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HEATS OF LINKAGE OF C-H AND N-H BONDS FROM VIBRATION SPECTRA

By Joseph W. Ellis

Abstract

The visible and near infra-red absorption data for several representative molecules are taken from a previous paper and fitted to the formula of an anharmonic vibrator, $\nu^n = \omega^0 n - bn^2$. The mechanical frequencies, $\omega^n = \omega^0 - 2bn$, are evaluated and plotted. Assuming that these frequencies originate in oscillations between a hydrogen atom and the remainder of the molecule, the restoring force residing in the C-H and N-H bonds, the heats of linkage of these bonds are calculated. The method originated by Birge and Sponer for the determination of the heats of dissociation of non-polar, diatomic, gaseous molecules is used. The heats of linkage for a hexane C-H bond is calculated to be 97,000 cal/mol in fair agreement with the 92,500 cal/mol value obtained thermochemically for its homologue, methane. The values for the heat of linkage vary among the different types of molecules, having the relatively high value of 117,000 cal/mol for benzene C-H bonds. The value for the N-H heat of linkage is calculated for one substance, aniline. It evaluates as 113,000 cal/mol and is believed to agree with the 101,000 cal/mol obtained thermochemically for an ammonia N-H bond within the limits of determination of the former value. A possible explanation of the doubleness of the absorption bands observed in the spectra of several substances, notably hexane and cyclohexane, is sought in two types of carbon valence. This doubleness indicates a slight inequivalence in the energy content of two types of C-H bond.

CONSIDERABLE success has been obtained by Birge[1] and others in the evaluation of the heats of dissociation of numerous non-polar, diatomic, gaseous molecules from band spectra data. The method rests upon the classical quantum theory of a quantized anharmonic vibrator and is made possible through the ability of the band spectroscopist to identify and evaluate successive mechanical oscillation frequencies characteristic of the molecule.

The quantum theory predicts the following stationary energy states due to vibration of a diatomic molecule in which the force coefficient varies with the amplitude of the motion:

$$E^n = h\omega^0 n - hbn^2 \tag{1}$$

Here n is a vibration quantum number defining the state, ω^0 the vibration frequency for an infinitesimal amplitude, b a constant arising from the non-linearity in the force law and h Planck's constant. The theory also postulates a series of radiation frequencies

$$\nu^n = \omega^0 n - bn^2 \tag{2}$$

to arise from transitions between these stationary states. Each stationary state has associated with it a mechanical frequency ω^n determined by

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[1] Birge, Molecular Spectra in Gases, Bull. Nat. Research Council, **57** (1927).

$$\omega^n=(1/h)\cdot(\partial E^n/\partial n)=\omega^0-2bn \tag{3}$$

The maximum vibrational energy which such a molecule can have is

$$E^n_{\text{max}}=h\int_0^{n_0}\omega^n dn=h(\omega^0)^2/4b \tag{4}$$

where n_0 designates the limiting stationary state, in which $\omega^n=0$ and beyond which the molecule dissociates. Putting $\omega^n=0$ in Eq. (3) gives $n_0=\omega^0/2b$. $E^n{}_{\text{max}}$ is equal to D, the work of dissociation of the molecule. If ν^n and ω^n are measured in spectroscopic frequency units, cm^{-1}, D may be calculated in calories per mol by

$$D=hc(\omega^0)^2N/4bJ \tag{5}$$

where N is the Avogadro number, J the mechanical equivalent of heat in ergs per calorie and c the velocity of light.

The heats of dissociation for non-polar diatomic molecules, obtained by Birge and others, have been calculated only after successive values of ω^n have been evaluated from the most general types of band spectra and identified with definite values of n. In many instances an expression for ω^n, less simple than that of Eq. (3), including additive terms in higher powers of n, has to be used. Graphically $E^n{}_{\text{max}}$ is obtained by plotting values of ω^n against values of n and measuring the area under the curve, the terminals of the curve being ω^0 and n_0 respectively; or rather, by plotting $\omega^{n+1/2}$ against $n+\frac{1}{2}$ since the values of n are obtained from optical data and $\omega^{n+1/2}$ is gotten from

$$\omega^{n+1/2}=\Delta\nu^n/\Delta n=\nu^{n+1}-\nu^n \tag{6}$$

The series of similar absorption bands in the spectra of organic liquids, data for some of which are tabulated in a previous paper,[2] are capable within the limits of experimentation of having their frequencies expressed by the quadratic formula of Eq. (2). This lends support to an hypothesis already advanced by the author that these absorption frequencies originate in anharmonic vibrations within the C-H and N-H bonds. A more definite physical picture of the molecular behavior is the vibration of the hydrogen atom with respect to the remainder of the molecule, the restoring force in the motion originating in the C-H and N-H bonds. Thus, for example, it will be assumed in this paper that the series for benzene arises from changes in vibrational energy of the hydrogen atom with respect to the phenyl radical. It is not assumed that the rest of the molecule represents a rigid structure. The similarities in the infra-red spectra of a large number of compounds indicate, however, that any other vibrations within the absorbing molecule influence the particular series in question only to a minor extent.

The above hypothesis would require that there be an electric moment existing within the chemical bond. That the bond is essentially homo-polar, however, is evident from the fact that the hydrogen atom comes off as an

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[2] Ellis, Phys. Rev. **32**, 906 (1928).

atom rather than as an ion. In the analogous case of a diatomic gas molecule it is for those types in which dissociation results in the separation into un-ionized atoms that the equations of the simple forms, (1)–(4) inclusive, are most nearly obeyed.

In Table I are tabulated the wave-lengths, frequencies and their first differences for members of the C-H series of hexane, cyclohexane, benzene, chloroform and aniline; and of the N-H series of aniline. In assembling the table the values considered most nearly correct are taken from Table I of the preceding article.[2] In Figs. 1–6 these data are plotted with values of n as ordinates and values of ν^n and ω^n as abscissas. The upper set of abscissa values are for the mechanical frequencies. The curves to the right and to the left are associated with the ω^n and ν^n values respectively.

TABLE I. *Wave-lengths, frequencies and their first differences, for certain organic liquids.*

n	λ	ν^n	ω^n	n	λ	ν^n	ω^n
		Hexane				Cyclohexane	
1	3.42μ	2,925 cm^{-1}		1	3.49μ	2,865 cm^{-1}	
2	1.74	5,750	2,825 cm^{-1}	2	1.75	5,720	2,855 cm^{-1}
3	1.195	8,370	2,620	3	1.20	8,340	2,610
4	0.920	10,880	2,510	4	0.930	10,750	2,420
5	0.749	13,340	2,460	5	0.758	13,180	2,430
6	0.640	15,650	2,300	6	0.648	15,410	2,230
7	0.562	17,800	2,150	7	0.571	17,510	2,100
		Benzene				Chloroform	
1	3.28μ	3,050 cm^{-1}		1	3.32μ	3,010 cm^{-1}	
2	1.68	5,950	2,900 cm^{-1}	2	1.69	5,920	2,910 cm^{-1}
3	1.145	8,730	2,780	3	1.15	8,700	2,780
4	0.874	11,440	2,710	4	0.880	11,350	2,650
5	0.713	14,020	2,580	5	0.721	13,880	2,530
6	0.608	16,430	2,410	6	0.614	16,300	2,420
7	0.532	18,800	2,370				
8	0.476	21,000	2,200				
		Aniline C-H				Aniline N-H	
1	3.25μ	3,075 cm^{-1}		1	2.90μ	3,450 cm^{-1}	
2	1.68	5,950	2,875 cm^{-1}	2	1.50	6,670	3,220 cm^{-1}
3	1.145	8,730	2,780	3	1.03	9,710	3,040
4	0.870	11,500	2,770	4	0.790	12,650	2,940
5	0.712	14,040	2,440	5	0.648	15,420	2,770
6	0.608	16,430	2,390				

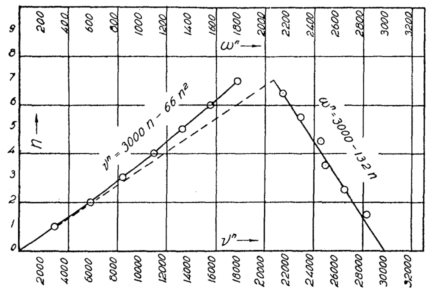

Fig. 1. Hexane.

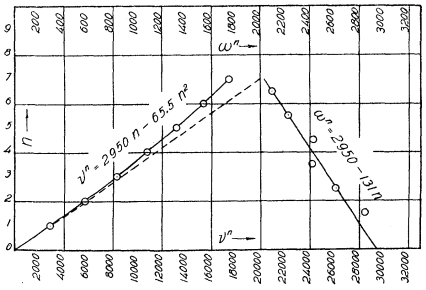

Fig. 2. Cyclohexane.

Since many of the bands for hexane and cyclohexane were observed as double, a mean wave-length value had to be used. Because of the approximately equal intensities of the components of the latter substance an arithmetical mean was used. The shorter wave-length component of the hexane bands was more intense than its companion; consequently, a wave-length value was arbitrarily chosen differing from the stronger component by an amount equal to one-third of the separation value.

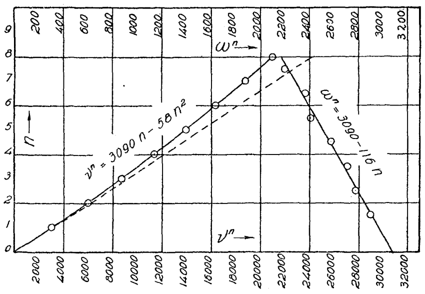

Fig. 3. Benzene.

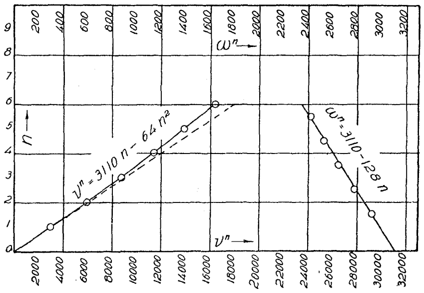

Fig. 4. Chloroform.

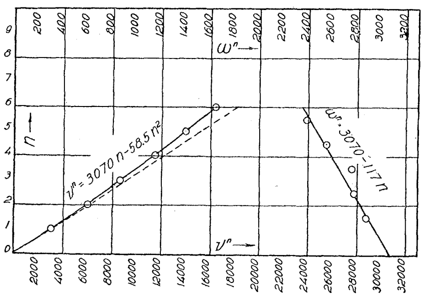

Fig. 5. Aniline C-H

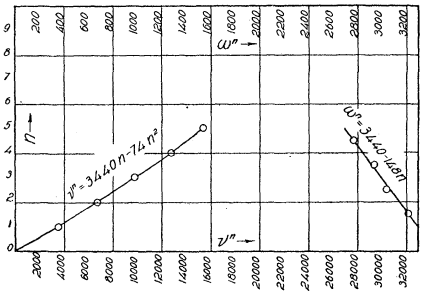

Fig. 6. Aniline N-H

There is no detectable deviation of any optical value from the parabolic curve. The broken line represents the form which the curve would take if the optical frequencies followed a truly harmonic law. This was calculated on the assumption that the frequency of the first series member was accurately determined. The points of the ω^n curve, calculated from the differences in successive ν^n values could scarcely be expected to yield a great degree of accuracy because of the lack of precision in determining the optical values. As mentioned above, ordinate values of $n+\frac{1}{2}$ have been used in the ω^n graph.

The ω^0 and n_0 values were determined from the intercepts of the ω^n curve while the b constant was determined from its slope.

Using the classical quantum[3] theory developed for diatomic gaseous

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[3] Although the classical quantum model is used throughout this paper, it is the author's understanding that the conclusions arrived at are equivalent to those which would be obtained from the newer wave-mechanics.

molecules, an attempt has been made to evaluate the heats of linkage, i.e., the heats of dissociation, of the C-H bonds for the five organic molecules listed above and for the N-H bonds of aniline. Eq. (5) has been used for this purpose. As an example of the use of this formula a calculation of D for the benzene C-H bond is shown:

$$D=\frac{6.55\times10^{-27}\times3\times10^{10}\times(3090)^2\times6.06\times10^{23}}{4\times58\times4.186\times10^7}=117{,}000 \text{ cal/mol.}$$

Values of ω^0, n_0, b and D are tabulated in Table II. The calculations of D are based upon the assumption that the ω^n curve is linear not only over the measured range but also over its extrapolated range. It is true that the ω^n values are not accurately enough determined to enable a detection of any possible slight regular deviation from linearity if it exists. The assumption that, even though there should be strict linearity over the lower range of ω^n values, there is no radical deviation from it in the extrapolated region finds its best support in the exact linearity over long ranges in the case of non-polar diatomic molecules.

TABLE II. *Calculated values of molecular constants for certain organic liquids.*

Liquid	ω^0	b	n_0	D
Hexane	3000 cm^{-1}	66	23	97,000 cal/mol
Cyclohexane	2950	65.5	23	94,000
Benzene	3090	58	27	117,000
Chloroform	3110	64	24	108,000
Aniline C-H	3070	58.5	26	117,000
Aniline N-H	3440	74	23	113,000

An attempt has been made to evaluate the accuracy of the measured values of D. This has been done entirely upon the basis of the deviations of the plotted points in the ω^n curves, assuming that Eq. (3) is obeyed throughout the region of extrapolation. In determining the values for the C-H bonds in hexane, benzene, chloroform and aniline it is believed that errors no greater than ±5 percent can arise from inaccurate drawing of the ω^n curves. Possible errors larger than this may arise in the other two instances.

It will be observed that the values of the heats of linkage of the C-H bond vary from 94,000 cal/mol for cyclohexane to 117,000 cal/mol for benzene. This variation lies well outside the limits of experimental determination. The chemist, having only indirect methods of measurement of this quantity, has frequently assumed its equality for all organic molecules.

The best value determined from thermochemical data with which to compare the D values of Table II must be sought in the methane molecule, CH_4. The energy to be associated with each of the four C-H linkages in this molecule may be obtained by taking one-fourth of the result obtained by adding together the heat of formation of methane, the heat of sublimation of carbon and twice the heat of formation of the hydrogen molecule. The best values obtainable for these are respectively 19,000,[4] 141,000[5] and 105,000 cal/mol.[6] These yield

$$\tfrac{1}{4}(19{,}000+141{,}000+2\times 105{,}000)=92{,}500 \text{ cal/mol}.$$

Experiments on the heats of combustion indicate that the heat of linkage of the C-H bond is about the same for all members of the paraffine series. Thus we are somewhat justified in comparing the 92,500 cal/mol value determined thermochemically for methane with the 97,000 cal/mol determined optically for hexane, which is a homologue of methane. It is probable that these two values check within the limits of the determinations of the constants involved. Since the contribution of the heat of formation of methane is small, and since the heat of formation of hydrogen is probably quite accurately determined, any appreciable inaccuracy in the chemical determination of D for the methane C-H bonds must be sought in the value of the heat of sublimation of carbon. It is doubtful whether any great accuracy can be assigned to the value quoted for this quantity, inasmuch as values ranging from about 100,000 cal/mol to 287,000 cal/mol are given in the literature. The two most recent determinations are by Ryschkewitsch[7] and Kohn and Gückel.[5] The former obtains a value around 100,000 cal/mol but considers the determination of the latter investigators as the more probable because of the better agreement of their value with that predicted by the Nernst heat theorem.

The optical determination yields a value expressing the energy necessary to remove the first hydrogen atom from the molecule, whereas the thermochemical value is a statistical one. It is entirely probable that this quantity varies with the number of atoms already removed.

The appreciably greater value for the unsaturated molecule, benzene, than for the saturated molecules, hexane and cyclohexane, is of interest. This variation seems reasonable; for, whatever be the nature of the distribution of the valence forces around a carbon atom in the benzene molecule, it would seem that the C-H bond as well as the C-C bonds should be affected by the lack of saturation. The greater value for the bonding force, manifest through the higher value of the fundamental frequency ω^0, and the greater value of the calculated heat of linkage for this molecule seem consistent with the above hypothesis.

It was pointed out in the preceding paper that many of the C-H series members are double. In fact, insofar as the resolving power of the instruments used permit a detection of a separation, it seems that a series is made up of either doublets or singlets throughout. Thus the bands of benzene, chlorobenzene, aniline and chloroform are single, while hexane, cyclohexane, acetone, ethyl acetate and the methyl groups of toluene and m-xylene yield doublets. The singleness of the benzene series and of that characteristic of

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[4] Landolt-Börnstein Tables.

[5] Kohn and Gückel, Naturwiss., **12**, 139 (1924).

[6] Bichowsky and Copeland, Jl. Amer. Chem. Soc., **50**, 1315 (1928).

[7] Ryschkewitsch, Zeits. f. Electrochem., **31**, 54 (1925).

the phenyl radical is consistent with the chemist's assertion of the equivalence of the six substitution positions of benzene. This conclusion has also been deduced by Brackett[8] from the relative sharpness of the benzene bands between 0.8μ and 2.6μ as compared with the corresponding bands of the paraffine compounds.

A possible cause for the duplicity of the bands of certain of the compounds is sought in this paper in the inequivalence of the four carbon valencies. Mrs. Lonsdale[9] has made an exhaustive study of the physical evidence indicating such an inequivalence and concludes that there are probably two each of two different types of carbon bond. The difference is geometrical but Mrs. Lonsdale asserts that corresponding physical and chemical differences might be anticipated.

The approximate equality in the intensity of the two components of the doublets of cyclohexane can be accounted for by assuming that successive hydrogenations of benzene involve the bringing into action of identical valence bonds, these being of the type opposite to those of the original benzene linkages.

There seems to be some discrepancy in the ratios of intensities as recorded by different observers for chain hydrocarbons, although the shorter wavelength components always appear with the greater intensity. Thus the record of Meyer, Bronk and Levin[10] of the 3.39, 3.48μ band of hexane[11] shows an intensity ratio of about 3 or 4 to 1. As nearly as can be visually estimated the ratio is at least that great for the higher frequency members of the hexane series determined in this investigation. Barnes and Fulweiler[12] give as a result of a microphotometer determination of the intensities of the two components of the 0.912, 0.932μ (our $n=4$) and the 0.745, 0.760μ (our $n=5$) bands of pentane, and for the corresponding bands for decane and tetradecane, a ratio of 4 to 3. A possible partial explanation for these apparent discrepancies may be found in the fact that isomeric forms may have been present in some of the investigations. Furthermore, the intensity of series members may decrease more rapidly for one component than for its companion.

It has been asserted that the bands of benzene are single. Higher resolution, however, shows that such bands are not monochromatic, but have in themselves a double structure. This is clearly shown in the record of Meyer, Bronk and Levin.[10] Similarly, the components of the bands of the chain compounds show a doubleness within themselves. This type of doubleness is assumed in the present paper to be the fundamental nature of a band arising from vibrational energy changes within a single type of C-H bond.

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[8] Brackett, Phys. Rev., **31,** 917 (1928).

[9] Lonsdale, Phil. Mag. **6,** 433 (1928).

[10] Meyer, Bronk and Levin, J.O.S.A. & R.S.I., **15,** 257 (1927).

[11] Although these investigators used hexane in a vapor form, this use of their data seems justifiable on account of the good agreement throughout of the positions of their bands with those determined with liquid hexane.

[12] Barnes and Fulweiler, Jl. Amer. Chem. Soc., **50,** 1033 (1928).

The first, second and fifth series members for toluene and m-xylene are of a three-fold nature; that is, in addition to the strong benzene type of bands there are the weaker doublets which are here credited to the C-H bonds of the methyl groups. This is of interest in connection with toluene, for this molecule may be considered as a phenyl derivative of methane. Although the data are not extensive enough to evaluate the heat of linkage for this type of bond in toluene, its value probably lies between those for benzene and hexane. This estimation is made from the fact that the ω^0 constant is about equal to that of hexane while the b constant, judged from the divergence from linearity among the frequency values observed, more nearly approximates that for benzene. The greater intensity of the shorter wave component for $n=1$ in the curve for toluene by Meyer, Bronk and Levin would permit us to assume that the bonding of a CH_3 group to the phenyl radical always involves the same type of bond, thus leaving within the methyl group two of one type of bond and one of the other. The observations of the present papers upon the second and fifth series members are not accurate enough to permit this interpretation.

It is difficult to reconcile some of the notions of this paper with the usual interpretation of some of the bands of hydrocarbon vapors and gases, for example, the 3.31μ band of methane which has been measured with a spectroscope of high resolving power by Cooley.[13] If it were permissible to identify this band of methane with vibrations between one of the H atoms and the remaining CH_3 group, the effect of increasing molecular weight upon the position of the band could be studied by comparing it with the analogous absorption maxima in higher homologous members of the methane series. From the theory of the quantized anharmonic oscillator there should be an approximately linear relation between the reduced mass of the vibrating molecule and the square of the fundamental frequency arising from these oscillations. Assuming that the 3.31, 3.39 and 3.43μ bands as given by the same observer, Coblentz,[14] arise from oscillations between one of the hydrogen atoms and the remaining alkyl radical, we might expect a linear relation between the squares of the wave-length values and the reduced mass of the vibrator. Table III gives the summarized data in this instance and Fig. 7 shows the resulting approximately linear relationship. The reduced mass here is calculated upon the basis of the mass of the hydrogen atom as unity.

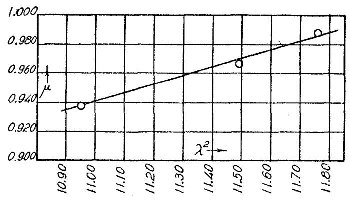

Fig. 7.

If the five percent difference between the value of the heat of dissociation determined thermochemically for a methane C-H bond and optically for a hexane C-H bond represents a true difference, and if the cause for this discrepancy were to be sought in the former determination, one or both of the

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[13] Cooley, Astrophys. J., **62**, 73 (1925).

[14] Coblentz, Publication of the Carnegie Institution, **35** (1905).

following two causes, already intimated above, might be suggested: (1) an inaccuracy in the value of the heat of sublimation of carbon used; (2) the fact that the value of the heat of formation of the methane molecule leads to an average value for the heat of linkage of a C-H bond.

TABLE III. *Comparison of reduced mass of vibrator with the square of the wave-length.*

Molecule	Liquid	M_R*	μ	λ	λ^2
Methane	CH_4	15	0.938	3.31μ	10.95
Ethane	C_2H_6	29	0.967	3.39	11.49
Hexane	C_6H_{14}	85	0.988	3.43	11.76

* M_R refers to the mass of the radical on the basis of the mass of the hydrogen atom as unity.

Of the diatomic molecules for which the heat of dissociation has been determined from band spectra data, only one, namely CO, contains a carbon atom. The value of D determined by Birge and Sponer[15] comes out too high. It is of interest to note that a slightly higher value for the heat of sublimation of carbon would bring into good agreement the optically and chemically determined values for both the CO molecule and the hexane C-H bond.

If the above possible discrepancy is to be accounted for on the basis of the statistical nature of the value of the heat of formation of CH_4, it would have to be assumed that successive removals of hydrogen atoms become easier, that is, that the bonding force in a CH molecule is looser than in a C-H bond of the methane molecule. This hypothesis finds some support in considerations of the following paragraph.

Certain electronic bands found at 3900A and 4300A in the spectra of burning hydrocarbons are now fairly definitely assignable to diatomic CH molecules.[16] From measurements upon these bands the value of ω^0 has been approximately determined as 2800 cm^{-1}.[17] Mulliken asserts that the CH molecules emitting these bands must exist in a low-lying energy state rather than in an electronically excited state. This fact makes it justifiable to compare the value of ω^0 for this molecule with that determined for a hexane C-H bond. Applying the equation of a harmonic vibrator, which would hold approximately for the motion with smallest amplitudes,

$$\omega^0 = (1/2\pi c)(K/\mu)^{1/2}$$

we get

$$\frac{K_1}{K_2} = \frac{\mu_1(\omega_1^0)^2}{\mu_2(\omega_2^0)^2} = \frac{0.987 \times (3000)^2}{0.923 \times (2800)^2} = 1.23$$

where K_1 and K_2 are the force coefficients for the hexane C-H bond and the CH molecule respectively, ω_1^0 and ω_2^0 the fundamental mechanical frequencies and μ_1 and μ_2 the reduced masses in these two instances. Thus we

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[15] Birge and Sponer, Phys. Rev., **28**, 259 (1926).

[16] Mulliken, Phys. Rev., **30**, 785 (1927).

[17] Molecular Spectra in Gases (Ref. 1, p. 230).

see that this calculation leads to a 23 percent greater value for the bonding force for the hexane C-H bond than for the CH molecule.

No great accuracy can be claimed for the calculated value of the heat of linkage of the N-H bond. It will be observed that, in addition to the three bands previously identified by the author as originating in the N-H bond[18] one more has been measured thermally for aniline and a fifth one, found in the records of Russell and Lapraik,[19] has been redetermined in connection with this investigation. The wave-length value for the second member of this series seems upon redetermination to be 1.50μ. The band at 2.8μ identified in Bell's[20] records as the fundamental band of the series seems to be slightly inaccurately located. If it is given the value of 2.90μ found in Bell's later record for diphenylamine[21] it fits the series more accurately. This reassignment of value is partially justified by the fact that the higher series members for both aniline and diphenylamine occupy the same positions in the spectrum. The five optical frequencies yield four values of ω^n, through which the most reasonable straight line has been drawn. This line yields a value of 113,000 cal/mol for the heat of linkage of the aniline N-H bond. An accuracy better than ±15 percent can scarcely be claimed for this value.

A chemical value can be obtained for this quantity in the case of ammonia, NH_3, by taking one-third of the sum of the heat of formation of ammonia[3] plus one-half of the heat of formation of nitrogen[22] plus three-halves of the heat of formation of hydrogen.[5] This yields

$$\tfrac{1}{3}(12{,}000+\tfrac{1}{2}\times 268{,}000+\tfrac{3}{2}\times 105{,}000)=101{,}000 \text{ cal/mol}.$$

It is believed that these two values check within the limits of the optical determination. If the higher value determined for aniline does represent a true difference, its larger value might be explained by the increased tightening of the N-H bonds in aniline due to the effect of the unsaturation of the adjoining phenyl radical. That such a tightening does occur is evidenced by the higher frequency values for all of the bands as compared with the corresponding bands of the alkyl amines.

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University of California at Los Angeles,
August 14, 1928.

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[18] Ellis, Jl. Amer. Chem. Soc., **50,** 685 (1928).

[19] Russell and Lapraik, Jl. Chem. Soc., **39,** 168 (1881).

[20] Bell, Jl. Amer. Chem. Soc., **47,** 2192 (1925).

[21] Bell, Jl. Amer. Chem. Soc., **48,** 813 (1926).

[22] The average of the optical and chemical values given by Birge and Sponer (Ref. 15) is used here.