCS$, with $E = 28.10$ v.e., has a resonance energy of 0.43 v.e.

The value $E = 20.01$ v.e. for cyanamide leads to a resonance energy of 0.20 v.e. relative to the structure $H_2N - C \equiv N :$, which is without doubt due to resonance with $H_2\overset{+}{N} = C = \overset{..}{N} : \overset{-}{}$.

It should be emphasized that the resonance energies calculated by the use of bond energies such as C=O from ketones do not include the energy of resonance between $C :: \overset{..}{O} :$ and $\overset{+}{C} : \overset{..}{O} : \overset{-}{}$. For example, if we were to assign to

$C :: \overset{..}{O} :$, that is, the normal covalent carbon-oxygen double bond, the estimated bond energy 6.60 v.e., then the ketones would show a resonance energy of 1.11 v.e. arising from the $R_2 = \overset{+}{C} : \overset{..}{O} : \overset{-}{}$ structure, and carbon dioxide a total resonance energy of 3.59 v.e. The procedure of using ketone C=O, etc., bond energies rather than the normal covalent energies has been adopted for two reasons. First, there is no satisfactory way of determining the value of $C :: \overset{..}{O} :$, for in no molecule is resonance to $\overset{+}{C} : \overset{..}{O} : \overset{-}{}$ prohibited. Second, since in every molecule con-

taining $C=O$ there is resonance between $\overset{..}{C::O:}$ and $\overset{+}{C}:\overset{..}{O}:\overset{-}{,}$, it must always be considered in interpreting the total resonance energy, and this is most easily done by simply using a $C=O$ bond energy which already includes this resonance energy.

## RESONANCE ENERGIES OF ALIPHATIC ACIDS, ESTERS, AMIDES, AND RELATED COMPOUNDS

### Carboxylic acids and esters

Data for acetic acid and eight other monobasic acids lead to a value of 1.20 v.e. for the resonance energy of the carboxyl group relative to the structure $R-C\overset{\displaystyle OH}{\diagdown\!\!\!\diagup_{\displaystyle O}}$ , with the use of the ketone value for $C=O$. Data for eight dibasic carboxylic acids lead to the value 1.19 v.e. per carboxyl group, in excellent agreement with the monobasic acid value.

In the carboxylic anions there is complete degeneracy between the structures $R-C\overset{\displaystyle O^-}{\diagup\!\!\!\diagdown_{\displaystyle O}}$

and $R-C\overset{\displaystyle O}{\diagup\!\!\!\diagdown_{\displaystyle O^-}}$ , so that appreciable energy of resonance between these two structures may well be expected. We have not obtained any empirical data for these ions. The extent to which the resonance is inhibited by attaching hydrogen to one of the two previously equivalent oxygen atoms cannot be predicted. Our value of 1.20 v.e. for the resonance energy in the carboxylic acids is a lower limit for the resonance energy in the corresponding anions.

It is to be expected from chemical evidence that the replacement of hydrogen by an aliphatic radical would have some further inhibiting effect on the carboxyl resonance. It is found, however, that to within the experimental error of about 0.2 v.e. the resonance energy is the same for methyl and ethyl esters as for carboxylic acids.

### Aliphatic amides

The values $E=23.55$ v.e. for formamide, $HCONH_2$, and 35.96 v.e. for acetamide, $CH_3$-$CONH_2$, lead to a resonance energy of 0.93 v.e. and 0.89 v.e., respectively, calculated relative to the structure

$$R-\underset{\underset{O}{\|}}{C}-NH_2.$$
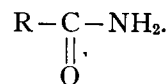
The expected resonance is between this structure and the structure

$$R-\underset{\underset{O^-}{|}}{C}=\overset{+}{N}H_2,$$
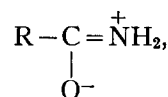
and the value 0.9 v.e. obtained is not greatly different from the related value 1.20 v.e. for the carboxyl group.

Oxamide, $(CONH_2)_2$, with $E=42.60$ v.e., has a total resonance energy of 2.05 v.e., or 1.03 v.e. per amide group, in agreement with the above value. Oxamic acid, $COOH\cdot CONH_2$, with $E=40.12$ v.e., has a total resonance energy of 1.99 v.e., nearly the sum of the values for the carboxyl group in oxalic acid and for the amide group in oxamide.

### Carbonic esters, urea, etc.

In the carbonate ion,

$$\overset{-}{O}-\underset{\underset{O}{\|}}{C}-\overset{-}{O},$$

guanidonium ion,

$$H_2N-\underset{\underset{\overset{+}{N}H_2}{\|}}{C}-NH_2,$$
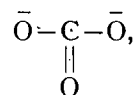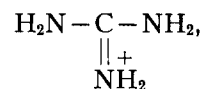
etc., there is complete degeneracy of the three structures corresponding to the three positions of the double bond, so that a resonance energy considerably larger than that in the carboxyl group is anticipated. Data on these symmetrical ions are not available, but data for similar unsymmetrical compounds, discussed below, in which resonance is only partially inhibited by the incomplete degeneracy lead to resonance energies of about 1.8 v.e.

Dimethyl carbonate, with $E=49.81$ v.e., and diethyl carbonate, with $E=74.46$ v.e., lead to a

carbonate resonance energy of 1.78 v.e. and 1.83 v.e., respectively. Urea, $CO(NH_2)_2$, with $E = 30.78$ v.e., and urethane, $C_2H_5OCONH_2$, with $E = 52.79$ v.e., have resonance energies of 1.59 v.e. and 1.89 v.e., respectively. No thermal data are available for guanidine.

## THE AROMATIC HYDROCARBONS

### Benzene

The value of $E'$ calculated for one of the Kekulé structures for benzene, $E' = 6C - H + 3C - C + 3C = C$, is 56.58 v.e. The data given in Table II for benzene and five other compounds

TABLE II. *Benzene and benzene derivatives.*

| Compound | Formula | $E$ | $E'$ | Resonance energy |
|---|---|---|---|---|
| Benzene | $C_6H_6$ | 58.20 | 56.58 | 1.62 v.e. |
| Toluene | $C_6H_5CH_3$ | 70.58 | 68.88 | 1.70 |
| Ethylbenzene | $C_6H_5C_2H_5$ | 82.90 | 81.18 | 1.72 |
| Propylbenzene | $C_6H_5C_3H_7$ | 95.27 | 93.48 | 1.79 |

lead to an average resonance energy between the two equivalent Kekulé structures, together with
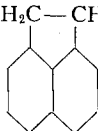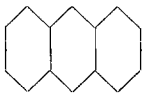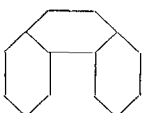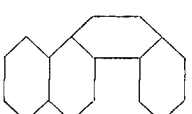
the additional contributions of the three excited states,[7] of 1.71 v.e.

The values of $E'$ and $E$ can be estimated from their internal consistency to be accurate to about $\pm 0.1$ v.e., the value of 1.71 v.e. for the resonance energy being accurate to about $\pm 0.15$ v.e. The quantum mechanical discussion of resonance in benzene and naphthalene is given in the preceding paper.[1]

### Naphthalene, anthracene, and other condensed ring systems

Data given in Table III lead to resonance energies relative to the usual structures with the maximum number of double bonds between adjacent carbon atoms of 3.24 v.e. and 3.07 v.e. for naphthalene and acenaphthene, 4.54 v.e. for anthracene, 4.78 v.e. for phenanthrene, and 6.53 v.e. for chrysene. These values are roughly equal to integral multiples of 1.71 v.e., the value found for benzene, the integral factor being in each case the number of benzene rings in the condensed ring system. The deviations are always in the direction of decreased resonance, the ratios for

TABLE III. *Condensed ring systems.*

| Compound | Formula | Structure | $E$ | $E'$ | Resonance energy |
|---|---|---|---|---|---|
| Naphthalene | $C_{10}H_8$ |  | 92.52 | 89.28 | 3.24 |
| Acenaphthene | $C_{12}H_{10}$ |  | 111.95 | 108.88 | 3.07 |
| Anthracene | $C_{14}H_{10}$ |  | 126.54 | 122.00 | 4.54 |
| Phenanthrene | $C_{14}H_{10}$ |  | 126.78 | 122.00 | 4.78 |
| Chrysene | $C_{18}H_{12}$ |  | 161.25 | 154.72 | 6.53 |

[7] See reference 1.

benzene and these five molecules being 1 : 1.90 : 1.80 : 2.66 : 2.80 : 3.82.

The saturated side ring in acenaphthene should not change the resonance energy from that of naphthalene, the small discrepancy observed (3.07 v.e. as against 3.24 v.e.) being attributed to experimental error. The ratio to 1.71 v.e. for acenaphthene, 1.80, is in better agreement with the quantum-mechanical ratio 1.82 than is the ratio 1.90 found for naphthalene itself, though in both the disagreement is within the experimental error.

## HETEROCYCLIC COMPOUNDS

Data are given in Table IV for heterocyclic compounds. For piperidine there is no difference between $E$ and $E'$, showing that the bond energies used are applicable to saturated heterocyclic molecules. Pyridine and quinoline differ from benzene and naphthalene only by the presence of one N in place of CH; and, as expected, the values 1.87 v.e. and 3.01 v.e., respectively, of the resonance energy are equal to within 10 percent to the values for the corresponding hydrocarbons.

Pyrrole, $C_4H_5N$, is found to have a resonance energy of 0.98 v.e., despite the fact that the structure

$$\begin{array}{ccc} HC & \!\!\!\!-\!\!\!\!- & CH \\ \| & & \| \\ HC & & CH \\ & \diagdown \; N \; \diagup & \\ & : N & \\ & H & \end{array}$$
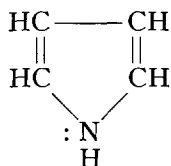
is the only structure that can be written for it in which each carbon atom forms four bonds with adjacent atoms. The large resonance energy requires that other structures contribute strongly to the normal state of this molecule. The most reasonable additional structures that can be written are the four of the type

$$\begin{array}{ccc} HC & \!\!=\!\! & CH \\ | & & | \\ HC^- & & CH, \\ & \diagdown_{+}\diagup & \\ & N & \\ & H & \end{array}$$
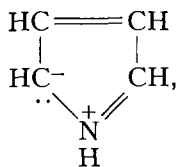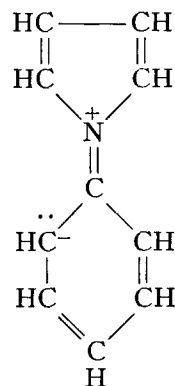
which differ from the first in that the two double bonds are shifted and the unshared electron pair

is on carbon rather than nitrogen. A negative carbon atom, with one unshared and three shared electron pairs, occurs rather often in resonating structures, as in carbon monoxide, the negative hydrocarbon free radicals, the ion $C_5H_5^-$ (in the alkali salts of pentadiene), which resonates among the five equivalent structures
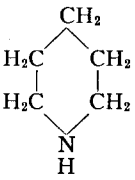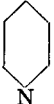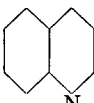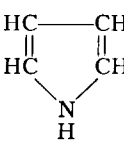
$$\begin{array}{ccc} HC & \!\!\!\!-\!\!\!\!- & CH \\ \| & & \| \\ HC & & CH, \text{ etc.} \\ & \diagdown_{-}\diagup & \\ & : C & \\ & H & \end{array}$$
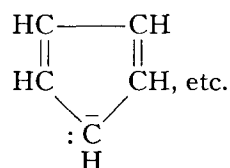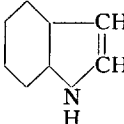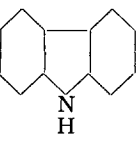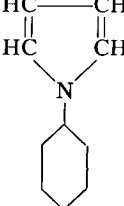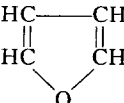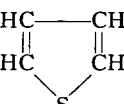
Indole, $C_8H_7N$, and carbazole, $C_{12}H_9N$, have resonance energies of 2.34 v.e. and 3.93 v.e., respectively, 0.63 v.e. and 0.51 v.e. greater than for the benzene rings in the indicated structures. For indole we expect the resonance energy to be somewhat smaller than the sum for benzene and pyrrole, because of the suppression of resonance from the sharing of two atoms by the two rings; in agreement with this argument, the observed value is 0.35 v.e. less than the sum $1.71+0.98 = 2.69$ v.e. Similarly for carbazole the observed resonance energy is 0.47 v.e. less than the sum $2\times1.71+0.98 = 4.40$ v.e. The resonance energy of phenylpyrrole, 3.29 v.e., is 0.60 v.e. greater than the sum of the pyrrole and benzene resonance energies; this additional stability is due to structures such as

$$\begin{array}{ccc} HC & \!\!\!\!-\!\!\!\!- & CH \\ \| & & \| \\ HC & & CH \\ & \diagdown_{+}\diagup & \\ & N & \\ & \| & \\ & C & \\ HC^- & & CH \\ | & & \| \\ HC & & CH \\ & \diagdown \; C \; \diagup & \\ & C & \\ & H & \end{array}$$

in which the unshared electron pair is on a carbon atom ortho or para to nitrogen.

The resonance energy of 0.93 v.e. for furane, $C_4H_4O$, arises from the same structures as for pyrrole.

TABLE IV. *Resonance energies of heterocyclic compounds.*

| Compound | Formula | Structure | $E$ | $E'$ | Resonance energy |
|---|---|---|---|---|---|
| Piperidine | $C_5H_{11}N$ | | 67.58 | 67.60 | — |
| Pyridine | $C_5H_5N$ | | 52.61 | 50.74 | 1.87 |
| Quinoline | $C_9H_7N$ | | 86.46 | 83.45 | 3.01 |
| Pyrrole | $C_4H_5N$ | | 44.84 | 43.86 | 0.98 |
| Indole | $C_8H_7N$ | | 78.91 | 76.57 | 2.34 |
| Carbazole | $C_{12}H_9N$ | | 113.22 | 109.29 | 3.93 |
| Phenylpyrrole | $C_{10}H_9N$ | | 98.45 | 95.16 | 3.29 |
| Furane | $C_4H_4O$ | | 42.18 | 41.25 | 0.93 |
| Thiophene | $C_4H_4S$ | | 41.21 | 39.86 | 1.35 |

Despite its five-membered ring, thiophene, $C_4H_4S$, shows a remarkably close resemblance to benzene in its properties. The resonance energy found for it, 1.35 v.e., is to be mainly attributed to the same structures as for pyrrole, though the structure

$$\begin{array}{ccc} HC & = & CH \\ | & & | \\ HC & & CH, \\ & \diagdown \diagup & \\ & S & \\ & \cdot\cdot & \end{array}$$
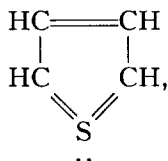
using five $M$ orbits in sulfur, may make a small contribution also.

## RESONANCE IN CONJUGATED SYSTEMS CONTAINING AROMATIC NUCLEI

### Biphenyl and related compounds

The thermochemical data for aliphatic hydrocarbons containing conjugated double bonds, such as butadiene, $CH_2 = CH - CH = CH_2$, etc., are not very reliable, but suggest a value of about 0.2 v.e. for the resonance energy. The data for molecules containing aromatic rings are more reliable, and show the existence of extra resonance accompanying increase in length of a conjugated system. Thus the value 3.77 v.e. for the resonance energy of biphenyl is 0.35 v.e. larger than the resonance energy of two benzene rings, the additional resonance being attributed to the contribution of structures such as

$\cdot \langle \rangle = \langle \rangle \cdot$, the dots representing single electrons on ortho or para carbon atoms. (These electrons are formally to be considered paired, in order to give a singlet state.) The resonance energy of fluorene should be the same as for biphenyl; the somewhat larger value given in Table V is probably due to error in the reported heat of combustion. For 1,3,5-triphenylbenzene, for which many quinone-type structures must be considered, the additional resonance energy is found to be 1.1 v.e.

For phenylethylene, in which a double bond conjugated with a benzene ring permits structures such as $\cdot \langle \rangle = CH - CH_2 \cdot$, the additional resonance energy is 0.29 v.e., and for stilbene, with two phenyl groups conjugated with the double bond, it is 0.67 v.e. The conjuga-

tion of a triple bond and a benzene ring in phenylacetylene provides extra resonance energy to the extent of 0.45 v.e. The extra resonance energy in 1,2-dihydronaphthalene is 0.32 v.e., in good agreement with the value for phenylethylene. The extra resonance energy in furylethylene is 0.25 v.e.

### Benzene derivatives

The extra resonance energy of phenylcyanide, benzoic acid, benzaldehyde, acetophenone, and other benzene derivatives in which a double or triple bond in a side chain is conjugated with the benzene ring should be about the same as for phenylethylene. The average value for these four compounds (Table VI) is 0.21 v.e. In benzophenone the larger extra resonance energy of 0.45 v.e. results from the conjugation of $C = O$ with the two benzene rings.

For symmetrical and unsymmetrical diphenylurea we expect some extra resonance energy in addition to that for two benzene rings and urea because of conjugation of these groups; the values found are 0.55 v.e. and 0.50 v.e., respectively.

In phenol, aniline, and other compounds in which an atom with unshared electron pairs is attached directly to the benzene ring, structures such as $: \langle \rangle = \overset{\cdot\cdot}{O} \overset{+}{:} H$ or especially

$\langle \rangle = \overset{\cdot\cdot}{O} \overset{+}{:} H$ may contribute appreciably to the normal state of the molecule; this is presumably the cause of the extra resonance energy of about 0.25 v.e. found for such compounds (Table VI). The high value for hydroquinone may indicate some additional resonance, the cause of which is not evident.

### The quinones

The data given in Table VII for the quinones show large extra resonance energies of 0.57 v.e. in quinone, 1.42 v.e. in anthraquinone, and 1.4 v.e. in phenanthraquinone, in addition to the resonance energy of two benzene rings in the last two compounds. These large values we attribute to structures such as $\cdot \overset{\cdot\cdot}{O} - \langle \rangle - \overset{\cdot\cdot}{O} \cdot$,

TABLE V. *Resonance energies of biphenyl and related compounds.*
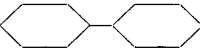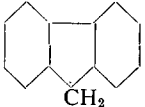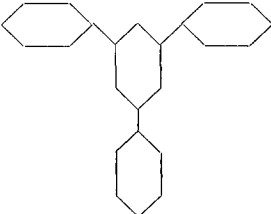
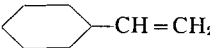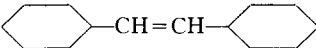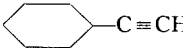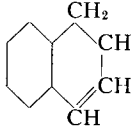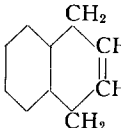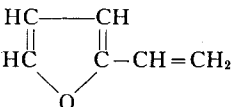| Compound | Formula | Structure | E | E' | Resonance energy | Extra resonance energy |
|---|---|---|---|---|---|---|
| Biphenyl | $C_{12}H_{10}$ | | 111.91 | 108.14 | 3.77 | 0.35 |
| Fluorene | $C_{13}H_{10}$ | | 119.57 | 115.44 | 4.13 | 0.71 |
| 1,3,5-Triphenylbenzene | $C_{24}H_{18}$ | | 219.2 | 211.3 | 7.9 | 1.1 |
| Phenylethylene | $C_8H_8$ | $-CH=CH_2$ | 77.42 | 75.42 | 2.00 | 0.29 |
| Stilbene | $C_{14}H_{12}$ | $-CH=CH-$ | 131.08 | 126.99 | 4.09 | 0.67 |
| Phenylacetylene | $C_8H_6$ | $-C\equiv CH$ | 70.99 | 68.83 | 2.16 | 0.45 |
| 1,2-Dihydronaphthalene | $C_{10}H_{10}$ | | 97.05 | 95.02 | 2.03 | 0.32 |
| 1,4-Dihydronaphthalene | $C_{10}H_{10}$ | | 96.73 | 95.02 | 1.71 | 0.00 |
| Furylethylene | $C_6H_6O$ | $-CH=CH_2$ | 61.28 | 60.10 | 1.18 | 0.25 |

TABLE VI. *Benzene derivatives.*

| Compound | Formula | $E$ | $E'$ | Resonance energy | Extra resonance energy |
|---|---|---|---|---|---|
| Phenyl cyanide | $C_6H_5CN$ | 66.89 | 64.97 | 1.92 | 0.21 |
| Benzoic acid | $C_6H_5COOH$ | 74.91 | 71.82 | 3.09 | 0.18 |
| Benzaldehyde | $C_6H_5CHO$ | 69.64 | 67.78 | 1.86 | 0.15 |
| Acetophenone | $C_6H_5COCH_3$ | 82.24 | 80.22 | 2.02 | 0.31 |
| Benzophenone | $C_6H_5COC_6H_5$ | 123.37 | 119.50 | 3.87 | 0.45 |
| Sym.-diphenylurea | $C_6H_5NH \cdot CO \cdot NHC_6H_5$ | 137.35 | 131.79 | 5.56 | 0.55 |
| Unsym.-diphenylurea | $(C_6H_5)_2N \cdot CONH_2$ | 137.30 | 131.79 | 5.51 | 0.50 |
| Phenol | $C_6H_5OH$ | 62.46 | 60.46 | 2.00 | 0.29 |
| Anisole | $C_6H_5OCH_3$ | 74.37 | 72.40 | 1.97 | 0.26 |
| Hydroquinone | $C_6H_4(OH)_2$ | 66.83 | 64.35 | 2.48 | 0.77 |
| Aniline | $C_6H_5NH_2$ | 64.89 | 62.99 | 1.90 | 0.19 |
| Methylaniline | $C_6H_5NHCH_3$ | 76.99 | 75.01 | 1.98 | 0.27 |
| Dimethylaniline | $C_6H_5N(CH_3)_2$ | 88.84 | 87.03 | 1.81 | 0.10 |
| Diphenylamine | $(C_6H_5)_2NH$ | 118.26 | 114.29 | 3.97 | 0.55 |

in which a benzene (or anthracene or phenanthrene) nucleus is formed by changing the $C=O$ bond to a single bond, leaving an odd electron on each oxygen (the two being formally paired).

TABLE VII. *Resonance energy of quinones.*

| Compound | Formula | $E$ | $E'$ | Resonance energy | Extra resonance energy |
|---|---|---|---|---|---|
| Quinone | $C_6H_4O_2$ | 61.01 | 60.44 | 0.57 | 0.57 |
| Anthraquinone | $C_{14}H_8O_2$ | 130.54 | 125.70 | 4.84 | 1.42 |
| Phenanthra-quinone | $C_{14}H_8O_2$ | 130.5 | 125.70 | 4.8 | 1.4 |

## UREIDES AND PURINES

Values of $E$ for some ureides and purines are given in Table VIII. For many of the substances it was necessary to estimate heats of vaporization or sublimation, in which cases $E$ is given only to 0.1 v.e. The values of $E'$ and the resonance energy $E-E'$ refer to the ketonic structures shown in the table; similar calculations may be easily made for enolic structures, leading usually to somewhat larger resonance energies. The ketonic resonance energies given do not include the energy of resonance of carbonyl between the structures $C::O:$ and $\overset{+}{C}:\overset{..}{O}:^-$, inasmuch as the ketone value $C=O=7.71$ v.e. was used in calculating $E'$.

The ureides hydantoin, parabanic acid, alloxan, barbituric acid, and 4-methyluracil show resonance energies of between 2.3 v.e. and 3.1

v.e., resulting from resonance of the double bonds among the various possible positions. These values seem not unreasonable when compared with the value 1.59 v.e. for urea. However, we should expect the resonance energy for hydantoin to be somewhat smaller than for the other four rather than somewhat larger.

Allantoin would be expected to have a resonance energy somewhat smaller than the sum for two urea groups and one amide group, since the amide and one urea group interfere through the sharing of NH. The experimental value, 4.7 v.e., is, however, somewhat larger than the corresponding sum $2\times1.59+0.91=4.09$ v.e.

The resonance energies of the seven purine derivatives given in Table VIII vary in an easily interpretable manner between 2.5 and 5.5 v.e. The value 2.5 v.e. for 7-methylpurine is probably a little too low, for the five-membered ring would be expected to contribute about 1.0 v.e. in addition to the 1.7 v.e. for the benzene-type six-membered ring. The introduction of an oxygen atom, with its accompanying increase in the number of possible positions for the double bond, increases the resonance energy to 3.5 v.e. for 8-oxypurine. Two oxygen atoms, in caffeine, theobromine, and xanthine, lead to an additional increase to 4.4 v.e., 4.7 v.e., and 4.9 v.e., respectively (the differences of the three values being probably without significance). Uric acid, containing three oxygen atoms, has a resonance energy of 5.2 v.e. In guanine, with one oxygen and one nitrogen atom providing extra resonance, the resonance energy is 5.5 v.e. Hence we learn

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TABLE VIII. *Ureides and purines.*

| Compound | Formula | Structure | $E$ | $E'$ | Resonance energy |
|---|---|---|---|---|---|
| Hydantoin | $C_3H_4N_2O_2$ | | 49.6 | 46.5 | 3.1 |
| Parabanic Acid | $C_3H_2N_2O_3$ | | 49.0 | 46.4 | 2.6 |
| Alloxan | $C_4H_2N_2O_4 \cdot H_2O$ | | 70.27 | 67.95 | 2.32 |
| Barbituric Acid | $C_4H_4N_2O_3$ | | 61.5 | 58.7 | 2.8 |
| 4-methyluracil | $C_5H_6N_2O_2$ | | 69.0 | 66.2 | 2.8 |
| Allantoin | $C_4H_6N_4O_3$ | | 75.9 | 71.2 | 4.7 |
| 7-methylpurine | $C_6H_6N_4$ | | 73.6 | 71.1 | 2.5 |
| 8-oxypurine | $C_6H_4N_4O$ | | 67.1 | 63.6 | 3.5 |
| Caffeine | $C_8H_{10}N_4O_2$ | | 108.5 | 104.1 | 4.4 |
| Theobromine | $C_7H_8N_4O_2$ | | 96.7 | 92.0 | 4.7 |

TABLE VIII. (*Continued*).

| | | | | | |
|---|---|---|---|---|---|
| Xanthine | $C_5H_4N_4O_2$ | NH — CO<br>CO    C — NH<br>                            >CH<br>NH — C — N | 73.0 | 68.1 | 4.9 |
| Guanine | $C_5H_5N_5O$ | NH — CO<br>CNH₂  C — NH<br>                            >CH<br>N —— C — N | 75.4 | 69.9 | 5.5 |
| Uric Acid | $C_5H_4N_4O_3$ | NH — CO<br>CO    C — NH<br>                            >CO<br>NH — C — NH | 77.7 | 72.5 | 5.2 |

that each oxygen atom attached to the purine group carries with it a contribution of about 0.9 v.e. to the resonance energy of the molecule, in addition to the resonance energy included in the ketonic C=O bond energy value. The data for guanine indicate that the contribution of a nitrogen atom is still larger, though this may be due to experimental error.

It may be mentioned that in heterocyclic systems as well as in hydrocarbon condensed ring systems the contribution to the normal state of structures associated with all of the possible positions of the double bonds is dependent on the existence of a coplanar arrangement of the pertinent atoms, with bond angles of about 120°, which requires that the rings contain five or six or possibly seven atoms.

## CONCLUSION

This study of thermochemical data for a very large number of substances has shown that in every case for which the data are reliable the observed energy of the molecule is equal to that calculated for an assumed distribution of bonds or differs from it in the direction corresponding to greater stability, in accord with the quantum-mechanical requirement that the actual energy for the normal state of any system is the lower limit for values of the energy integral calculated for any wave function. For molecules for which several electronic structures make appreciable contributions to the wave function for the normal state, values of the resonance energy of 0.2 v.e. to 10 v.e. are found. Thus in benzene, pyridine, etc., the resonance energy is about 1.7 v.e. or 39,000 cal./mole, in naphthalene and quinoline about 3.1 v.e., and larger in larger condensed ring systems. In the carboxylic acids and other compounds in which a double bond resonates between two positions the energy of this resonance is about 1.2 v.e.; and in compounds such as urea, with three positions for the double bond, the resonance energy is about 1.8 v.e. Additional resonance energy is also found to accompany any increase in length of the conjugated system, as in phenylethylene, biphenyl, etc. In the preceding paper there has been given the quantum-mechanical discussion of benzene and naphthalene, and a similar treatment of open-chain conjugated systems, biphenyl, the hydroaromatic hydrocarbons and other systems will be published later.