

ABSTRACT OF THESIS

The Apparent Energies of the Nitrogen - Nitrogen
and the Carbon - Carbon Bonds
and
The Determinations of the Heats of Combustion of
Hydrazobenzene and Hippuric Acid

by

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W. V. June 1. 1947

The present study was undertaken in order to complete the nitrogen - nitrogen bond energy series by calculating this energy in hydrazobenzene from its heat of combustion. In view of the wide discrepancies in the known values for this quantity the heat of combustion was determined in an adiabatic calorimeter after standardization with benzoic acid. To establish the validity of this result, as well as of those reported earlier from this laboratory, the heat of combustion of the secondary standard, hippuric acid, was also measured and found to agree with the accepted value.

In addition to the calculation of the bond energy in hydrazobenzene this data also permitted calculation of the nitrogen - nitrogen double bond energy in azobenzene.

From semi-empirical equations estimations of the bond multiplicities and interatomic distances have been made, correlation of thermochemical bond energies with results of kinetic studies have been presented to clarify some apparent discrepancies reported earlier, and evidence has been presented which indirectly supports the newly proposed

heat of dissociation of nitrogen, and recalculation of the N - N bond energies in the hydrazines for which reliable thermochemical data is available has been presented to show the influence of this new energy term on the apparent energies of the N - N bond.

An analysis of the several factors contributing to bond stabilization is presented and future studies proposed which should prove most fruitful in view of the current interpretations.

To demonstrate the marked influence of certain fundamental assumptions usually made in the calculation of apparent bond energies, the calculations have been extended to the carbon -carbon bonds where large discrepancies arise directly as a result of these assumptions.

It now appears that only qualitative overall effects can be demonstrated in a thermochemical approach to the analysis of a bond energy, although the value of thermal data in supplementing spectral, kinetic, and other approaches to this problem should not be underestimated.

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HYDRAZOBENZENE AND HIPPURIC ACID

by

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A THESIS

submitted to the
OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1947

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ACKNOWLEDGEMENT

The author gratefully acknowledges
the suggestions and friendly criti-
cisms of

Professor E. C. Gilbert
who suggested and so capably super-
vised this study.

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INTRODUCTION

A full interpretation of the bond energies of certain functional groups within polyatomic organic molecules must await the accumulation of combustion data of structurally related molecules, their heats of fusion, heats of vaporization, estimation of resonance energies from bond length measurements, and the correlation of these energies and lengths with the results of other studies on bond strengths. Certain apparent discrepancies in the fundamental thermochemical data also require further study and consideration before a complete analysis of a bond energy can be accomplished. One of these is the wide variation in the heats of sublimation of carbon, values of from 110 Kcal./mole to 170 Kcal./mole are currently being used by different authors. Another results from a recent interpretation of the nitrogen spectrum by Gaydon (26) which may change the heat of dissociation of nitrogen from 169 Kcal. to 225 Kcal./mole. An accurate determination of these and similar data is necessary for the calculation of the heats of formation of substances from the atoms and, hence, profoundly influences bond linkage calculations.

Further, thermal and photochemical kinetic studies yield values of the bond energies of polyatomic molecules which disagree markedly with values determined more directly from heat of combustion data although a consideration of the equation relating the activation energies determined from kinetic studies with the heats of dissociation

$$\Delta H_D = E_S - E_\alpha$$

reveals that the energy of dissociation ΔH_D is not equal to the activation energy of dissociation E_S but rather to the difference $E_S - E_\alpha$ where E_α is the activation energy of the association process. For many processes a very low value of E_α would be expected and

$$\Delta H_D \cong E_S$$

and since

$$\Delta H_D \cong \Delta H_\beta$$

where ΔH_β is the heat of linkage or bond energy, it would be expected that

$$\Delta H_\beta \cong E_S$$

However, until such time as measurements of E_α confirm this expectation, better practice would dictate the following interpretation. The bond energy ΔH_β cannot be expected to be equivalent to the activation energy for bond dissociation except in those cases where the activation energy for association is zero. Furthermore once ΔH_β and E_S are known from heat of combustion and reaction - rate data E_α may be calcu-

lated and much can be learned of the mechanism of organic reactions from the results of such calculations.

An example of an apparent discrepancy in the several approaches to bond energy is presented in this thesis to demonstrate the application of the preceding principles and to justify an extension of the calculation of bond energies from heat of combustion data although attainment of absolute accuracies cannot be realized until more is known of the heats of fusion, sublimation, and vaporization of organic compounds, their resonance energies, and variations of bond strengths with respect to their intramolecular positions. The absolute values of these quantities are of such magnitude, however, that errors arising from estimates made thereon would only slightly alter the overall qualitative effects of substituents and the nature of the bond itself on its energy.

The earlier investigations of Anderson and Gilbert (4) and this author (16) indicated the necessity of redetermining the heat of combustion of hydrazobenzene whose earlier values (72, 61) yield nitrogen - nitrogen bond strengths in disagreement with those expected from the substituted hydrazobenzene series (16). This thesis therefore also presents the results of the recalibration and restandardization of the adiabatic calorimeter used in earlier work in this laboratory (41, 51) and the determination of the heat of combus-

tion of hydrazobenzene from which a new nitrogen - nitrogen bond was calculated and shown to fit the series mentioned above. The heat of combustion of hippuric acid was also determined and compared with a recent value reported by Huffman (39) to check certain approximations which have been made in the calculation of the heats of combustion of nitrogen - containing substances from the temperature rises of the calorimeter recorded experimentally.

With the intention of better illustrating the influence of substituents, resonance, and dipolar charge on bond strengths demonstrated herein for the nitrogen - nitrogen single and double bonds, hereafter designated N - N and N = N, the calculations have been extended to the carbon - carbon single and double bonds, hereafter designated C - C and C = C, making use of combustion data reported by Anderson (3) and this author (16) in earlier theses.

BOND ENERGY AND ACTIVATION ENERGY OF DISSOCIATION

From studies on the thermal dissociation of tetraphenylhydrazine, Cain and Wiselogle (12) have determined the activation energy of dissociation E_s to be 30.0 Kcal./mole which is greater than the energy of dissociation of hydrazine, in marked contrast to the lowering of bond strength and activation energy observed by substituting phenyl groups for hydrogen atoms in the ethane series. These authors were led to believe that the nitrogen - nitrogen bond energy itself would be decreased whereas they found it to be apparently increased. Lewis and Lipkin (51) have taken the view that the heat of dissociation of tetraphenylhydrazine may be considerably greater than hydrazine itself on the basis of the reasoning that resonance stabilization results in distribution of the basic properties of each of the lone electron pairs of the nitrogen atoms among the several ortho and para positions in the rings. However, these authors further point out that resonance stabilization of the biphenyl-nitrogen radicals formed on dissociation should exceed that of the original molecule and no observable strengthening of the nitrogen-nitrogen bond should be noted. Still another factor to which apparently little attention has been given is the molecular-weight labilization of the nitrogen - nitrogen bond. For this reason the N - N bond in tetraphenyl hydra-

zine may be expected to be less than that in hydrazine in spite of the resonance stabilization. This has already been demonstrated in the ethane series and evidence presented in the section of this thesis on C - C bond energies indicates that this effect has a measurable influence on the substituted ethylenes as well. In fact, in the case of the N - N bond, Anderson and Gilbert (4) have calculated the bond energy in tetraphenylhydrazine to be only 10.5 Kcal./mole from heat of combustion data in considerable difference with the value obtained for the activation energy of dissociation, 30.0 Kcal. Although these two values appear to disagree considerably a consideration of the equation relating the heat of dissociation ΔH_D to the activation energy of dissociation of the given bond

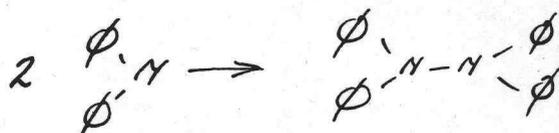
$$\Delta H_D = E_S - E_\alpha$$

reveals that ΔH_D does not equal E_S but rather is the difference in the activation energies of association E_α and dissociation. Assuming that ΔH_D is equivalent to the energy of the bond undergoing dissociation ΔH_B there results

$$\Delta H_B = E_S - E_\alpha$$

Therefore ΔH_B cannot be expected to equal E_S . Assuming that $\Delta H_D = \Delta H_B$ is probably valid for the unimolecular dissociations involving the production of free radicals; in fact, the bond energy of the nitrogen - nitrogen triple bond, the hydrogen -

hydrogen single bond, oxygen - oxygen double bond, etc. are taken to be the heats of dissociation of the respective gaseous molecules. The error in this assumption has been shown to be large, 5 Kcal. in 35 Kcal., only in the case of the oxygen - oxygen single bond as calculated by Lewis and Lipkin (51) from the heat of formation of hydrogen peroxide. This apparent error results from their particular choice of the bond energy of the oxygen - hydrogen bond. For the present, therefore, the assumption will be presumed valid. The foregoing experimental results may in turn be used to calculate E_a , the energy of activation for the association process of the biphenyl - nitrogen radicals. Such a calculation yields 19.5 Kcal./mole for the association reaction



where ϕ represents a phenyl group. This value appears high until consideration is taken of the increased resonance stabilization of the free radical by the odd electron pair.

The $-\text{NH}_2$ radical formed in the gaseous dissociation of hydrazine should, however, have an activation energy of association of or nearly zero. A calculation of the activation energy for this process is possible from ΔH_f for the N - N bond calculated by Pauling (59) from the heat of combustion data of Hughes, Corrucini, and Gilbert (41). A similar cal-

calculation by Skinner (67) yields 43 Kcal. for the ΔH_3 of the N - N bond while Sokolov (68) has calculated this energy to be approximately 48 Kcal. by a semi-empirical quantum-mechanical method. Before the activation energy of association can be calculated, an estimate of the activation energy of dissociation E_s will have to be made.

Fugassi (25) has derived an empirical equation relating the symmetrical vibration frequency of any bond with its activation energy of dissociation from which E_s can be calculated for hydrazine. The equation,

$$E_s = 2.8581 \bar{\nu} \left[35.5 - \frac{900.45 \bar{\nu}}{D_e} \right]$$

where

E_s = the activation energy of dissociation

D_e = the heat of dissociation or bond energy

$\bar{\nu}$ = the symmetrical valence vibration of the given bond,

can be seen to be related to the Morse equation for the vibrational energy of a molecule

$$E_{vib} = (n + \frac{1}{2}) N h \nu - (n + \frac{1}{2})^2 \left(\frac{N h \nu}{4 D_e} \right)^2$$

where

n = the vibrational quantum number

N = Avogadro's number

h = Planck's constant.

Using Pauling's N - N bond value and the spectral data of Kahovec and Kohlrausch (42), E_{δ} becomes negative, while using Gaydon's value of 43 Kcal. for the N - N bond energy, E_{δ} becomes 42.8 Kcal. in good agreement with the bond energy. Hence the activation energy of association is very nearly zero for the amino radical, $-NH_2$. This result is not unreasonable since the amino radicals would be expected to associate more readily than the biphenyl-nitrogen radicals because of resonance stabilization of the latter as well as steric factors which hinder its association. Since the activation energy for the association of the biphenyl-nitrogen radicals was unreasonably larger than expected, this value was recalculated using a new bond energy of 27.4 Kcal. calculated from the thermal data of Anderson and Gilbert (4) and Skinner's new estimate of the N - H bond energy of 92 Kcal. E_{α} now becomes 2.6 Kcal., a far more plausible result.

Thus the former apparent discrepancies in bond energy determinations from heats of combustion and thermal and photochemical kinetic studies may prove not to be in disagreement in view of this interpretation. Objections, therefore, to the heat of combustion approach to bond energies may be reduced to differences in resonance energies which may be determined later from bond length measurements, to differences in heats of fusion, sublimation, vaporization which may

be determined by well-known techniques, and to errors in the establishment of the normal energy values for the carbon - carbon, carbon - hydrogen, oxygen - hydrogen, nitrogen-hydrogen, and nitrogen - nitrogen bonds and the variations of these normal values with respect to their particular intramolecular positions. A consideration of the usual approximations will reveal that the overall qualitative effects will be altered only slightly at such a time when accurate values of the forementioned quantities are made available. In addition to the foregoing theoretical considerations, bond energies, even though known with little accuracy, may still serve beneficially in practical problems. Especially is this true in a homologous series where errors resulting from the foregoing estimates are reduced still further.

Accepting the foregoing interpretation, calculations of $N - N$, $N \equiv N$, $C - C$, and $C = C$ bond energies can now be made with assurance that at least overall qualitative effects of substituents may be made from our present knowledge of the thermochemical properties of certain of the molecules.

An indirect conclusion resulting from the interpretation presented in this section lies in the fact that the fundamental data used by Gaydon and Skinner in the calculation of the $N - N$ bond yields a bond energy in good agreement with its activation energy of dissociation.

Since there is little or no molecular - weight labilization to alter the pure bond energy in hydrazine the good agreement between the bond energies calculated from thermal and spectral data supports the heat of dissociation of nitrogen gas of 225.0 Kcal./mole proposed by Gaydon and an improved N - H bond energy in hydrazine of 92 Kcal. proposed by Skinner. For comparative purposes and until such time as Gaydon's and Skinner's values are well established, the previously accepted value for the heat of dissociation of nitrogen gas of 169.0 Kcal./mole will be used in the following calculations in this thesis.

APPARENT ENERGY OF THE NITROGEN - NITROGEN BOND

A. The energy of the nitrogen - nitrogen single bond

Calculations of the bond energies involving nitrogen (4, 16, 59) have been based on the equivalence of the energy of the three nitrogen - hydrogen bonds in ammonia, i.e. 83.7 Kcal. which is one-third of the heat of complete dissociation of the ammonia molecule in the gaseous state to its atoms. No improvement in the qualification of this assumption has been evolved since the last writing by this author on N - N bonds (16) although Skinner has proposed a newer value for this bond as mentioned earlier. However, assumption of either one of these values in preference to the other alters the overall qualitative results only slightly although differences in the basicity of substances such as aniline, hydrazine, and hydrazobenzene, for example, must be regarded as being an indication of the difference in bond strengths of the nitrogen - hydrogen bonds in these various substances as well as in ammonia itself.

Quantitative evidence of this bond strength variation in the case of the oxygen - hydrogen bond has been demonstrated by Dwyer and Oldenberg (22) who have made absorption spectra measurements with a spectrograph of high resolving power on hot mixtures of oxygen and water vapor. These authors have found that ΔH_2 of the first bond requires 118

Kcal. while the second requires but 100 Kcal.; the thermo-chemist has chosen 110 Kcal. from one-half the heat of formation of water from atomic hydrogen and oxygen.

Ultimate analyses of the variations in N - H bond energies in substituted hydrazines and hydrazobenzenes will contribute much toward a better understanding of the intramolecular forces. Recent improvements (9,27,28,29) in equipment used in high frequency absorption studies (0.5 to 3.0 cm.) by a method originally proposed in 1933 by Cleeton and Williams (15) furnish a promising tool for supplementing electron diffraction studies currently yielding valuable information on bond length variations.

The energy of the N - N bond was originally calculated by Pauling (59) from the heat of combustion of hydrazine determined by Hughes, Corrucini, and Gilbert (41) earlier in this laboratory. More recently Anderson and Gilbert (4) have made measurements leading to the N - N bond energies in tetraphenylhydrazine, dibenzoylhydrazide, and phenylhydrazine. More recently this author has calculated the bond energy in 4, 4'-dinitrohydrazobenzene from its heat of combustion and that of para-nitroaniline. The apparent energy of the nitrogen bond in hydrazobenzene is in considerable disagreement with that expected from the known energies of the N - N bond if the combustion data of Swietoslawski and Bobin -

ska (72) are used, whereas that calculated from the data of Petit (61) gives a somewhat lower energy than that expected for the unsubstituted hydrazobenzene. Since this latter datum was determined in 1889 a redetermination of the heat of combustion of hydrazobenzene was obviously necessary before any conclusions as to the nitrogen bond energy in this molecule could be made. Evaluation of the Lewis - Lipkin explanation also depended partially on the results of this redetermination. A new heat of combustion of hydrazobenzene was determined and the results presented in the last section of this thesis.

Although the energy of a given bond is specific for the particular atomic species, there are several factors which prohibit ready prediction of bond strengths. The effect of resonance stabilization has been mentioned in the preceding section. A more complete interpretation of this effect and its relation to increased molecular weight labilization is included herein to emphasize the relative effects of these two factors. However, there is still another factor which is believed to be of such magnitude as to influence the bond energies. Lewis and Lipkin (51) believe that the magnitude of the dipolar negative coulombic repulsion acting between the two nitrogens is sufficiently great to appreciably weaken the N - N linkage. Any dimunition of these coulombic charges will therefore strengthen the N - N bond. Phenyl groups have

this strengthening effect by the partial withdrawal of the lone electron pair into the phenyl resonating system although the increased molecular weights more than offset this stabilization. The phenyl - group resonance stabilization of the N - N bond is well demonstrated in the mono- substituted hydrazine, phenylhydrazine, for which Anderson and Gilbert (4) have calculated a bond energy of 24.3 Kcal. The difference in bond energies in unsubstituted and in substituted hydrazines may be given by the expression

$$\epsilon'_p = \Delta H''_p - \Delta H'_p$$

where

$\Delta H''_p$ = the nitrogen - nitrogen bond energy in the substituted hydrazine

$\Delta H'_p$ = the nitrogen - nitrogen bond energy in hydrazine

ϵ'_p = the excess stabilization energy if positive; the excess labilization energy if negative,

from which ϵ'_p for phenylhydrazine is +4.3 Kcal.; however, this does not represent pure resonance stabilization energy since the additional weight of the phenyl group has reduced the stabilization somewhat. At least for the first phenyl substituent the stabilization due to resonance is greater than the reduction due to increased molecular weight. For the second phenyl group in the symmetrical hydrazine the resonance stabilization very nearly equals the molecular

weight labilization. Similar calculations for other N - N bonds are presented in Table I using the bond energies listed in Table II.

A similar treatment may be applied to substituted and unsubstituted hydrazobenzenes to determine the extent of increased resonance (stabilization) by the withdrawal of the lone electron pair of the nitrogens into the ring by acidic substituents or decreased resonance (labilization) by forcing the electron pair back to the nitrogens by basic substituents on the phenyl groups. However, as pointed out in the discussion of current data on nitrogen - nitrogen bond energies the heat of combustion of hydrazobenzene is in such a state of uncertainty that no quantitative calculations can be made from previous data. However, using the bond energy of 20.9 Kcal. whose calculation is presented later in this section from the new heat of combustion reported in the last section of this thesis, an energy difference may be calculated from

$$\epsilon_p'' = \Delta H_p'' - \Delta H_p'$$

where

$\Delta H_p''$ = the energy of the nitrogen - nitrogen bond in a substituted hydrazobenzene

TABLE I

CALCULATED STABILIZATION - LABILIZATION ENERGIES
 BASED ON THE N - N BOND IN HYDRAZINE

Compound	
Phenylhydrazine	+4.3 Kcal./ mole
Hydrazobenzene	+0.9 Kcal./ mole ^a
	+(4.7)Kcal./ mole ^b
	-(7.6)Kcal./ mole ^c
Hydrazine	0.0 Kcal./ mole
Dibenzoylhydrazine	- 2.3 Kcal./ mole
4,4'-dinitrohydrazobenzene	- 3.2 Kcal./ mole
Tetraphenylhydrazine	- 9.5 Kcal./ mole

a calculated from the new heat of combustion reported in the last section of this thesis.

b calculated from the data of Swietoslawski and Bobinska (72).

c calculated from the data of Petit (61).

TABLE II

SUMMARY OF THE APPARENT N - N BOND ENERGIES

Compound	N - N Bond Energy
Phenylhydrazine	24.3 Kcal./ mole ^a
Hydrazobenzene	20.9 Kcal./ mole ^b
	24.7 Kcal./ mole ^c
	12.4 Kcal./ mole ^d
Hydrazine	20.0 Kcal./ mole ^e
Dibenzoylhydrazine	17.7 Kcal./ mole ^a
4,4'-dinitrohydrazobenzene	16.8 Kcal./ mole ^f
Tetraphenylhydrazine	10.5 Kcal./ mole ^a

a determined by Anderson (3).

b calculated from data reported in this thesis.

c calculated from data of Swietoslawski and Bobinska (72).

d calculated from data of Petit(61).

e calculated by Pauling (59) from data of Hughes, Corrucini, and Gilbert (41).

f determined by this author (16).

$\Delta H'_0$ = the energy of nitrogen - nitrogen bond in hydrazobenzene

ϵ''_p = the excess stabilization energy if positive;
the excess labilization energy if negative.

The apparent resonance stabilization energy studies are of more significance in the hydrazobenzene series than in the hydrazine series since the former series may be expected to be less sensitive to molecular weight labilization than in the comparisons made on page 17. Some idea of the difference in extents of the effects of molecular weight may be derived from a consideration of the percentage differences in comparisons with 4,4'-dinitrohydrazobenzene. In the preceding energy comparison, the reference substance, hydrazobenzene, has a molecular weight which is 67.2 per cent of that of the substituted molecule while hydrazine has a molecular weight which is only 11.6 per cent of that of the substituted molecule.

The N - N bond data is still limited for substituted hydrazobenzenes although ϵ''_p for 4,4'-dinitrohydrazobenzene can be calculated to be - 4.1 Kcal./mole from its bond energy of 16.8 Kcal./mole and that of 20.9 Kcal./mole in the unsubstituted hydrazobenzene. This latter value was calculated from $-\Delta H_r$ of 1590.84 Kcal./mole reported in the last section of this thesis with the heat of combustion data of Anderson and Gilbert (4) of aniline in the following way.

The heat of the reaction for the combustion of hydrazobenzene may be written:

$$\Delta H'_R = 12 \Delta H_{f(\text{CO}_2)} + 6 \Delta H_{f(\text{H}_2\text{O})} - 2 \Delta H_{f(\phi-N)} - 2 \Delta H_{f(N-H)} - \Delta H_{f(N-N)}$$

and for the combustion of two moles of solid aniline

$$\Delta H''_R = 12 \Delta H_{f(\text{CO}_2)} + 7 \Delta H_{f(\text{H}_2\text{O})} - 2 \Delta H_{f(\phi-N)} - 4 \Delta H_{f(N-H)}$$

where $\Delta H'_R$ and $\Delta H''_R$ are the isobaric heats of combustion of hydrazobenzene and two moles of solid aniline, - 1590.84 and - 1616.06 Kcal. respectively. The subscripts f denote the heats of formation of the substances or bonds in parentheses. Subtracting the first equation from the second yields

$$-25.22 = \Delta H_{f(\text{H}_2\text{O})} - 2 \Delta H_{f(N-H)} + \Delta H_{f(N-N)}$$

where $\Delta H_{f(N-H)}$, the energy of the nitrogen - hydrogen bond, is assumed to be one-third the heat of formation of solid or gaseous ammonia, i.e. - 85.9 and 83.7 Kcal. respectively, from which

$$-\Delta H_{f(N-N)_s} = 25.32 \text{ Kcal.}$$

and

$$-\Delta H_{f(N-N)_g} = 20.92 \text{ Kcal.}$$

in contrast to the earlier values of 24.7 Kcal. (4) and 12.4 Kcal. (16).

An attempt to correlate the resonance stabilization and molecular weight labilization effects mathematically met with two difficulties, namely, the effect of steric hindrances on bond energies and the partial weakening of the nitrogen - nitrogen bond as a result of symmetrical resonance stabilization. The magnitudes of these two factors are not known although the former is presumed to be extremely small. The order of magnitude of the latter awaits the results of future studies proposed at the end of this section.

The fact that the N - N bond energy in hydrazobenzene is nearly that of the N - N bond energy in hydrazine may be taken to mean that the sum of the energies of labilization, $\sum \epsilon_l$, are equal to the sum of the stabilization energies, $\sum \epsilon_s$, where

$$\sum \epsilon_s = \epsilon_{sr} + \epsilon_{srd}$$

and

$$\sum \epsilon_l = \epsilon_{lm} + \epsilon_{lrb} + \epsilon_{lrs}$$

and

ϵ_{sr} = the energy of pure ortho, para resonance stabilization

ϵ_{srd} = the energy of resonance stabilization by withdrawal of the lone electron pair into the ring by acidic substituents

ϵ_{lm} = the energy of molecular weight labilization

ϵ_{lrb} = the energy of resonance labilization by repulsion of the lone electron pair away from the ring by basic substituents

ϵ_{lrs} = the energy of resonance labilization arising from distribution of the lone electron pairs along the N - N bond in symmetrically substituted hydrazobenzenes.

A program of study of the nitrogen - nitrogen bond energies of the following should yield much information of value in the ultimate quantitative interpretation of the several factors contributing to the bond strength. Comparisons of the N - N bond in 4,4'-dimethylhydrazobenzene and sym-dibenzylhydrazobenzene may be used to reduce the molecular weight labilization effects to zero and demonstrate the ortho resonance contributions. This study could then be extended to 2,2'-dimethyl and 2,6,2',6'-tetramethylhydrazobenzenes to demonstrate the effects of mixed ortho - para resonance and pure para resonance respectively, on the nitrogen - nitrogen bond. In the tetramethyl comparisons use of the effects of molecular weight differences on nitrogen - nitrogen bond would have to be applied to compensate for the two additional methyl groups. Finally, these results should be compared to results obtained from studies on the 3,3'-dimethyl and 3,5,3',5' tetramethylhydrazobenzenes to demonstrate the slight effect, if any, of meta-substitutions on the resonance stabilization and to further coordin-

ate the molecular weight labilization studies.

Extension of the data on the nitro-substituted hydrazobenzenes presented herein is to be encouraged. Investigations on 2,2'-dinitro-, 3,3'-dinitro-, 2,6,2',6'-tetranitro-, and 3,5,3',5'-tetranitrohydrazobenzenes would be the most fruitful in view of the present interpretations.

From an academic point of view, the possibility of investigating the effects of still other substituents including both acidic and basic groups cannot be precluded. Similarly, data on the N - N bond energy in unsymmetrically substituted nitro-, methyl-, amino-, halogen-, and acyl hydrazobenzenes would be desirable. The results of this study would reveal whether the symmetrical resonance labilization energy ϵ_{LRS} is of sufficient magnitude to be detected.

B. The energy of the nitrogen - nitrogen double bond

From the heat of combustion of hydrazobenzene reported in the section on thermochemical measurements, the energy of the nitrogen - nitrogen double bond, $N = N$, may be calculated using the heat of combustion of azobenzene (18) and the assumptions of the previous section with respect to the nitrogen - hydrogen bond energy.

Consideration of the molecular structures of hydrazobenzene and azobenzene reveals that the difference in their

heats of combustion arises from the difference in the N - N and N = N bonds, the energy of two N - H bonds, and the heat of combustion of two hydrogen atoms to liquid water. Neglecting the slight difference in crystal lattice energies and assuming that the resonance energies are of the same order of magnitude, the N = N bond energy in cis and trans azobenzene may be calculated from their heats of combustion, -1555.5 Kcal./mole and -1545.6 Kcal./mole (18) according to the following heat balances. For solid hydrazobenzene

$$12 \Delta H_{f(\text{CO}_2)} + 6 \Delta H_{f(\text{H}_2\text{O})}^* - 2 \Delta H_{f(\phi\text{-N})} - 2 \Delta H_{f(\text{N-H})} \frac{2}{3} - \Delta H_{f(\text{N-N})} = -1590.84 \text{ Kcal.}$$

and for solid cis azobenzene

$$12 \Delta H_{f(\text{CO}_2)} + 5 \Delta H_{f(\text{H}_2\text{O})}^* - 2 \Delta H_{f(\phi\text{-N})} - \Delta H_{f(\text{N=N})} = -1555.5 \text{ Kcal.}$$

subtracting

$$\Delta H_{f(\text{H}_2\text{O})}^* - 2 \Delta H_{f(\text{N-H})} \frac{2}{3} - \Delta H_{f(\text{N-N})} + \Delta H_{f(\text{N=N})} = -35.34 \text{ Kcal.}$$

where

$\Delta H_{f(\text{CO}_2)}$ = the standard heat of formation of carbon dioxide

$\Delta H_{f(\text{H}_2\text{O})}^*$ = the heat of formation of water from hydrogen atoms and molecular oxygen

$\Delta H_{f(\phi\text{-N})}$ = the heat of formation of the phenyl-nitrogen radical

$\Delta H_{f(N-H)}$ = the heat of formation of the N - H bond from solid ammonia (subscript s) or gaseous ammonia (subscript g)

$\Delta H_{f(N-N)}$ = the heat of formation of the N - N bond in solid hydrazobenzene from solid nitrogen or gaseous nitrogen atoms (subscripts s or g).

Substituting, using heats of formation in the solid state gives

$$-(171.7) - 2(-85.9) - (-25.32) + \Delta H_{f(N=N)_s} = -35.34 \text{ Kcal.}$$

and

$$-\Delta H_{f(N=N)_s} = 60.76 \text{ Kcal./mole}$$

while using gaseous heats of formation there results

$$-(171.7) - 2(-83.7) - (-20.92) + \Delta H_{f(N=N)_g} = -35.34 \text{ Kcal.}$$

and

$$-\Delta H_{f(N=N)_g} = 51.96 \text{ Kcal./mole.}$$

Since the N = N bond has an energy of formation of -51.96 Kcal./mole and since the N - N bond has an energy of formation of -20.92 Kcal./mole the formation of the second bonding pair requires approximately -31 Kcal.

Similar calculations of the N = N bond energies in trans azobenzene yield 70.66 and 61.86 Kcal, from which the energy of formation of the second bond in the trans isomer yields approximately 41 Kcal. for the gaseous bond. The difference in the two results from the cis and trans iso-

mers cannot be taken to mean that the true energy of the bond in one configuration is greater than in another since the crystal lattice energy difference in the two isomers is not known, however, the energy of formation of the second bond must prove to be > 35 Kcal. and less than 40 Kcal. since trans isomers are known to be generally more stable than cis isomers.

Using Gaydon's proposed change in the heat of dissociation of nitrogen the N - N bond energy is 43 Kcal. while the unsubstituted azobenzene N = N bond is 85.6 Kcal. which means that an additional 42.6 Kcal. are evolved on formation of the second bond.

Since the energy of the N = N double bond is of a greater order of magnitude than the single bond, errors arising from thermochemical measurements will be reduced proportionally in the azo compounds. The lone electron pairs in the azobenzenes are still available for resonance as they are in the hydrazobenzenes and other substituted hydrazines. For these reasons substituted azobenzenes lend themselves well to further investigations.

Since the results presented in this section of the present thesis indirectly support the new heat of dissociation of nitrogen, the N - N bond energies have been recalculated from the existing thermochemical data and presented in Table III.

TABLE III

SUMMARY OF THE APPARENT N - N BOND ENERGIES^a

Compound	N - N Bond Energy
Azobenzene (N = N)	82.6 Kcal./mole ^b
Hydrazine	43.0 Kcal./mole ^c
Phenylhydrazine	42.7 Kcal./mole ^d
Hydrazobenzene	37.5 Kcal./mole ^e
Dibenzoylhydrazide	34.3 Kcal./mole ^d
4,4'-dinitrohydrazobenzene	33.4 Kcal./mole ^f
Tetraphenylhydrazine	27.4 Kcal./mole ^d

a calculated using Gaydon's heat of dissociation of nitrogen of 225.0 Kcal./mole (26) and an energy for the N - H bond of 92.0 Kcal. estimated by Skinner (67).

b calculated from data of Corrucini and Gilbert (18).

c calculated from data of Hughes, Corrucini, and Gilbert (41).

d calculated from data of Anderson and Gilbert (4).

e calculated from data of this thesis.

f calculated from data of this author(16).

C. Bond energy and interatomic distances

Clark (14), Cherton (13), Kavanau (43,44), Fox and Martin (24), and Lagemann (48) have proposed empirical equations to describe the curves resulting from plotting the bond energy (and energy of dissociation), bond order, and interatomic distance for carbon - carbon bonds. Correlations involving these properties of the nitrogen - nitrogen bonds have received less attention. However, Lagemann (48) has extended an earlier equation of Kavanau (44)

$$D = a + b \left(\frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N$$

where

D = the interatomic distance in Angstroms

n_1, n_2 = the principal quantum numbers of the valence electrons in the bonded atoms

N = the bond order or multiplicity

a, b = constants determined by the specific atom pair,

by noting that a was proportional to the reciprocal of the sum of the atomic numbers Z and that b was directly proportional to Z so that

$$D = \frac{K_1}{Z} + K_2 Z \left(\frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N$$

where

K_1 = a constant, 12.45

K_2 = a constant, 0.0676.

Although this equation yields calculated bond lengths for hydrazine, azobenzene, and nitrogen which agree to better than one per cent with observed values (43) an extension of this equation is not possible until more is known of the multiplicity term N .

For the carbon - carbon bonds, $C - C$, $C = C$, and $C \equiv C$, Kavanau (44) has shown the multiplicity N to be related to the energy of the bond E and defines N by

$$N = N_0 \left[1 - \left(1 - \frac{E}{133} \right)^{1/2} \right]$$

where $N_0 =$ a constant, 4.00, which, when inserted in the above equation gives an expression by which the interatomic distances can be calculated from the energies of the bonds.

Development of a similar expression for the nitrogen bonds proved impossible since data for this series is limited.

However, an equation can be evolved for the nitrogen - nitrogen series based a hypothetical $X - N \equiv N - X$ structure whose triple bond energy was estimated to be ~ 85 Kcal. X is a low molecular weight atom or group.

The general form of this equation is similar to that proposed by Cherton (13) for the carbon - carbon bond series

$$E = (K - D)m$$

where K and m are constants for any given series, i.e. carbon - carbon, nitrogen - nitrogen, etc. Using the inter-

atomic distance for $X-N \equiv N-X$ structure as that in nitrogen gas, 1.095 A, and E of 20.0 Kcal. and D of 1.47 A in hydrazine (43) and solving the two simultaneous equations there results

$$E = (1.585 - D) 173.6$$

Using the bond length reported by Kavanau for azobenzene, 1.23 A, E can be calculated to be 61.67 Kcal. which agrees with the value from the calculations presented earlier of 61.86 for transazobenzene to 0.3 per cent. On this basis the interatomic distances for the nitrogen - nitrogen bonds whose energies have been reported can therefore be calculated from

$$D = 1.585 - E/173.6$$

The results of these calculations are presented in Table IV. From these bond lengths the multiplicities were calculated from the equation

$$D = \frac{K_1}{Z} + K_2 z \left(\frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N$$

which has been tested for azobenzene and hydrazine to better than 1.0 per cent (48). The results of these calculations are also presented in Table IV for tetraphenylhydrazine, dibenzoylhydrazide, hydrazobenzene, phenylhydrazine, and 4,4'-dinitrohydrazobenzene with the previously known values

for hydrazine and azobenzene. These calculations are based on assumptions for the hypothetical structure $X-N\equiv N-X$ and will therefore necessarily require revision when the nitrogen dissociation energy has been established and when further data is available on the N - N bond distances in other hydrazines and hydrazobenzenes.

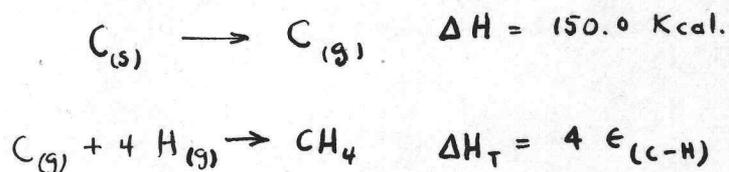
TABLE IV

N - N BOND DISTANCES AND MULTIPLICITIES
CALCULATED FROM THE EXPERIMENTAL BOND ENERGIES

Compound	E Kcal.	D A.	N
- N \equiv N -	(85.1)	1.095	3.00
Azobenzene	61.7	1.23	1.99
Phenylhydrazine	23.3	1.45	1.02 ₂
Hydrazobenzene	20.9	1.46 ₆	0.97
Hydrazine	20.0	1.47	0.96
Dibenzoylhydrazide	17.7	1.48 ₃	0.91
4,4'-dinitrohydrazobenzene	16.8	1.48 ₈	0.89 ₅
Tetraphenylhydrazine	10.5	1.52 ₅	0.77 ₅

APPARENT ENERGY OF THE CARBON - CARBON BOND
IN SOME STILBENES

The basis for most calculations of bond energies involving carbon is the equivalence of the four carbon - hydrogen bonds in methane similar to the assumption of equivalence of the three nitrogen - hydrogen bonds in ammonia. Using this assumption and the heats of sublimation of carbon, the energy of the carbon - hydrogen bond may be calculated from the following thermochemical equations

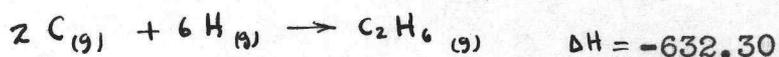


where ΔH_T is four times the energy necessary to decompose gaseous methane into normal atoms of hydrogen and carbon, using an average value for the heat of sublimation of carbon of 150,000 Kcal. From the heat of dissociation of hydrogen (10) and the heat of formation of methane, - 18,240 Kcal./mole (11)

$$4 \Delta H_b = -18,240 - 2(103,800) - 150,000$$

where ΔH_b is the energy, heat of linkage, or heat of formation of the carbon - hydrogen bond (C - H) and is therefore 93.96 Kcal.

This treatment may be extended to calculate the energy of the carbon - carbon single bond from the heat of formation of ethane, - 20,960 Kcal./mole (11) and from the equations



and

$$6 \Delta H_{f(C-H)} + \Delta H_{f(C-C)} = -632.30$$

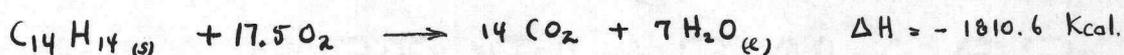
where

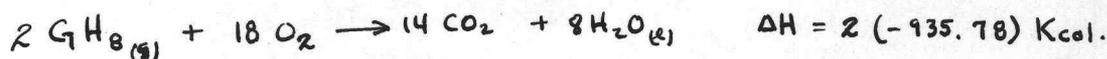
$$-93.96 \text{ Kcal.}$$

from the preceding calculation. The apparent energy of formation of the C - C bond is therefore -68.54 Kcal.

The C - C bond energy in the symmetrical diphenyl ethane, dibenzyl, may be calculated from the heats of combustion of solid dibenzyl and liquid toluene, -1810.6 Kcal. and -934.2 Kcal. using the heat of fusion of toluene of -1.58 Kcal./mole reported by Parks and Huffman (57).

Writing heat balances for the combustion reactions,





$$14 \Delta H_{f(\text{CO}_2)} + 7 \Delta H_{f(\text{H}_2\text{O})\text{g}} - \Delta H_{f(\text{C}_7\text{H}_8)} - \Delta H_{f(\text{C-C})} = -1810.6 \text{ Kcal.}$$

$$14 \Delta H_{f(\text{CO}_2)} + 8 \Delta H_{f(\text{H}_2\text{O})\text{g}} - \Delta H_{f(\text{C}_7\text{H}_8)} - 2 \Delta H_{f(\text{C-H})} = -1871.56 \text{ Kcal.}$$

Subtracting the two heat balances

$$\Delta H_{f(\text{H}_2\text{O})\text{g}} - 2 \Delta H_{f(\text{C-H})} + \Delta H_{f(\text{C-C})} = -60.96 \text{ Kcal.}$$

and substituting

$$-171.7 - 2(-93.96) + \Delta H_{f(\text{C-C})} = -60.96$$

from which an energy of the C - C bond of 77.18 Kcal. was calculated whereas a value of < 68.54 Kcal. would be expected as a result of molecular weight labilization and no resonance stabilization. Part of this apparent discrepancy may be attributed to this author's particular choice of the heat of sublimation of carbon. There has been much controversy concerning this value and there is evidence which points to each of the three values - 125.0 Kcal., - 136.0 Kcal., and - 170.0 Kcal. Pauling (59) has chosen the lowest value from which a bond strength of 68.5 Kcal. was calculated. Had the maximum value been chosen, 170 Kcal., the C - C bond strength would be approximately 79 Kcal.

Skinner (67) has pointed out that the simple assump-

tion that the C - H bond energy can be put equal to $\Delta H_{\rho(C-H)}$ in methane seems justifiable only in cases where C - H has the same bond length as it has in methane. For instance, spectroscopic measurements have shown the C - H bond length in ethylene to be 1.071 Å while in acetylene it is only 1.057 Å. Whereas this distance is 1.09₃ Å in methane, a calculation of the ideal covalent C - H bond is given by the sums of one-half the C - C and H - H bonds to be 1.142 Å. In fact, Stevenson has shown by electron impact studies that the bond strength of C - H in methane is 101 Kcal. while in ethane he found it to be reduced to 96 Kcal. Similar studies on the C - C bond strength showed it to vary from 83 Kcal. in ethane to 78 Kcal. in the central link in butane.

Using Stevenson's reduction of 5 per cent in the C - H bond energy in going from methane to ethane, a new C - C bond strength in ethane was calculated to be 96.44 Kcal. while in dibenzyl the C - C bond energy now becomes 67.8 Kcal., a far more reasonable value in view of the expected molecular weight labilization.

Here, as in the case of the N - N bonds discussed earlier, the relative magnitudes of the influence of various structures and substituents on C - C bond strengths may still be demonstrated. For the present purpose it would appear that any one of the sets of fundamental values could be assumed as a basis for comparisons until such time as more is known

of the heat of sublimation of carbon and until definite trends in variation of C - H bond energies with respect to their intramolecular positions are well established.

Considerable work has been done to establish the validity of one of the several proposed heats of sublimation of carbon (2,7, 32,34,35,46,47,53,55,76). Assuming the three values, 125.0, 136.0, and 170.0 Kcal., as the heats of sublimation, C - H and C - C bond energies have been calculated and are presented in the following table to indicate the influence of the heat of sublimation of carbon on these values.

Sublimation heat, Kcal.	C - H Kcal.	C - C Bond Energy, Ethane Kcal.	Dibenzyl Kcal.
125.0	87.7	56.16	64.66
136.0	90.5	61.6	70.18
(150.0	93.96	68.6	77.18)
170.0	98.96	78.6	87.18

The values in parenthesis were calculated using the mean heat of sublimation, -150 Kcal. The influence of variation of the C - H energy with position can easily be seen from this table since it would be expected that the C - C bond in dibenzyl would be less than that in ethane.

The energy of the carbon - carbon double bond, C = C, may be calculated from its heat of combustion to be 112.8 Kcal. if the heat of sublimation of 125.0 Kcal is used; if

- 136.0 Kcal. is used the bond energy becomes 123.76 Kcal. Applying Stevenson's correction of 5 per cent to the C - H bond, these energies become 130.3 Kcal. and 141.84 Kcal. respectively. A calculation of the energy of the carbon - carbon double bond in a substituted ethylene may be made from the heats of combustion of stilbene and solid toluene from the heat balances

$$14 \Delta H_f(\text{CO}_2) + 6 \Delta H_f(\text{H}_2\text{O}) - 2 \Delta H_f(\phi^{\text{CH}}) - \Delta H_f(\text{C}=\text{C}) = -1765.0 \text{ Kcal.}$$

$$14 \Delta H_f(\text{CO}_2) + 8 \Delta H_f(\text{H}_2\text{O}) - 2 \Delta H_f(\phi^{\text{CH}}) - 4 \Delta H_f(\text{C}-\text{H}) = -1871.6 \text{ Kcal.}$$

from which

$$\Delta H_f(\text{C}=\text{C}) = -106.6 - 2 \Delta H_f(\text{H}_2\text{O}) + 4 \Delta H_f(\text{C}-\text{H})$$

and substituting

$$\Delta H_f(\text{C}=\text{C})_s = -106.6 - 2(-171.7) - 4(90.46)$$

and

$$- \Delta H_f(\text{C}=\text{C})_s = 125.04 \text{ Kcal.}$$

$$\Delta H_f(\text{C}=\text{C})_g = -106.6 - 2(-171.7) - 4(87.7)$$

and

$$- \Delta H_f(\text{C}=\text{C})_g = 114.0 \text{ Kcal.}$$

Applying the 5 per cent correction the energies of these bonds become 96.5 Kcal. and 107.0 Kcal depending on the use of 125 or 136 Kcal. for the heat of sublimation of carbon.

Similar heat balances may be made from the heats of combustion of cis 4,4'-dinitrostilbene, - 1572.95 Kcal./

mole and trans 4,4'-dinitrostilbene, -1568.75 Kcal./mole determined by Anderson (3) and for cis paranitrostilbene, -1723.00 Kcal./mole and for trans paranitrostilbene, -1716.19 Kcal./mole determined by this author (16).

For two moles of paranitrotoluene, $-\Delta H_R = 888.6$ Kcal. per mole as reported by Kharasch (45),

$$14 \Delta H_f(\text{CO}_2) + 7 \Delta H_f(\text{H}_2\text{O}) - 2 \Delta H_f(\text{C}_6\text{H}_4\text{NO}_2) - 4 \Delta H_f(\text{C-H}) = -1777.2 \text{ Kcal.}$$

and for one mole of cis 4,4' dinitrostilbene

$$14 \Delta H_f(\text{CO}_2) + 5 \Delta H_f(\text{H}_2\text{O}) - 2 \Delta H_f(\text{C}_6\text{H}_4\text{NO}_2) - \Delta H_f(\text{C=C}) = -1572.95 \text{ Kcal.}$$

and subtracting

$$2 \Delta H_f(\text{H}_2\text{O}) - 4 \Delta H_f(\text{C-H}) + \Delta H_f(\text{C=C}) = -204.25 \text{ Kcal.}$$

from which

$$-\Delta H_f(\text{C=C}) = 222.7 \text{ Kcal.}$$

using a C - H bond energy of 90.46 Kcal. and

$$-\Delta H_f(\text{C=C}) = 211.7 \text{ Kcal.}$$

using a C - H bond energy of 87.7 Kcal. Applying the Stevenson correction here yields 204.6 Kcal. and 194.1 Kcal. respectively.

Similar calculations on the trans isomer yield 226.9 Kcal., 216.05 Kcal., 208.8 Kcal. and 198.3 Kcal.

From the heat of combustion of one mole of para nitrotoluene, -888.6 Kcal. and of one mole of solid toluene, -935.78 Kcal.

$$14 \Delta H_f(\text{CO}_2) + 7.5 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_4\text{NO}_2) - \Delta H_f(\text{C}_6\text{H}_5) - 4 \Delta H_f(\text{C-H}) = -1824.38$$

and from cis paranitrostilbene

$$14 \Delta H_f(\text{CO}_2) + 5.5 \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}^{\text{CH}}_{\text{NO}_2}) - \Delta H_f(\text{C}^{\text{CH}}) - \Delta H_f(\text{C}=\text{C}) = -1723.0$$

and subtracting

$$2 \Delta H_f(\text{H}_2\text{O}) - 4 \Delta H_f(\text{C}-\text{H}) + \Delta H_f(\text{C}=\text{C}) = -101.36 \text{ Kcal.}$$

from which

$$- \Delta H_f(\text{C}=\text{C}) = 119.82 \text{ Kcal.}$$

using a C - H bond energy of 90.46 Kcal. and

$$- \Delta H_f(\text{C}=\text{C}) = 108.78 \text{ Kcal.}$$

using a C - H bond energy of 87.7 Kcal. Applying the bond correction here yields 101.7 Kcal. and 91.24 Kcal.

While the trans isomer has an apparent bond energy of 126.63 and 115.59 Kcal., a much lower energy than this would be expected from the decreased molecular weight labilization in the mono-nitrostilbene as compared to the di-nitro stilbene. Had any other values been chosen for the heat of sublimation of carbon the apparent energy in the cis and trans para nitrostilbenes would be still less than that in the 4,4' dinitro compounds. Since the heats of fusion of these substances do not differ markedly and since errors in these values of fifty per cent would alter the bond energies by only a few per cent some other factors are apparently contributing. The resonance energy differences may be of a greater order of magnitude than would be expected on the basis of the present knowledge of aromatic molecules or there may be wider variation in the C - H bond energy than originally anticipated.

Some quantitative measurements of these two factors will have to be made before a full interpretation of the preceding results can be presented. Pauling and coworkers (60), Sherman (66), and Van Vleck and Sherman (75) have estimated resonance energies by taking the differences between the energy of the molecule computed from additivity of bond energies and experimental results. However, Van Vleck (75) points out that such results are more of qualitative than quantitative significance. Kistiakowsky (46) has estimated resonance energies with somewhat greater precision from studies on the heats of hydrogenation of hydrocarbons. As mentioned earlier a more reliable method for detecting the existence of resonance and estimating the magnitude of the resonance energy is based on the measurements of internuclear distances by means of electron diffraction studies and hence falls outside the scope of the present thesis. Electron impact and similar studies will have to be made on many ethylene derivatives before quantitative corrections can be made to the C - H bond.

THERMOCHEMICAL MEASUREMENTS

The necessity for the redetermination of the heat of combustion of hydrazobenzene has been realized for some time (4)(16) and since the interpretation of the foregoing N - N bond energies depends on an accurate value for this quantity its heat of combustion was redetermined by means of an adiabatic calorimeter similar to that proposed originally by Holman (38) and Richards (62,64) and modified to advantage by Daniels(20), Hatland (33), Maass and Barnes (52), Roth and Eyman (65), and Swietoslowski (71). Discussions of the adiabatic calorimeter have been treated fully by Barry (6) and White (77,78,80) while special emphasis has been placed on various phases of its use by Adams and Brown (1), Aston and Eidinoff (5), Beauseigneur (8), Conn, Kistiakowsky, and Roberts (17), Daniels (21), Ewing (23), Gucker, Pickard, and Planck (31), Hess and Gramkee (36), Higgins (37), Lange and Monheim (49), Lange and Rounsefell (50), Matui (54), Parr and Staley (58), Richards and Burger (63), Sturtevant (70), Uchida (73), Urban (74), White (79), Williams and Daniels (81), and Winand (82). The specific heat of the calorimeter was redetermined and shown to be in agreement with earlier values from this laboratory (3,16,19,40).

A recalibration of the thermometric bridge was made and a determination of the heat of combustion of a nitrogen-

containing secondary standard was also determined to further establish the validity of the results determined in this laboratory and to show that certain approximations made in the calculations of the heats of combustion of nitrogen-containing substances influence the results to such a small amount as to be within experimental error. After the specific heat of the calorimeter had been determined to be equivalent to the earlier value of 2607.34 cal./degree Centigrade, the heat of combustion of hydrazobenzene was determined to be 1590.84 Kcal./mole. Since the 34-junction thermocouple was inadvertently broken before the heat of combustion of hippuric acid could be determined a new thermocouple was constructed as nearly similar to the previous one as possible. A new determination of the specific heat of the calorimeter was then made and the effective specific heat shown to be 2608.13 cal./degree Centigrade.

The heat of combustion of hippuric acid was then determined and shown to agree, perhaps fortuitously, exactly with the more precise value of 1007.8 Kcal./mole determined by Huffman (39).

The Bureau of Standards, United States Department of Commerce, supplied standard sample number 39f for both calibrations of the calorimeter. Freezing point measurements indicated a purity of 99.98 per cent. The data obtained from the combustion of the benzoic acid is given in Tables

V and VI for the calibration before and after the installation of the new thermocouple.

The hippuric acid was Eastman Kodak Company White Label and was recrystallized three times from distilled water and dried at 105° C. for 48 hours and over P_2O_5 for from 72 to 96 hours. The heats of combustion determined thereon fall well within the limits of Huffman's deviations on a considerably larger number of determinations. These results are presented in Table VII.

The hydrazobenzene was prepared by the reduction of azobenzene with sodium hydroxide and zinc dust in an inert atmosphere. After drying over P_2O_5 for 72 hours under vacuum in a desiccator flushed three times with nitrogen, the melting point in air was recorded to be $128.5 - 129.5^{\circ}$ C. Further drying in vacuum for 200 hours failed to produce any measurable change in the melting point. However, this is of little consequence since the calorimetric results themselves are more sensitive to impurities than variations of the physical constants. The results of the determinations of the heats of combustion of hydrazobenzene are presented in Table VIII.

TABLE V

DETERMINATION OF THE ENERGY EQUIVALENT
OF THE CALORIMETER AT 25.0° CENTIGRADE

True mass of sample in grams	Corrected ^a ΔR ohms	Heat cap- acity of calorimeter and products	Energy equivalent of calori- meter	Dev. ^b from mean
0.51066	0.12461	2611.65	2607.89	+ 0.49
0.53041	0.12953	2609.62	2605.85	- 1.55
0.68513	0.16714	2612.33	2608.47	+ 1.07

a ΔR was corrected for the heat of stirring and for the heat of combustion of the iron wire used to ignite the sample.

b Since only a limited number of runs were made these results were used as qualitative check only of the earlier determination by this author.

Average $S_p = 2607.40$ cal./°C.

Average deviation from mean ± 1.03 cal./°C.

TABLE VI

DETERMINATION OF THE ENERGY EQUIVALENT
OF THE CALORIMETER AT 25.0° CENTIGRADE

True mass of sample in grams	Corrected ^a ΔR ohms	Heat cap- acity of calorimeter and products	Energy equivalent of calori- meter	Dev. from mean
0.50552	0.12313	2613.07	2609.36	+ 1.23
0.58240	0.14222	2609.74	2605.93	- 2.20
0.32212	0.07860	2611.74	2608.07	- 0.06
0.50740	0.12378	2612.38	2608.61	+ 0.48
0.48355	0.11799	2611.75	2608.00	- 0.13
0.68742	0.16771	2612.16	2608.29	+ 0.16
0.54458	0.13308	2611.59	2607.80	- 0.33
0.63933	0.15593	2612.95	2609.13	+ 1.00
0.55031	0.13432	2610.97	2607.18	- 0.95
0.48527	0.11841	2611.75	2608.00	- 0.13
0.64614	0.15763	2612.30	2608.46	+ 0.33

a ΔR was corrected for the heat of stirring and for the heat of combustion of the iron wire used to ignite the sample.

Average $S_p = 2608.13$ cal./°C.

Average deviation from mean $\pm 0.63_6$ cal./°C.

TABLE VII

HEAT OF COMBUSTION OF HIPPURIC ACID

Run	True mass of sample in grams	ΔT^a °C.	Total ^a heat cal.	Heat from HNO ₃ calories	cal./gm.	Dev. from mean
1	0.62611	1.35121	3529.30	6.28	5626.89	- 1.73
3	0.55161	1.19102	3134.38	5.95	5628.83	+ 0.21
4	0.65667	1.41881	3705.92	7.08	5628.61	- 0.01
5	0.49490	1.06900	2792.13	5.14	5631.41	+ 2.79
7	0.53290	1.15056	3005.18	6.35	5627.37	- 1.25

a corrected for the heat of stirring and for the combustion of the iron wire.

Average $-\Delta U_{\theta} = 5628.62$ cal./ gm.

Average deviation 1.25 cal./ gm.

$-\Delta U_{\theta} = 1008.46 \pm .22$ Kcal./ mole

$-\Delta U_R = 1007.67 \pm .22$ Kcal./ mole

$-\Delta H_R = 1007.82 \pm .22$ Kcal./ mole

TABLE VIII

HEAT OF COMBUSTION OF HYDRAZOBENZENE

Run	True mass of sample in grams	ΔT^a °C.	Total ^a heat cal.	Heat from HNO ₃ calories	cal./gm.	Dev. from mean
2	0.52382	1.73607	4533.19	8.06	8638.70	+5.18
4	0.57457	1.90300	4969.13	9.52	8631.86	-1.66
5	0.54255	1.79623	4690.27	8.06	8630.01	-3.51
6	0.62410	2.06713	5397.77	10.30	8632.40	-1.12
8	0.53667	1.77770	4641.95	8.05	8634.53	+1.01
9	0.54006	1.78870	4670.80	8.16	8633.58	+0.06

a corrected for the heat of stirring and for the heat of combustion of the iron wire.

$$\text{Average } -\Delta U_B = 8633.52 \text{ cal./gm.}$$

$$\text{Average deviation } \pm 2.09 \text{ cal./gm.}$$

$$-\Delta U_B = 1590.61 \pm .39 \text{ Kcal./mole}$$

$$-\Delta U_R = 1589.65 \pm .39 \text{ Kcal./mole}$$

$$-\Delta H_R = 1590.84 \pm .39 \text{ Kcal./mole}$$

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