235. *The Heats of Formation of the* —N=N— *and* >C=N— *Bonds.*

By G. E. Coates and L. E. Sutton.

The apparent heats of formation of bonds, or bond energy terms, are still very useful data, notwithstanding that the technical difficulties attending their derivation from combustion data and their theoretical limitations have recently been emphasised.

The terms for the N=N and the C=N bond have been obtained by burning azo*iso*propane and *n*-butyl*iso*butylideneamine (Q_c = $1053{\cdot}_4$ and $1295{\cdot}_4$ kcals./mole respectively). On the basis of graphite $\longrightarrow$ carbon gas (^3P) − 126·3 kcals./mole and $N_2(g) \longrightarrow 2N(g)$ − 170·2 kcals./mole, these bond terms are 63·1 and 106.

Q_c values for benzylideneanil ($1639{\cdot}_3$), dibenzylidene-ethylenediamine ($2116{\cdot}_5$), dibenzylidene-azine ($1808{\cdot}_1$), and diphenylbutadiene ($2023{\cdot}_1$) have also been measured. From resonance energies in these and related compounds it is concluded that the bond energy term for C=N may vary from 96 to 106.

The chemical consequences of this variation and of that in the C=O bond are illustrated. The relevance of the new values to the polymerisation of multiple-bonded substances, and to the resonance energy in polyene systems is discussed.

From available data it is tentatively concluded that the π bonds in C=C, N=N, and C=N have much the same strength, though the σ bonds vary greatly. In triple bonds there appears to be a drastic reorganisation resulting in a regular change of strength from C≡C, through C≡N, to N≡N.

Great importance attaches to the amount of energy evolved when a bond in a molecule is formed. Direct methods of measuring such values in polyatomic molecules have been developed, *e.g.*, spectrographic methods (see review by Samuel, *Rev. Mod. Physics*, 1946, **18**, 103), electron-impact methods (Smyth, *ibid.*, 1931, **3**, 347; Smith, *Physical Rev.*, 1937, **51**, 263; Hipple, *ibid.*, 1938, **53**, 530; Stevenson, *J. Chem. Physics*, 1942, **10**, 291), and the identification of the heats of activation of certain thermal reactions with the energy necessary to break a particular bond (Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19; Andersen and Kistiakowsky, *J. Chem. Physics*, 1943, **11**, 6; Kistiakowsky and Van Artsdalen, *ibid.*, 1944, **12**, 469; Andersen and Van Artsdalen, *ibid.*, p. 479; Andersen, Kistiakowsky, and Van Artsdalen, *ibid.*, 1942, **10**, 305).

These methods are still not of wide application, however, and most values have been obtained by analysing the heats of forming a whole molecule from its constituent atoms, on the assumption that this gross energy is the sum of the heats of forming the individual bonds (Sidgwick and Bowen, *Ann. Reports*, 1931, **28**, 386; Sidgwick "The Covalent Link in Chemistry", Cornell, 1933, Chap. IV; Pauling and Yost, *Proc. Nat. Acad. Sci.*, 1932, **18**, 414; Pauling, "The Nature of the Chemical Bond", Cornell, 1940, Chap. IV). We have in this way sought to obtain values for the C=N and the N=N bond.

The difficulties attending the indirect thermochemical method are several. The primary assumption implies that all the bonds are strictly " localised " or independent; and if this is not so, the method fails, or at least runs into complications. The discrepancy between the actual values for the heats of forming certain molecules and those predicted on the assumption of additivity have indeed been used to detect and to measure the effects of particular kinds of non-localisation, especially that termed " resonance " (Pauling, *loc. cit.*; cf. Lennard-Jones and Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811); but other kinds are possible, *e.g.*, the overlap of bonding functions of adjacent or neighbouring bonds, hyperconjugation, steric repulsion, dipolar interaction, changes of bonding orbital; and the sorting out of these contributions has not been carried very far. Some deviations from additivity of up to 5—6 kcals./mole are observed in the paraffins, olefins, and alcohols (Rossini, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 21; Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1935, **57**, 876; Rossini, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 189) in which no " resonance " of the above-mentioned kind is to be expected.

Furthermore, the true heat of breaking a bond is a function not only of the molecule in which it is, but also of the fragments into which this is broken. If one or more radicals are formed, these may be stabilised or destabilised by changes in resonance energy, in bonding orbitals, or in steric energy.* This will cause the true value to differ from the average value which the analysis gives. There may be variations of heats of formation which compensate and so produce no obvious departure from additivity in the molecule as a whole. The actual heat of formation or dissociation of a particular bond cannot, therefore, be accurately identified with the average value of forming it from atoms, which is all that the thermochemical analysis can give. The distinction may be recognised by using different names for them; the energy for a particular bond, such as would be measured by a direct method, may be called the *bond energy*, while the thermochemical average may be called the *bond energy term* (Butler and Polanyi, *loc. cit.*). Long and Norrish (*Proc. Roy. Soc.*, 1946, *A*, **187**, 337) and Walsh (*Trans. Faraday Soc.*, 1947, **43**, 60) use " dissociation energy ", and " bond energy " or " bond heat of formation " respectively.

There are other difficulties too. One of the most serious is the continuing uncertainty about the heats of atomising some of the elements from their standard states, especially carbon and nitrogen (see later). The heat of promotion of carbon from its ^3P ground state into that in which it is ready to form four valencies (often said to be the ^5S state) is also very uncertain; and indeed the relevance of this energy to that of rupturing the first of four linkages formed by carbon (as in $CH_4 \longrightarrow CH_3 + H$) is not clear. If there is no demotion during rupture, this promotion energy, supposing it can be determined, gives the correct basis for making the bond energy terms approximately equal to the bond energies; but if there is any such demotion, it obviously does not. As a result of these uncertainties, the nominal bond energy terms may be very different from the true bond energies.

A further difficulty is that in general the thermochemical data cannot be corrected to absolute zero, but are reduced to some room temperature (18°, 20°, or 25°), so that the bond energy terms may be affected by the thermal energy of bond stretchings and bendings and group rotations.

The fraction which such a contribution makes to bond energy is small; and its importance in a discussion of absolute bond strengths would be trivial. In some hydrocarbons where it can be calculated, it is only about 0·5 kcal. per bond (Aston, *Chem. Reviews*, 1940, **27**, 59). Dewar has, however, suggested (*Trans. Faraday Soc.*, 1946, **42**, 767) that the total of the contributions may have an important effect upon the resonance energies as calculated by subtracting the sum of the bond energy terms for a normal structure from the observed heat of formation, and that this is the cause of the discrepancies between values so calculated and those derived from hydrogenation data (Dolliver, Gresham, Kistiakowsky, and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 831). This discrepancy proves to be caused by failure to use the appropriate value for H_a (C=C) (Cottrell and Sutton, *J. Chem. Physics*, 1947, **15**, 685). Kistiakowsky and his co-workers found that the heat of hydrogenation of a C=C bond increases as more alkyl groups are attacked, and they therefore used a value from *cyclo*hexene in deriving the benzene resonance energy. This was not done in calculations from combustion data : but when appropriate values from normal, or branched-chain olefins are used (see later), the discrepancies disappear. This substitution effect is almost as great at 0° K., and appears therefore to arise from some

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* Attempts to correlate bond energies and stretching force-constants (see, *e.g.*, Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223) are limited by the fact that the latter relate to quite small perturbations of the initial state, so the effect on them of such changes in the final states is uncertain, and may be small. The same may be true of bond lengths and electric dipole moments. All these characteristics do, however, afford an indication of whether an anomalous bond energy arises from a change in the initial or in the final state.

bonding change, though until zero-point vibrational energies are eliminated this is not certain (see Cottrell, *J.*, in the press).

Fortunately, for the calculation of differences in processes not involving a change in the total number of bonds, *e.g.*, heats of reaction, or resonance energies as differences between actual and additive heats of formation, bond energy terms are adequate, and the difficulties concerning heats of atomisation are irrelevant; but for the discussion of reaction velocity in relation to absolute bond strengths, or in the comparison of the strengths of different bonds, bond energies are necessary. Our primary aim was to obtain information for the first purpose.

The only compounds containing an N=N bond which are free from extra resonance appear to be the azo-paraffins. Azomethane is a gas at room temperature and is not suited to the combustion technique used in the present work, namely bomb calorimetry. Azo*iso*propane boils at 88·6° and was chosen instead. A compound containing the smallest possible number of bonds is, other things being equal, the best for this purpose, since the unknown bond energy is then a larger part of the total heat of formation. Azobenzene has the advantage of being readily obtainable and easily purified; but it is likely to have extra resonance. Published data for it are discussed later.

Compounds not stabilised by extra resonance and containing a C=N bond are not at all common. The only possibilities appeared to be some azomethines which result from the condensation between primary aliphatic amines and some higher aliphatic aldehydes. Lower aliphatic aldehydes give more complex, often polymerised products with amines. *n*-Butyl*iso*butylideneamine ($CH_3{\cdot}[CH_2]_3{\cdot}N{:}CH{\cdot}CHMe_2$) was chosen for the present purpose. The more readily accessible aromatic azomethines are of course likely to be stabilised by extra resonance; and by using the C=N value from the above compound we may expect to determine this. Combustion data were, therefore, obtained for benzylideneanil and dibenzylidene-ethylenediamine. In order to obtain further data, for related carbon and nitrogen systems, dibenzylideneazine (CHPh:N·N:CHPh) and diphenylbutadiene were also measured.

Heats of Atomisation.—The dissociation energy of hydrogen (H_a = 102·48 ± 0·02 kcals./mole at 0° K., for nH_2, Beutler, *Z. physikal. Chem.*, 1935, *B*, **29**, 315) and of oxygen (H_a = 117·0 kcals./mole at 0° K., Herzberg, " Molecular Spectra and Molecular Structure ", New York, 1939, p. 491) are known with a fair degree of certainty.

That of nitrogen, and the heat of atomising graphite are still uncertain. The choice appears to lie between high values for both, if the importance of the non-crossing rule be accepted (Gaydon and Penney, *Proc. Roy. Soc.*, 1945, *A*, **183**, 374), or low ones for both if the arguments of Herzberg (*Chem. Reviews*, 1937, **20**, 145; *J. Chem. Physics*, 1942, **10**, 306) and of van der Ziel (*Physica*, Eindhoven, 1937, **4**, 373) be preferred. Both possible values, in each case, are accurately known, but the choice between them is a matter of dispute (cf. Long and Norrish, *loc. cit.*; Valatin, *J. Chem. Physics*, 1946, **14**, 568). We shall not try to resolve this difficulty; so where absolute values are discussed we shall quote values on both bases, calling the lower ones the A series, and the higher ones the B series.

The heats of atomisation (in kcals./mole) which we shall take are given in Table I.

TABLE I.

		H_a (0° K.).	H_a (293·1° K.).
Carbon (^3P from graphite)	A	125·1	126·3
	B	170·4	171·6
Hydrogen		51·24	51·71
Oxygen		58·5	58·9
Nitrogen	A	84·6	85·1
	B	112·5	113·0

In all the values at 20° the atomic gases are assumed to be perfect. The carbon A values are based on 9·14 e.v. for H_a(CO) at 0° K. to give ^3P carbon (Herzberg, *loc. cit.*); the B values on 11·11 e.v. (Gaydon and Penney, *loc. cit.*); $-\Delta H_0$ for C(graphite) + 1/2 $O_2 \longrightarrow$ CO (gas) is taken as 27·2 kcals./mole (Rossini, *J. Res. Nat. Bur. Stand.*, 1939, **22**, 407); the value of $H_{293\cdot1} - H_0$ taken for graphite (0·25 kcal./g.-atom) is that given by Rossini and Jessup (*ibid.*, 1938, **21**, 491; cf. Pitzer, *Chem. Reviews*, 1940, **27**, 53).

The values of $H_{293\cdot1} - H_0$ for hydrogen and oxygen are those given by Pitzer (*loc. cit.*); that for nitrogen is from Giauque and Clayton (*J. Amer. Chem. Soc.*, 1933, **55**, 4885). The A values for nitrogen are based on 7·38 e.v. for H_a (N_2) at 0° K. (van der Ziel, *loc. cit.*) and the B values on 9·764 e.v. (Gaydon and Penney, *loc. cit.*).

EXPERIMENTAL.

Preparation of Materials.—Azo*iso*propane was prepared by the method of Lochte, Noyes, and Bailey (*J. Amer. Chem. Soc.*, 1922, **44**, 2556); b. p. 88·6° ± 0·1° (corr.). *n*-Butyl*iso*butylideneamine, prepared by the condensation of purified *iso*butaldehyde and *n*-butylamine, was dried over potassium carbonate and twice fractionated, the fraction of constant b. p. 142·7° ± 0·1° (corr.)/755 mm. being taken for combustions (Found : N, 11·13. Calc. : N, 11·02%). Since this work was done a series of other similar compounds has been described by Campbell, Sommers, and Campbell (*ibid.*, 1944, **66**, 82).

Benzylideneanil was prepared as described in *Org. Synth.*, Coll. Vol. I, p. 73, and was crystallised three times from alcohol, m. p. 52° ± 0·2° (corr.). Before use it was dried in a vacuum. Dibenzylidene-ethylenediamine, from benzaldehyde and ethylenediamine (Mason, *Ber.*, 1887, **20**, 267), kindly supplied by British Celanese Ltd., was crystallised from alcohol; m. p. 54° ± 0·2° (corr.).

Dibenylideneazine and diphenylbutadiene were prepared according to *Org. Synth.*, Coll. Vol. II, p. 395 and p. 229, respectively; m. p.s 93° ± 0·3° and 153° ± 0·3°.

Benzoic, hippuric, and salicylic acids, for use as calorimetric standards, were each thrice crystallised from distilled water, and dried in a vacuum over concentrated sulphuric acid, and then in a vacuum over phosphoric oxide. Gelatine capsules for the combustion of liquids were kept all together in a closed bottle for several months before use, so that they all attained the same water content.

Calorimetric Method.—The Griffin–Sutton bomb calorimeter (*J. Sci. Instr.*, 1933, **10**, 286) was used in this work and the normal procedure for measuring heats of combustion was followed. Temperatures were measured with a mercury thermometer, reading to 0·01°, which had been calibrated at the N.P.L. The water equivalent was determined by means of eight combustions of benzoic acid (R.M.S. error 0·1%) [heat of combustion = q = 6·319 kcals.$_{15}$/g. (vac.), First Report of the Permanent Thermochemical Commission, 1933, p. 2], and checked by eight combustions of hippuric acid and three of salicylic acid. The measured heat of combustion of hippuric acid was 5·637 ± 0·013 kcals/g., which is 0·15% greater than the accurate value 5·628$_8$ found by Huffmann (*J. Amer. Chem. Soc.*, 1938, **60**, 1171). The heat of combustion of salicylic acid, q = 5·240 ± 0·015 kcals./g., was 0·10% greater than the value given by Keffler (*J. Physical Chem.*, 1929, **33**, 37). The bomb was filled with oxygen at 25 atm., but heats of combustion were corrected to atmospheric pressure by the method of Washburn (*Bur. Stand. J. Res.*, 1933, **10**, 525). The vacuum correction was applied to all weights. The random error is estimated to be not more than ± 0·25%, a degree of accuracy which is poor in comparison with that attained by modern precision technique, but sufficient for the purpose of obtaining bond energies in view of the numerous other errors which arise.

Results.

(All energy terms are given in kcals./mole.) *Azo*iso*propane.* From five combustions, Q, the heat of combustion per mole, was 1053·$_4$ ± 0·3 kcals. n-*Butyl*iso*butylideneamine.* Five combustions, Q = 1295 ± 2·4. *Benzylideneanil.* Five combustions, Q = 1639 ± 1·7. *Dibenzylidene-ethylenediamine.* Four combustions, Q = 2116·5 ± 2·0. *Dibenzylideneazine.* Five combustions, Q = 1808·0 ± 3·1. *Diphenylbutadiene.* Five combustions, Q = 2023·0 ± 1·6. The following approximate heats of vaporisation and sublimation, obtained by means of Trouton's rule, were corrected to 20° (latent heats of fusion were assumed to be 4) : azo*iso*propane, $L_{v.}^{20°}$ = 8·5 ± 0·5; *n*-butyl*iso*butylideneamine, 10 ± 0·5; benzylideneanil, $L_{s.}^{20°}$ = 20·5 ± 0·5; dibenzylidene-ethylenediamine, 22 ± 0·5; dibenzylidene-azine, 22·3 ± 0·5; diphenylbutadiene, 22·3 ± 0·5.

Heats of formation were calculated with the use of Rossini's data for the heats of combustion of graphite and hydrogen (*loc. cit.*), *viz.*, $\mathrm{C(graphite)} + \mathrm{O_2} = \mathrm{CO_2}$, $\Delta H_{25}° = -94{\cdot}03$; $\mathrm{H_2} + 1/2\ \mathrm{O_2} = \mathrm{H_2O_{(l.)}}$, $\Delta H_{25}° = -68{\cdot}32$. Using these values and the heats of atomisation given in Table I, the atomic heat of formation (H_a) at 20° of a gaseous compound $\mathrm{C}_a\mathrm{H}_b\mathrm{O}_c\mathrm{N}_d$ is related to its (positive) heat of combustion Q by

$$-H_a\ (\mathrm{A}) = Q + L_{v(s.)}^{20°} - (126{\cdot}3 + 94{\cdot}0)a - (51{\cdot}71 + 34{\cdot}16)b - 58{\cdot}9c - 85{\cdot}1d$$

and

$$-H_a\ (\mathrm{B}) = Q + L_{v(s.)}^{20°} - (171{\cdot}6 + 94{\cdot}0)a - (51{\cdot}71 + 34{\cdot}16)b - 58{\cdot}9c - 113{\cdot}0d$$

The errors in these standard values are so much less than those in Q and L_v that they have no appreciable effect upon the uncertainty in H_a.

In these equations, bond energies and atomic heats formation derived from series A in Table I are labelled (A), and those from series B are labelled (B). In the following calculations A values will be used : B values will be given later.* Hence the atomic heats of formation (A) of the compounds examined are : Azo*iso*propane, H_a = 1632 ± 0·5; *n*-butyl*iso*butylideneamine, 2002 ± 2·6; benzylideneanil, 2234 ± 2·0; dibenzylidene-ethylenediamine, 2930 ± 2·2; dibenylideneazine, 2454·5 ± 3·3; diphenylbutadiene, 2681·5 ± 1·8.

The numbers represent, in the language of the additivity rule, the sum of the energy terms of all the bonds in the molecule and any extra resonance energy. In order to derive the energy terms for the C=N and N=N bonds, it is, therefore, necessary to decide those for the other bonds, *viz.*, C–C, C=C, C–H, and C–N.

In the paraffin series the increase in Q per CH$_2$ group becomes constant at 157·4 kcals./mole† at pentane (g.) and hexane (g.) (Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 263). Hence, from the expression for H_a, the energy of one C–C bond and of two C–H bonds is 234·6 kcals./mole. By combining this with the heats of formation of the individual paraffins, a series of values for H_a(C–C) and

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* The formula for conversion from A into B values is $H_a(\mathrm{B}) = H_a(\mathrm{A}) + 11{\cdot}3x + 9{\cdot}3y$, where x and y are the numbers of ends of single bonds attached to carbon or nitrogen respectively for the bond in question.

† These and other values given by Rossini are actually for 298° K., not 293° : the difference is negligible.

H_a(C–H) are obtained which become steady at hexane (practically at pentane) at 60·3 for C–C and 87·15 for C–H [cf. 59·6 and 87·8, respectively, used by Pauling, *op. cit.*, p. 53, corrected to 126·3 for H_a(C, graphite)]. These values will be taken because the hydrocarbon radicals in the compounds we have examined contain three or more carbon atoms.

By combining these values with the heats of forming *n*-1-olefins (Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 269) a series of values for the C=C bond may be obtained which becomes steady at *n*-pent-1-ene at 101·2 kcals./mole which will be adopted (Pauling's value, *op. cit.*, p. 131, is 102).

For evaluating the resonance energy in benzene a different value is, however, appropriate, namely, that from *cis*-hex-3-ene, which is 102·9 kcals./mole; while for substituted benzenes, with carbon replacing hydrogen, each substitution is accompanied by a change in one double-bond value to 106·4, that taken from 2-methylbut-2-ene (cf. Cottrell and Sutton, *loc. cit.*).

To obtain the C–N bond energy term from the heats of combustion of amines (Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359) it is in most cases necessary to know the N–H bond energy term; this will be taken as 83·7 kcals./mole from data on ammonia (Pauling, *op. cit.*; *loc. cit.*). The following are the C–N terms calculated by using the above values for the C–C, C–H and N–H terms: Methylamine 47·8, ethylamine 48·1, *n*-propylamine 48·4, butylamines 54·8, *iso*amylamine 55·5, *n*-hexylamine 55·9, *n*-heptylamine 56·4, dimethylamine 45·4, diethylamine 51·0, di*iso*butylamine 53·4, di*iso*amylamine 54·8, triethylamine 53·1, tri*iso*butylamine 55·1, tri*iso*amylamine 50·4. The average value 52·5 will be used (Pauling gives 49·0, corrected to our value for H_a of C), but it cannot be regarded as very definite.

From the above data we calculate H_a for the –N=N– bond to be 65·7 kcals./mole in azo*iso*propane, without correcting for the possible difference in the *iso*- and *n*-propyl radicals: assuming the correction to be the same whether nitrogen or carbon is attached, the value is 63·1. The value of the >C=N bond in *n*-butyl*iso*butylideneamine is 106·1 kcals./mole or 104·8 corrected for the "iso-effect" (Pauling, *loc. cit.*, estimates this as 96).

For comparison with the –N=N– and the >C=N– bond, the energies of >N–N< and of –C≡N have been calculated from the heat of formation of hydrazine ($-\Delta H^{\circ}_{25^{\circ}\,\text{C.}\,(\text{g.})} = 22{\cdot}250$; Corruccini, Hughes, and Gilbert, *J. Amer. Chem. Soc.*, 1939, **61**, 2639) and the heat of combustion of methyl cyanide (Rossini and Bichowsky, "Thermochemistry of Chemical Substances", New York, 1936) as 20·4 and 151·6 kcals./mole, respectively. The C–O and C≡C bond energy terms have similarly been calculated from the data of Rossini (*J. Res. Nat. Bur. Stand.*, 1934, **13**, 189; *Amer. Pet. Inst. Rep.*, 1945) as 74·1 and 132·7 kcals./mole, respectively, the latter being the steady value from 1-ynes; Pauling gives 70·65 and 126·0, respectively.

From data in Bichowsky and Rossini's and Kharasch's compilations the value for H_a(C=O) is calculated as 143 kcals./mole in formaldehyde, 153·4 in acetaldehyde, 153·7 in propaldehyde, 156 in acetone, and 155 in methyl propyl ketone (cf. Pauling, *loc. cit.*).

The values are collected in Table II (p. 1193), which also includes values for O–O and O=O. The former is derived from water and hydrogen peroxide; the latter is Pauling's estimate of the value for the $^1\Delta$ state of molecular oxygen.

It may be re-emphasised that these are bond energy terms, *i.e.*, values chosen primarily to make possible the calculation of molecular heats of formation by simple addition. Different values for N–N and O–O have been proposed, *e.g.*, by Skinner (*Trans. Faraday Soc.*, 1945, **41**, 645; see, however, Glockler and Matlack, *J. Chem. Physics*, 1946, **14**, 504), by Walsh (*Trans. Faraday Soc.*, 1947, **43**, 60), and for O–O by Bolland and Gee (*ibid.*, 1946, **42**, 244); but these are bond energies, more appropriate in discussions of absolute bond characteristics, but not necessarily suitable for the above purpose. From the nature of the process used in deriving bond energy terms, which is to take as primary certain bonds which occur very often, *e.g.*, C–H and C–C, and to treat others as secondary or even tertiary, a variation in the heat of formation of the molecule as a whole may correspond to large variations in the term for one particular secondary bond. Thus, we see that the C=O term varies from 143 to 156; but, according to Skinner (*loc. cit.*), the change in the C=O bond itself is small, the alterations being mainly in the other bonds. This must be remembered if bond energy terms are used, *faute de mieux*, for bond energies. Artificial as the convention may seem, it is the simplest one.

DISCUSSION.

From the energy terms found for the –N=N– and the >C=N– bond we may now attempt to calculate resonance energies in some conjugated systems containing nitrogen.

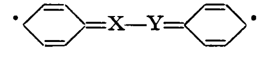
Corruccini and Gilbert (*J. Amer. Chem. Soc.*, 1939, **61**, 2925) and Richardson and Parks (*ibid.*, p. 3543) give values for the heats of combustion of *trans*-azobenzene and of stilbene, respectively. From them and from our own value for benzylideneanil the total resonance energies may be calculated. These may be uncorrected either for the benzene rings being substituted (p. 1188) or for the "*iso*-effects" in the –N=N– and the >C=N bond (see above); or corrections may be made for both, it being assumed where appropriate that the effect of substitution of hydrogen by nitrogen is the same as that by carbon.

Subtraction of the resonance energy in the benzene rings (36 kcals./mole in each) then gives that peculiar to the molecule as a whole. These values are collected below:

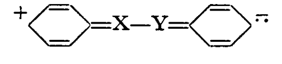
	Azobenzene.	Benzylideneanil.	Stilbene.
Uncorr.	12·7	5·1	15·7
Corr.	8·3	–0·6	8·7

There is no apparent theoretical reason why the value for benzylideneanil should be so low or so different from the others. Using the electron-pair-bond description, we should say that the main structures, besides the " normal " ones, contributing to the overall resonance are * (*a*), (*b*), (*b*′), (*c*), and (*c*′) together with corresponding ortho-structures.

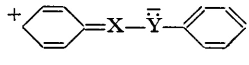
(*a.*)



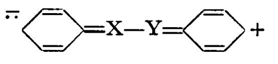
(*b.*)



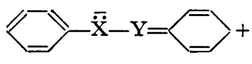
(*c.*)



(*b*′.)



(*c*′.)



The resonance energies will depend inversely upon the differences of energy between them and the " normal " structure. Now the differences for type (*a*) can be calculated from the bond energy terms given, and are 23·2, 42·6, and 42·6 kcals./mole for azobenzene, benzylideneanil, and stilbene, respectively. The corresponding ones for structures of type (*b*) would bear the same relation among themselves as would those above, though they would differ from the latter by the energy needed for the electron transfer common to all. The structures of type (*c*) and (*c*′) would show different relations. Nitrogen having a greater electronegativity than carbon, these energy differences would rise in the order azobenzene $<$ benzylideneanil $<$ stilbene. The resonance energy should therefore be, on the above arguments, greatest in azobenzene, least in stilbene, and intermediate in benzylideneanil; and not in that supposedly observed, *viz.*, stilbene $\gg$ azobenzene $>$ benzylideneanil.

The corrected particular resonance energies in dibenzylideneazine and in diphenylbutadiene are 4·4 and 23·6, respectively. Here also the difference is far larger than would be expected.

There is a further anomaly. If the above bond energy terms are used to calculate the total resonance energy in dibenzylidene-ethylenediamine, the value 58·7 (uncorr.) to 54·3 (corr.) kcals./mole is obtained; but this is 13·3 to 17·7 kcals./mole *less* than that in the two benzene rings alone. This result is highly improbable.

Yet again, these bond values give also a resonance energy of only 27·2 kcals./mole in pyridine, compared with 36 in benzene, which also seems unlikely.

It is probably significant that if a value of 96 kcals./mole be used as the energy term for the $C=N$ bond, instead of the 106 used above, then (i) the differences between the (*a*) type structures and the normal ones are nearly equal at 43·5, 42·6, and 42·6 kcals./mole for azobenzene, benzylideneanil, and stilbene; and the differences for the (*b*) type structures are likewise equal; so the resonance energies expected would be nearly equal in all these compounds; (ii) the extra resonance energy calculated in benzylideneanil from the observed Q_c rises to 15·2 (uncorr.) or 9·6 (corr.) kcals./mole, and so is nearly equal to those in azobenzene and in stilbene; (iii) the resonance energy in dibenzylideneazine becomes 24·4; (iv) the extra resonance energy in dibenzylidene-ethylenediamine is calculated as 7 (uncorr.) to 2·6 (corr.) kcals./mole; (v) that in pyridine is calculated to be 37·3 kcals./mole.

The use of this lower value, therefore, resolves several anomalies; but it would mean : (i) that while our values for the heats of combustion of azo*iso*propane, benzylideneanil, dibenzylideneazine, and dibenzylidene-ethylenediamine are probably good, that of *n*-butyl*iso*butylideneamine is 10 kcals./mole (0·8%) too low, *i.e.*, by about three times the random error which we deem probable; or (ii) that certain bond energies which we have supposed to be constant are not so; or (iii) that some of the bond energy terms used are slightly in error.

It has been shown that the anomalies exist whether or not the resonance energies are corrected for known constitutional effects. Furthermore, uncertainties in certain secondary terms such as that in the C–N bond are irrelevant to the present discussion. The resonance energy of azobenzene, for example, may be expressed : R(azobenzene) $=$ H_a(azobenzene, obs.) $-$ H_a(azo*iso*propane, obs.) $-$ $6H_a(C=C)$ $-$ $2H_a(C-C)$ $+$ $4H_a(C-H)$. Similar expressions may be written for the resonance energies of benzylideneanil, dibenzylidene-ethylenediamine, and pyridine.

We conclude, therefore, that the anomalies are due either to causes (i) or (ii) of those

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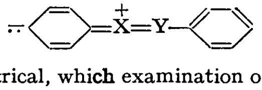
* Structures (*d*) or (*d*′) prove less likely to be important, because they would require the molecule to

(*d.*)



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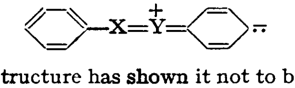


(*d*′.)

be axially symmetrical, which examination of the crystal structure has shown it not to be in stilbene and azobenzene.

considered. The possibility of the experimental value for *n*-butyl*iso*butylideneamine being erroneous can only be eliminated by further measurements on this and similar compounds.*

It is quite possible that the energy terms for the C=N and the C-N bond vary from compound to compound.† The aliphatic amines give a range of values for the latter (see above). Furthermore, the C=O bond term differs in formaldehyde, acetaldehyde, and the ketones by 13 kcals./mole (Pauling, *op. cit.*, and above).

We incline, therefore, to believe that this last explanation is the most probable; and we ascribe a value of 96—106 kcals./mole to the apparent heat of forming the C=N bond.

TABLE II.

Bond energy terms.

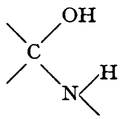
	(A)	(B)		(A)	(B)		(A)	(B)
C—C	60·3	83·0	N—N	20·4	39	C—N	52·5	73·1
C=C (1-ene)	101·2	146·5	N=N	63·1	100·3	C=N	96—106	137·5—147·5
C=C (*cis*-3-ene)	102·9	148·2				C≡N (HCN)	145·2	207·2
C≡C (1-yne)	132·7	200·5	N≡N	170	226	C≡N (cyanides)	151·6	213·6
C≡C (2-yne)	136·3	204·1						
	(A)	(B)					(A)	(B)
C—O	74·1	85·5	O—O	34·9		C—H	87·15	98·45
C=O (formaldehyde)	143	166·3	O=O	(96)		N—H	83·7	93·0
C=O (acetaldehyde)	153·4	176·7	O—H	110				
C=O (ketones)	156	179·3						

(A) based on low values for atomisation of carbon and nitrogen.
(B) on high values (p. 1189).

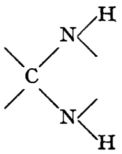
Some Applications of the Results.—Addition and condensation reactions. These bond energy terms are of interest in connection with certain organic reactions for they enable us to calculate roughly the heats of reaction (— ΔH) in the vapour phase for alternative courses, and thus to predict the probable course. No exact correlation can be expected because (*a*) the range of the calculated ΔH values is rather large (see below), (*b*) the reaction heats in condensed phases will be somewhat different, (*c*) changes of entropy may have an important effect, (*d*) dehydrating agents, which are often used, can increase the heat evolved by about 10 kcals. per mole of water formed. It is nevertheless of interest to see to what extent such simple predictions are useful.

The common reactions of primary amines with carbonyl compounds produce one of the groupings (1)—(3); (3) may follow from (1) (cf. Sprung, *Chem. Reviews*, 1940, **26**, 297).

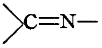
(1)



(2)



(3)



$>C=N-$

For (1), as the value of H_a for >C=O varies from 143 to 156, $-\Delta H$ ranges from 9·9 to − 3·1 kcals./mole; for (2) correspondingly (if H_a for C-N be taken as 52·5) from 14·6 to 1·6 kcals./mole; while for (3), if H_a for C=N be 96, it ranges from + 5·6 to − 7·4 kcals./mole, or, if H_a(C=N) be 106, from 15·6 to 2·6 kcals./mole.

We should, therefore, expect that the grouping (1) would be produced only by aldehydes, and then possibly only as an unstable intermediate, while the imino-group would be formed only if its individual heat of formation is near the upper limit (106 kcals./mole), or if it is stabilised by resonance, as in hydrazones, oximes, anils, or hydrobenzamide. As we have seen, the thermal data suggest that the >C=N- bond heat of formation will be large in imines only when it has large alkyl groups attached.

The grouping (2) is otherwise the most likely to be formed. Still more energy per N atom obviously can be liberated by further condensation to give a ring or chain product, with the

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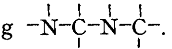
* Since the foregoing was written, Dr. H. D. Springall, using the bomb calorimeter at Manchester, has very kindly measured the heat of combustion at constant pressure of a sample of liquid *iso*butyl-*n*-butylideneamine supplied by Mr. K. B. Everard and one of the present authors (L. E. S.). He found a value of 1295 ± 2·5 kcals./mole which agrees within the limits of experimental error with the value which we found for the isomer (1295 ± 2·4).

† It may be noted that we are concerned here only with the variation of their *sum*.

‡ These would favour the formation of OH groups, for the hydrogen-bonding which results therefrom would stabilise the system.

repeating grouping  $-\overset{|}{N}-\underset{|}{\overset{|}{C}}-\overset{|}{N}-\underset{|}{\overset{|}{C}}-$. If the condensation is with ammonia, three C−N bonds per N atom might be formed. This, however, would produce a highly ordered structure, so it is likely to occur only if the molecules are small, *i.e.*, if the numbers of configurations which they can have relative to each other is small enough to make the attainment of the desired one reasonably probable. This may be one reason why it happens only with formaldehyde, a further reason being that the internal energy change is then greatest. The experimental facts are, on the whole, in agreement with these conclusions.

A reaction which appears to be made possible by resonance stabilisation in the product is the isomerisation of an azo-compound to a hydrazone. This involves the change $-N{=}N{-}CH_2- \longrightarrow -NH{-}N{=}CH-$ for which $-\Delta H$ is calulated to be only $-$ 5·8 to $+$ 4·2, if resonance energy be ignored. It may be remarked, however, that the azo-compounds for which this change is best known (see Taylor and Baker, " Sidgwick's Organic Chemistry of Nitrogen ", Oxford Univ. Press, 1937, p. 434) are those with one group aromatic, *e.g.*, $Ph\cdot N{:}N{-}CH_2{-}CH_3$, wherein there would be resonance stabilisation in both reactant and product, but more in the latter.

Polymerisation : resonance energy in polyene systems. Sidgwick (*loc. cit.*) drew attention to the fact that for the single, double, and triple bonds in the carbon–carbon series the ratios of the heats of formation are as $1 : <2 : <3$, whereas for the nitrogen–nitrogen series they are as $1 : (>2) : >3$, while for the carbon–nitrogen series they appear to be fairly accurately as 1 : (2) : 3. The exact values of the ratios depend upon the latent heat values taken for carbon and nitrogen. The qualitative nature of the relation is independent of these, however; and so, too, are the calculated heats of the bond reactions (ignoring resonance energies) (*a*) $X{=}Y \longrightarrow 2X{-}Y$ or (*b*) $3X{\equiv}Y \longrightarrow 3X{=}Y + 3X{-}Y$, which are given in Table III. The tendencies to polymerise, or not, are clearly marked save in the carbon–nitrogen and carbon–oxygen series. Polymerisation in these two will turn upon the bond energy term value for the particular compound considered, on temperature and concentration, and on possible resonance or steric energy, or the complication in shape of the molecules.

TABLE III.

$-\Delta H$ (kcals./mole).

	C—C bonds.	N—N bonds.	C—N bonds.	C—O bonds.
(*a*)	19·4	− 22·3	−1 to +9	−7·8 to +5·2
(*b*)	87·3	−259·5	−9·3 to +20·7	—

If, after the fashion of Fox and Martin (*J.*, 1938, 2106), the curves of bond energy against bond order are drawn for carbon–carbon, carbon–nitrogen, and nitrogen–nitrogen bonds, the accompanying figure is obtained; and it might be expected, following these authors' line of thought, that from bond orders as defined by Penney (*Proc. Roy. Soc.*, 1937, *A*, **158**, 306) the heats of formation of bonds in polyene systems could be derived by interpolation.* Were this so, the resonance energy in, *e.g.*, benzene would be six times the difference between the ordinate from the carbon–carbon curve, for order 1·623, and the ordinate for order 1·5 from the *chord* drawn between the points on this curve for orders 1 and 2. On this view, we could say that it arises partly from the change in order, which changes the ordinate obtained from the chord (and so gives rise to the contribution R_1), and partly from the effect of curvature, which gives rise to the additional contribution R_2. Now Penney defines the bond order as a function of the spin vectors of the π electrons on the six atoms on the ring : it is, therefore, independent of the nature of the atoms. The same is true of the bond order as defined by Coulson (*Proc. Roy. Soc.*, 1939, *A*, **169**, 413) provided that the atoms are all the same. For the hypothetical molecule N_6 the bond order would also be 1·623, but because the curvature of the energy–order graph for nitrogen–nitrogen bonds is positive, R_1 and R_2 are opposed; so there should be much less resonance energy—roughly one-quarter of that in benzene.

Further consideration of the problem shows, however, that no such simple interpretation of energy–order curves is theoretically justified (Cottrell and Sutton, *Quart. Reviews*, in the press). Penney intended his bond order to be applied to the chord between the points for order 1 and 2; and Coulson applied his order either to the chord or to a curve giving a correction for compression of the single bond and for stretching of the double one, which curve would have *positive* curvature

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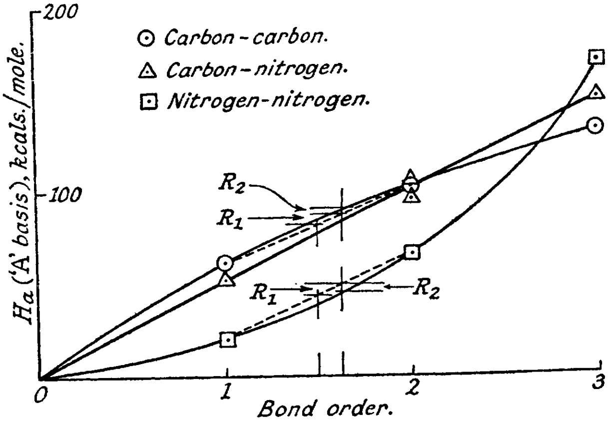
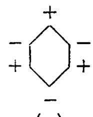
* This could only be done absolutely if the correct latent heat of vaporisation of graphite to quadrivalent carbon were known; for the slope and curvature of the energy–order curve depends on it.

instead of the negative curvature apparent in the figure for carbon–carbon bonds. Furthermore, it is not even an empirical truth that the correct bond energy in benzene can be obtained by interpolation in the way first indicated : the value so obtained is too high. If Pauling's bond order (1·5) be used, the value is too low. For the present, therefore, the only conclusion to be drawn is that measurements of resonance energy in azines and azoles are badly needed to throw light on this question.

In passing, it may be noted that the definition of bond order is less simple for carbon–nitrogen bonds than for the others. The electronegativities of carbon and nitrogen being different, there may be polar contributions in these bonds. Penney's definition of bond-order is based on the electron-pair-bond approximation and it therefore takes no account of polar structures. The molecular orbital method brings these in, though arbitrarily; so it might be expected that Coulson's definition (*loc. cit.*), based on this approximation, would be more suitable.



The part of this bond order due to π electrons, the mobile bond order, is, however, a function of the products of the coefficients a_r, a_s, etc., of the atomic orbitals required to build up the molecular orbital; it is large only when the products of the coefficients for neighbouring atoms are simultaneously large : the products for non-neighbours do not count. For the extreme case of a fully ionic structure (*e*) the mobile bond order would, therefore, be zero; and it is a maximum when a_r, a_3, etc., are all equal, *i.e.* it is really a measure of the covalent bond order, and in fact approximates very closely to the order as defined by Penney (in benzene it is 1·667). The use of such energy–order curves as the above to discuss resonance energy is even less justified, therefore, when the system contains carbon–nitrogen bonds.



(*e*.)

Bond energies. In conclusion, some remarks will be made about the absolute values of the bond energy terms, *i.e.*, regarded as bond energies. Values on both the A and the B basis will be considered in the hope of reducing the uncertainty of the discussion.

For this purpose, the B values are probably more useful, because for C–H and C–C they are roughly equal to the observed bond energies 103 and 83 respectively (Butler and Polanyi, *Nature*, 1940, **146**, 129; Bangham, *ibid.*, 1941, **147**, 542; Stevenson, *loc. cit.*; Anderson and Kistiakowsky, *loc. cit.*). In fact, the effective quadrivalent atomisation energy for carbon may be taken to be 170—190 kcals./g.-atom from these observations. A similar " practical " basis for nitrogen is still lacking.

On either basis, the absolute differences between the heats of forming double and single bonds are not very different for carbon–carbon, nitrogen–nitrogen, carbon–nitrogen (lower limit for C=N), and possibly oxygen–oxygen (see Table IV). That for carbon–oxygen is, however, markedly different; and that for carbon–nitrogen is also appreciably different if the upper limit value for C=N be taken. The differences between the values for triple and double bonds vary greatly.

The difference, Δ, between H_a(C=N) and the arithmetic mean of H_a(C=C) and H_a(N=N) is almost the same (12·5 kcals./mole) as the Δ value for single bonds (12·1), if the lower-limit value of 96 for H_a(C=N) be used. This would mean that for the second bond in the C=N bond the effective electronegativity difference between carbon and nitrogen is zero. If the upper limit of 106 be used, the double-bond difference is about twice as great (22·5) as the single-bond one, so

TABLE IV.

	H_a (X=X)—H_a (X—X).		H_a (X≡X)—H_a (X=X).	
	(A)	(B)	(A)	(B)
C—C	40·9	63·55	31·2	53·9
N—N	42·7	61·3	104·3	123·1
C—N	43·5—53·5	64—74	45—55·5	66—76·5
O—O	(61)			
C—O	69—82	81—94		

the electronegativity difference for the second bond of the double bond is then the same as that for the first (0·7).

The H_a values for C–O and C=O exceed the corresponding arithmetic means by 26·5 and 51, *i.e.*, the effective electronegativities are much the same for both parts of the double bond (0·9); H_a(C≡N) is almost exactly the arithmetic mean of H_a(C≡C) and H_a(N≡N) [151·2 (A) or 213·2 (B) kcals./mole].

The variation in the H_a values for triple bonds is much less than in those for single bonds; H_a(N≡N) is 1·28 (A) or 1·13 (B) times H_a(C≡C), but H_a(N–N) is only 0·34 (A) or 0·47 (B) of H_a(C–C).

These data suggest certain conclusions. One is that the strength of the $p\pi$ bond in C=C and N=N is nearly independent of the nature of the atoms, and of the strength of the σ bond. This may be so in C=N also; but under some conditions the $p\pi$ bond is stronger, presumably because it develops partial ionic character. It may be true also in O=O; but it certainly is not in C=O, again probably because the bond has partial ionic character.

In going from the double to the triple bonds, there seems to be a drastic reorganisation. This is not altogether surprising. In the double-bonded state, the σ bond can be formed by a variety of atomic orbitals, from p to hybridised sp^2: the only condition is that one p orbital on each atom shall be left free to form the π bond. This may explain the relatively constant character of the first π bond. When, however, a second π bond has to be formed, to give a triple bond, the bonding orbitals for the σ bond are much more restricted: they must be formed from one s and one p atomic orbital. This may involve a considerable change in the σ bond.

The similarity and regularity of the three triple-bond energy terms may arise from this fixation of atomic bonding orbitals; and they may also indicate that the C≡N bond is predominantly covalent. Nitrogen is more electronegative than carbon; so in a tertiary amine there is some piling up of negative charge on the nitrogen atom. In a triple C≡N bond, there is, however, a further compression of the bonding electrons, and the repulsion energy which this causes might reduce the contribution per electron to ionic character. The polarity of the C≡N bond may arise largely from the unshared nitrogen electrons.*

The surprisingly large ratio of H_a(N≡N) to H_a(N–N), *viz.*, 8·33 (A) or 5·8 (B), has been said to show that the N≡N bond is abnormally strong. As we have seen, however, it is not much stronger than C≡C; so a more significant observation appears to be that the N–N is abnormally weak compared with C–C. The reason for this weakness is not at present clear. Obviously it is insufficient to say that the atomic bonding orbitals used by nitrogen may be p orbitals, which form less strong bonds than do the sp^3 orbitals which must be used by tetrahedral carbon, unless we explain why these poor orbitals are used. The usual point made is that nitrogen forms only three bonds, so hybridisation is less complete; but the weakness is so pronounced that this explanation hardly seems adequate. The same problem appears to arise in the O–O bond.

The authors wish to thank Professor C. A. Coulson for helpful discussions, Messrs. T. L. Cottrell and L. Orgel for checking some of the calculations, and Imperial Chemical Industries Ltd. for a grant toward the cost of the research.

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* Pauling (*loc. cit.*) offers the alternative explanation that the N≡N bond is largely ionic.