Ground States of Conjugated Molecules. XII.[1] Improved Calculations for Compounds Containing Nitrogen or Oxygen[2]

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Abstract: This paper describes an extension of the completely self-consistent treatment of part XI[1] to conjugated molecules containing nitrogen or oxygen. In this the total heat of atomization is expressed as a sum of bond energies of localized σ bonds, the compression energies being calculated using Morse potential functions, and of the total π-bond energy, calculated by a semiempirical SCF MO method. The key parameters in this, *i.e.*, the one-electron core resonance integrals $\beta_{ij}{}^c$, are found by the Dewar–Schmeising thermocycle method. Preliminary calculations in part VII had treated the σ-bond energies as additional parameters; in order to use values corresponding to the thermocycle, we found it necessary to allow for the polarity of σ bonds. It is assumed that the formal charges ($\pm\delta Q$) on atoms X and Y due to polarity to a σ bond linking them are given by $Q(I_x - I_y)$, where I_x and I_y are Mulliken electronegativities and Q is a universal constant; the corresponding changes in the valence-state ionization potentials (W) are found from empirical relations between W and q.

Previous papers of this series[1,4] have described a semiempirical SCF–MO treatment of conjugated molecules, based on the Hückel σ–π approximation, which enables their heats of atomization to be estimated with quite unexpected accuracy. The heat of atomization is expressed as a sum of bond energies of localized σ bonds, and of the π-bond energy which is calculated theoretically.

The success of this treatment is due to the procedure used to estimate the key parameters in it, *i.e.*, the one-electron core resonance integrals, $\beta_{ij}{}^c$. Previous workers have used values designed to fit observed spectroscopic data; these, however, are unsuitable for calculations of ground-state properties. In our work we have estimated $\beta_{ij}{}^c$ by the thermocycle method of Dewar and Schmeising;[5] this is equivalent to a comparison of the calculated and observed π-bond energies of a simple diatomic π bond, stretched to the length at which $\beta_{ij}{}^c$ is to be estimated.

This diatomic π-bond energy is found by difference between the corresponding bond energies of pure single and pure double bonds between the atoms in question; these in turn are found from the equilibrium bond energies by subtracting the corresponding stretching or compression energies, which in turn are estimated by assuming Morse potential functions for the bonds. Thus the energies of the σ bonds in a molecule are incidentally determined during the estimation of the corresponding core resonance integrals; the heat of atomization should then be given by adding together a sum of these σ-bond energies and the calculated total π-bond energy.

In the earlier papers of this series,[4a-g] σ-bond energy was treated as an independent parameter, since good heats of formation could not be obtained by using the values found from the thermocycle. In part XI,[1] this restriction was removed in the case of hydrocarbons; here we describe an analogous completely self-consistent treatment of conjugated compounds containing nitrogen or oxygen.

Theoretical Approach and Estimation of Integrals

The basic theory of our method has been described in detail in earlier papers[1,4] of this series and need not be repeated here. The Pople F matrix[6] in our notation[1,4] is given by

$$F_{ii} = W_i + \frac{1}{2}q_i(ii,ii) + \sum_{j \neq i}(q_j - c_j)(ii,jj) \qquad (1)$$

$$F_{ij} = \beta_{ij}{}^c - \frac{1}{2}p_{ij}(ii,jj) \qquad (i \neq j) \qquad (2)$$

As in part VII,[4f] the one-center repulsion integrals (ii,ii) were found from the corresponding valence-state ionization potentials (W_i) and electron affinities (A_i) by the Pariser–Parr method;[7] W_i and A_i being determined from spectroscopic data using the promotion energies of Hinze and Jaffé.[8] Table I shows the values of W_i and (ii,ii) for carbon, pyridine-type nitrogen, pyrrole-type nitrogen, carbonyl-type oxygen, and ether-type oxygen.

An interesting check on these values is provided by an estimation of the corresponding effective nuclear

(1) Part XI: M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc*" **91**, 789 (1969).

(2) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

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(4) (a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); (b) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965); (c) *ibid.*, **87**, 692 (1965); (d) M. J. S. Dewar and C. C. Thompson, Jr., *ibid.*, **87**, 4414 (1965); (e) M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, **21**, 1817, 3423 (1965); (f) *J. Chem. Phys.*, **44**, 759 (1966); (g) M. J. S. Dewar, G. J. Gleicher, and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **88**, 1349 (1966); (h) M. J. S. Dewar, J. Hashmall, and C. G. Venier, *ibid.*, **90**, 1953 (1968); (i) M. J. S. Dewar and J. Kelemen, *J. Chem. Phys.*, **49**, 499 (1968).

(5) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

Table I. One-Center Integrals for Carbon, Nitrogen, and Oxygen

Atom or ion	Valence state	W_i, eV	(ii,ii), eV	Z_1	Z_2
C	trtrtrπ	-11.16	11.13	(3.18)	(3.18)
N	tr^{2}trtrπ ($>$N)	-14.12	12.34	3.58	3.52
N$^+$	trtrtrπ ($>$NH)	-28.59	16.63	5.10	4.75
O	tr^{2}tr^{2}trπ ($>$C=O)	-17.70	15.23	4.01	4.35
O$^+$	tr^{2}trtrπ ($>$O)	-33.90	18.60	5.55	5.32

(6) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1379 (1953).

(7) See R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

(8) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

charges, Z. If we assume our p AO's to be hydrogenlike, their energies should vary as Z^2, and their dimensions as Z^{-1}; hence the one-center repulsion integrals should vary as Z. Thus if W_c, (cc,cc), and Z_c are, respectively, the valence-state ionization potential, the one-center integrals, and effective nuclear change, for carbon, the corresponding values for some other atom X should be related to these by

$$Z_x = Z_c \left(\frac{W_x}{W_c}\right)^{1/2} \quad (3)$$

$$Z_x = Z_c \left[\frac{(xx,xx)}{(cc,cc)}\right] \quad (4)$$

These two estimates of Z_x are listed in the last column of Table I; as will be seen, they agree quite well with one another in each case. The effective nuclear charge of carbon was assumed to be 3.18.
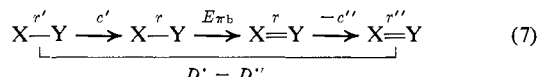
The two-center repulsion integrals (ii,jj) were estimated by a procedure equivalent to that of part XI,[1] using an expression equivalent to that of Ohno,[9] viz.

$$(ii,jj) = e^2[r_{ij}^2 + (R_i + R_j)^2]^{-1/2} \quad (5)$$

where r_{ij} is the internuclear distance between atoms i and j, and where

$$2R_i = e^2/(ii,ii); \quad 2R_j = e^2/2(jj,jj) \quad (6)$$

As in the previous papers,[4] β_{ij}^c was found from the following thermocycle[5]

$$X\overset{r'}{-}Y \overset{c'}{\longrightarrow} X\overset{r}{-}Y \overset{E_{\pi b}}{\longrightarrow} X\overset{r}{=}Y \overset{-c''}{\longrightarrow} X\overset{r''}{=}Y \quad (7)$$
$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}_{D' - D''}$$

Here r' and D' are the equilibrium bond length and bond energy of a pure σ bond between atoms X and Y in their appropriate valence states, r'' and D'' are corresponding quantities for a pure X=Y double bond, c' and c'' are the energies required to compress or stretch the X—Y and X=Y bonds to the common length r at which β_{xy}^c is to be estimated, and $E_{\pi b}$ is the π binding energy (i.e., minus the π-bond energy) of the X=Y bond stretched to length r.

In our SCF-MO treatment, it can be shown that

$$E_{\pi b} = q_x[W_x + \frac{1}{4}q_x(xx,xx)] + q_y[W_y + \frac{1}{4}q_y(yy,yy)] +$$
$$2p_{xy}\beta_{xy}^c + (q_x - c_x)(q_y - c_y)(xx,yy) -$$
$$\frac{1}{2}p_{xy}^2(xx,yy) - W_x - W_y \quad (8)$$

Combining eq 7 and 8

$$\beta_{xy} = \frac{1}{2p_{xy}}\Big[(1 - q_x)W_x + (1 - q_y)W_y -$$
$$\frac{1}{4}q_x^2(xx,xx) - \frac{1}{4}q_y^2(yy,yy) -$$
$$(q_x - c_x)(q_y - c_y)(xx,yy) +$$
$$\frac{1}{2}p_{xy}^2(xx,yy) + D' - D'' - c' + c''\Big] \quad (9)$$

(9) K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).

In order to apply this equation, we need to know the charge densities q_x and q_y, the bond order p_{xy}, and the quantities D', c', D'', and c'' that appear in the thermocycle; the remaining integrals are given by Table I and eq 5 and 6.

In part VII,[4f] we made the simplifying assumption, that q_x, q_y, and p_{xy} could be set equal to the charge densities and bond order of the bond in a conjugated molecule whose β_{ij}^c we are calculating; this enabled β_{ij}^c to be found directly from eq 9. However q_x, q_y, and p_{xy} in fact refer to an entirely different situation, i.e., a diatomic molecule containing a two-center π bond; in this case they must be found independently by an iterative SCF treatment of the diatomic system. In the present investigation we adopted the latter more rigorous approach.

As in the case of hydrocarbons,[4b] we have assumed that there is a linear relation between bond order and bond length for any bond in a conjugated system; this relation is used to recalculate the lengths of all the bonds in a conjugated molecule at each step in the iterative treatment, and all the two-center integrals involving pairs of adjacent atoms are in turn recalculated at each step (variable β treatment[4]). Ideally, one should recalculate the entire geometry of the molecule at each step in the iteration, and then recalculate *all* the two-center integrals; since, however, we have not as yet devised any convenient procedure for calculating the geometry of a molecule in terms of bond lengths,[10] we have made the simplifying assumption[4b] that integrals between nonadjacent atoms remain unchanged. As in the case of hydrocarbons,[4b] we have tested this approximation for a number of molecules by recalculating the geometry by hand from the final bond lengths given by the SCF-MO treatment, and then repeating the calculation using this as the initial geometry; the results given by the second SCF treatment were in all cases almost identical with those given by the first, even when the geometry originally assumed differed considerably from the final one.

Estimation of Bond Energies, Bond Lengths, and Compression Energies. The quantities D', r', and c' refer to a theoretical abstraction, i.e., a "pure σ" bond between a pair of sp^2-hybridized atoms. In order to estimate their values, one is forced to use empirical relationships between bond length and other bond properties. Following Dewar and Schmeising,[5] we used the tractrix relation of eq 10 between bond energy (d) and bond length (r), and the inverse power series relation of eq 11 between force constant (k) and bond length

$$Br = A \ln [A + (A^2 - d^2)^{1/2}] - A \ln d - (A^2 - d^2)^{1/2} \quad (10)$$

$$k = Cr^{-2} + Dr^{-4} + Er^{-6} \quad (11)$$

where A, B, C, D, and E are parameters.

In the case of carbon–carbon bonds, the constants A and B were found[1] by fitting the bond lengths and carbon–carbon bond energies for diamond and ethylene,

(10) The trouble, of course, is that the geometry is not determined by the bond lengths alone, but also by the condition that the total angle strain should be a minimum; it is very difficult to devise a computer program to solve this problem for arbitrary molecules.

and C, D, and E by fitting[1] the force constants for ethane, ethylene, and acetylene. Using the bond order/bond length relation established by data for ethylene, benzene, and graphite, and extrapolating to $p = 0$, r' was found to be 1.512 Å; D' and k were then found from eq 10 and 11, and these in turn gave the value a' for the corresponding constant in the Morse function

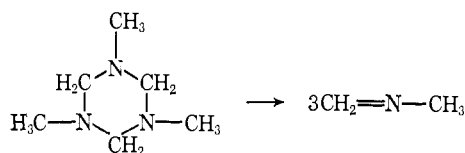$$c' = D'\{1 - \exp[a'(r' - r)]\}^2 \qquad (12)$$

It is, however, much more difficult to estimate the corresponding quantities for bonds involving nitrogen or oxygen, for two reasons. Firstly, there are few reliable heats of formation for organic compounds containing nitrogen or oxygen, and it is therefore difficult to estimate bond energies for the various CN, CO, and NN bonds; secondly, complications arise in the case of pyrrole-type nitrogen and ether-type oxygen, since the corresponding double bonds involve ionic species ($>C\!=\!N^+<$ and $>C\!=\!O^+\!-$) whose heats of formation cannot easily be estimated. We have therefore been forced to make a simplifying assumption that the σ bonds formed by pyridine-type nitrogen and pyrrole-type nitrogen are similar, and likewise the bonds formed by carbonyl-type oxygen and ether-type oxygen.

The heats of atomization at 25° used in this work were as follows, being taken from the National Bureau of

Table II. Bond Energies (25°) and Bond Lengths Used in Determining the Parameters in the Tractrix Equation

Bond	D, kcal/mole	r, Å	A, kcal/mole	B, kcal/mole
C—N	71.37[a]	1.480[b]	3636.49	8904.83
C=N	119.377[c]	1.270[d]		
C—O	82.515[e]	1.427[b]	16068.29	55904.20
C=O	163.759[f]	1.230[b]		
N—N	47.833[g]	1.449[h]	7233.52	23522.60
N=N	94.38[i]	1.240[i]		

[a] From the heat of formation of methylamine (-6.70 kcal/mole: National Bureau of Standards and JANAF Tables). [b] L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958. [c] Estimated from the enthalpy (35 kcal/mole: B. G. Gowenlock and K. E. Thomas, $J.$ $Chem.$ $Soc.$, B, 409 (1966)) for the reaction

$$
\begin{array}{c}
CH_3 \\
| \\
H_2C\stackrel{N}{\diagup}CH_2 \\
| \quad | \\
H_3C\!-\!N\diagdown \diagup N\!-\!CH_3 \longrightarrow 3CH_2\!=\!N\!-\!CH_3 \\
CH_2
\end{array}
$$

assuming the difference in bond energy between N–C (sp²–sp³) and N–C (sp³–sp³) bonds to be the same as that (3.5 kcal/mole) between C–C (sp²–sp³) and C–C (sp³–sp³) bonds. [d] L. Merrit and E. Lanterman, $Acta$ $Cryst.$, **5**, 811 (1952). [e] From the heat of formation of methanol (-48.08 kcal/mole: National Bureau of Standards and JANAF Tables). [f] From the heat of formation of formaldehyde (-27.7 kcal/mole: National Bureau of Standards and JANAF Tables), assuming $D(CH) = 99.297$ kcal/mole. [g] J. A. Kerr, $Chem.$ $Rev.$, **66**, 465 (1966). [h] Y. Morino, T. Iijima, and Y. Murata, $Bull.$ $Chem.$ $Soc.$ $Japan$, **33**, 46 (1960). [i] From the heat of combustion of azoisopropane measured by G. E. Coates and L. E. Sutton ($J.$ $Chem.$ $Soc.$, 1187 (1948)), assuming the C–N (sp²–sp³) bond energy to be 74.87 kcal/mole (see footnote c above). [j] R. J. W. LeFebre, F. M. O'Dwyer, and R. L. Werner, $Australian$ $J.$ $Chem.$, **14**, 315 (1961).

Standards and JANAF Tables. The bond energies and bond lengths used in determining the constants in eq 10 are shown in Table II, together with the derived values for A and B.

Table III shows the data used to determine the constants in eq 11, together with the derived values of C, D, and E.

Table III. Data Used to Determine Parameters in Eq 11

Bond	Molecule	$10^{-5}k$, dynes/cm	C, Å²	D, Å⁴	E, Å⁶
C—N	CH₃NH₂	3.347[a]			
C=N		10.500[b]	-22.292	67.003	-6.018
C≡N	HCN	18.583[c]			
C—O	CH₃OH	3.280[d]			
C=O	CH₂O	10.800[e]	-20.067	52.681	3.629
C≡O	CO	18.530[b]			
N—N	H₂NNH₂	3.600[f]			
N=N		13.250[b]	-56.632	179.565	-94.043
N≡N	N₂	22.900[b]			

[a] E. L. Wu, G. Zerbi, S. Califano, and B. Crawford, Jr., $J.$ $Chem.$ $Phys.$, **35**, 2060 (1961). [b] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955. [c] A. E. Douglas and D. Sharma, $J.$ $Chem.$ $Phys.$, **21**, 448 (1953). [d] G. Zerbi, J. Overend, and B. Crawford. Jr., $ibid.$, **38**, 122 (1963). [e] S. Bratox and S. Besnainou, $ibid.$, **34**, 1142 (1961). [f] G.-M. Schwab, K. Koller, and K. Lorenzen, $Angew.$ $Chem.$, **73**, 219 (1961).

The data for single bonds in Tables II and III refer to saturated molecules in which the atoms have essentially sp³ hybridization. In the absence of adequate experimental data concerning the effect of hybridization on bond length, we assumed that the contraction on passing from a bond of sp³–sp³ type to one of sp²–sp² type would be the same for CN, CO, and NN bonds as for CC bonds, i.e., -0.032 Å.[1] Using values found in this way for the equilibrium σ-bond lengths, D' and k' were found using eq 10 and 11 and the data in Tables II and III, and a' was calculated from k' using eq 12. The corresponding values for r'', D'', and a'' were found directly from the data for double bonds in Tables II and III. Table IV shows the final values of the various quantities determined in this way, together with the constants F and G in the assumed linear relation between bond order and bond length.

$$r = F - Gp \qquad (13)$$

Table IV. Thermocycle Data for the Calculation of Core Resonance Integrals

Bond	D'', eV	D', eV	r'', Å	r', Å	a'', Å⁻¹	a', Å⁻¹	F, Å	G, Å
CC	5.5600	3.9409	1.338	1.512	2.3177	2.0022	1.512	0.174
CN	5.1766	3.3463	1.270	1.448	2.5161	1.9209	1.448	0.178
CO	7.1011	3.9987	1.230	1.395	2.1787	1.7870	1.395	0.165
NN	4.0926	2.3017	1.240	1.417	3.1787	2.5290	1.417	0.177

Allowance for σ Polarization. In the present approach, the heat of atomization (ΔH_a) of a molecule is written in the form

$$\Delta H_a = \Sigma E^\sigma + E_{\pi b} \qquad (14)$$

where the sum is over the bond energies (E^σ) of the

σ bonds. In order to apply this in practice, one must also have estimates of the bond energies of bonds to hydrogen. The value for CH is that deduced in part XI[1] for hydrocarbons, *viz.*

$$E(\text{CH}) = 102.368 \text{ kcal/mole} \qquad (15)$$

No other quantity is needed for calculations involving oxygen compounds, or nitrogen compounds of pyridine type; in the case of pyrroles, one also needs to know the bond energy for the NH bond.

Extensive trials, using the parameters established in the preceding section and all reasonable variants of them, failed, however, to give satisfactory estimates of heats of formation. A clue to this discrepancy was provided by the results in part VII,[4f] where it was shown that very different values had to be assumed for the σ bond energies of pyridine-type, and pyrrole-type, CN bonds. This result suggested that one of two factors might be responsible; either our assumption that the CN σ-bond energies for pyridine-type and pyrrole-type bonds is incorrect, or errors might be introduced by our failure to allow for the polarity of σ bonds, an effect which would be different in the case of pyridine-type nitrogen, where the nitrogen atom is linked to two neighboring atoms by polar σ bonds, from the case of pyrrole-type nitrogen with three neighboring atoms. Since it would be difficult to allow for differences between the σ-bond energies of CN bonds of different types, because of the lack of thermochemical data, we decided to try introducing a correction for σ polarization into our treatment.

As a first approximation, we assumed that the formal charges (δQ) developed in two atoms, X and Y by the existence of a polar σ bond between them, are proportional to the difference between their Mulliken electronegativities I_x and I_y, *viz.*

$$\delta Q_x = -\delta Q_y = (I_x - I_y)Q \qquad (16)$$

where the proportionality factor, Q, has the same value for all bonds. The total formal charge on a given atom (X) is assumed to be a sum of contributions (δQ_x) by the various σ bonds it forms. Such formal charges in the σ framework will lead to corresponding changes in the valence-state ionization potentials, W_i. In order to estimate these we assumed a parabolic relation between the valence-state ionization potential (W) of a given atom and the total valence-shell electron density (q) on it, *viz.*
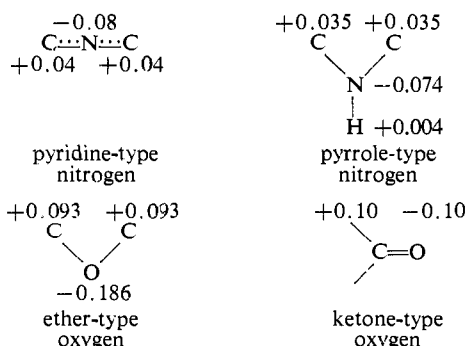
$$W = a + bq + cq^2 \qquad (17)$$

where a, b, and c are parameters found by fitting the ionization potentials of an atom and two ions derived from it. Table V shows the data used to determine these parameters for the various atoms in which we are interested, together with the corresponding eq 17. The values of W are again taken from the compilation by Hinze and Jaffé.[8]

The optimum value of Q was established by extensive calculations for a wide variety of conjugated compounds of nitrogen and oxygen. The best values for the partial charges for bonds of various types are shown in Figure 1, while Table VI shows values of W_i and (ii,ii) for nitrogen and oxygen, and for the adjacent carbon atoms, in several molecules, using the results shown in Figure 1 together with the equations listed in the first column of Table V. Corresponding values for the effective nuclear charges (Z^e) are also listed for comparison with the "normal" values in Table I.

Results and Discussion

The rest of this paper presents the results of calculations for a wide variety of conjugated compounds containing nitrogen or oxygen, carried out by the

Table V. Data Used to Determine the W *vs.* q Relation for Various Atoms, and the W *vs.* q Relations for Them

Type of atom and W/q relation	Valence states	W, eV	q
Trigonal carbon	$C^-(\text{tr}^3\text{trtr}\pi)$	-1.28	4
$W = -55.9860 + 18.7385q$	$C(\text{trtrtr}\pi)$	-11.16	3
$-1.2655q^2$	$C^+(\text{trtr}\pi)$	-23.571	2
Trigonal nitrogen (pyridine)	$N^-(\text{tr}^2\text{tr}^2\text{tr}\pi)$	-3.307	5
$W = -101.363 + 30.6085q$	$N(\text{tr}^2\text{trtr}\pi)$	-14.12	4
$-2.1995q^2$	$N^+(\text{tr}^2\text{tr}\pi)$	-29.332	3
Trigonal nitrogen (pyrrole)	$N^-(\text{tr}^2\text{trtr}\pi^2)$	-14.12	4
$W = -89.402 + 24.6265q$	$N(\text{trtrtr}\pi^2)$	-28.586	3
$-1.4515q^2$	$N^+(\text{trtr}\pi^2)$	-45.955	2
Trigonal oxygen (furan)	$O^-(\text{tr}^2\text{tr}^2\text{tr}\pi^2)$	-17.697	5
$W = -136.787 + 33.3355q$	$O(\text{tr}^2\text{trtr}\pi^2)$	-33.901	4
$-1.9035q^2$	$O^+(\text{tr}^2\text{tr}\pi^2)$	-53.912	3
Trigonal oxygen[a] (carbonyl)	$O^-(\text{tr}^2\text{tr}^2\text{tr}^2\pi)$	?	6
$W = -101.597 + 16.7809q$	$O(\text{tr}^2\text{tr}^2\text{tr}\pi)$	-17.697	5
	$O^+(\text{tr}^2\text{tr}^2\pi)$	-34.477	4

[a] The promotional energy for $O^-(\text{tr}^2\text{tr}^2\text{tr}^2\pi)$ is not listed in the tables by Hinze and Jaffé. We assumed the W *vs.* q relation to be linear.

**Table VI.** Values for W_i and (ii,ii), Allowing for σ Polarization

Atom	Core charge	W, eV	Z^c	(ii,ii),[d] eV
Pyridine C^a	1.040	-11.6078	3.24	11.3511
N	0.920	-13.0931	3.42	11.8838
Pyrrole C^a	1.035	-11.5516	3.24	11.3236
N	1.926	-27.4161	4.82	16.2842
Furan C^a	1.093	-12.2075	3.33	11.6406
O	1.814	-30.5989	5.16	17.6709
Carbonyl C^a	1.100	-12.2872	3.34	11.6786
O	0.900	-16.0190	3.98	14.4871
Pyrimidine C^b	1.080	-12.0597	3.31	11.5700

[a] This is the carbon atom bonded to the heteroatom. [b] This is the carbon atom between the two heteroatoms. We assume as a first approximation that charges due to bond polarity are additive. [c] In order to estimate Z values, W and Z values of reference atoms listed in Table I were used. [d] In order to estimate (ii,ii) values, (ii,ii) and Z of reference atoms listed in Table I and Z listed in Table VI were used.

Figure 1. Formal charges (in units of the electronic charge) due to polarity of σ bonds.

procedure indicated above. For convenience, the various types of compound corresponding to the different kinds of nitrogen (pyridine-type or pyrrole-type) and oxygen (ether-type or ketone-type) will be treated separately.

A. Compounds Containing Pyridine-Type Nitrogen.
Table VII shows heats of atomization (ΔH_a) calculated for a wide variety of aromatic compounds containing pyridine-type nitrogen, together with experimental values where these are available.

I   II   III

IV   V   VI

VII   VIII   IX

X   XI   XII

XIII   XIV   XV
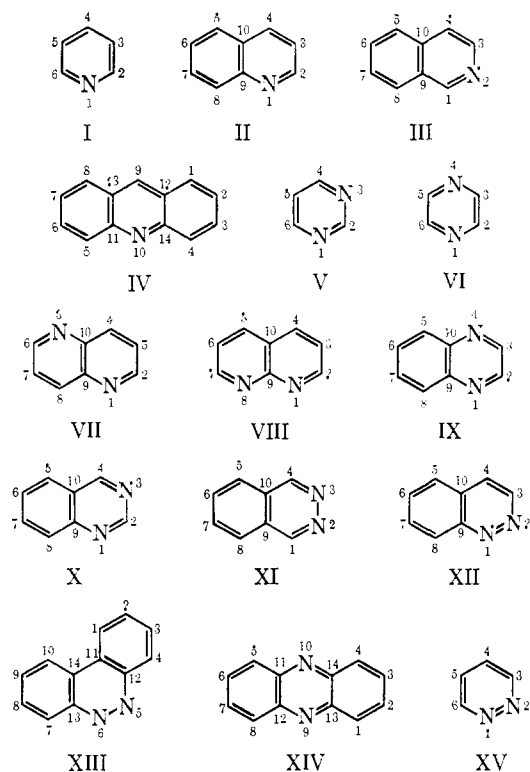
The agreement between the calculated and observed values is very satisfactory, particularly in view of the fact that heats of combustion for nitrogen compounds are still subject to much greater errors than those for hydrocarbons. It is unfortunate that so few heats of formation have been measured for compounds of this type; perhaps our calculations will encourage work in this area to test the accuracy of our predictions.

In view of the apparent success of our procedure, both here and for the other types of compounds discussed below, we have included results for some other ring systems of biological and chemical interest, on the grounds that these will probably remain for some time the best available estimates of their heats of formation.

B. Derivatives of Pyrrole and Aromatic Amines.
In order to calculate heats of atomization of pyrroles or aromatic amines we need to know the bond energy of the NH (sp²) bond. Unfortunately there is no way of estimating this directly, but one would expect it to be somewhat greater than the NH (sp³) bond energy in a secondary amine (3.96 eV). We have assumed the value

$$D(\mathrm{NH,\ sp^2}) = 93.2\ \mathrm{kcal/mole} = 4.042\ \mathrm{eV}\quad(18)$$

this giving good results for a number of compounds of different types. Values for the heats of atomization of the following pyrroles and aromatic amines are listed in Table VIII.

XVI   XVII   XVIII

XIX   XX

XXI   XXII
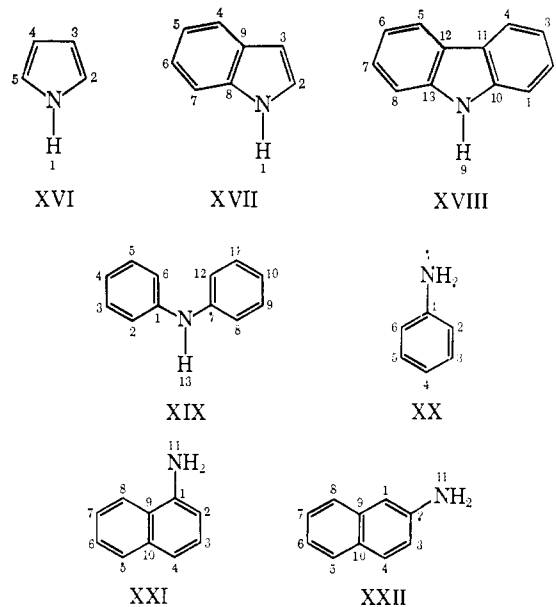
The calculated heats of atomization agree very well with experiment, except for indole and carbazole where the differences are considerably greater than the claimed limits of error. However, one might expect the effects of successive annelations of pyrrole with benzene to be additive, and indeed the calculated increments in ΔH_a for XVI → XVII (33.67 eV) and XVII → XVIII (33.74 eV) are almost identical; the corresponding differences between the experimental values (33.29, 33.85 eV) for ΔH_a, on the other hand, differ by over 0.5 eV. We therefore feel somewhat dubious about the accuracy of the thermochemical data.

C. Pyrazole, Imidazole, and Related Compounds.
Table IX lists calculated and observed heats of atomization for the azole derivatives XXIII–XXIX. Here again the agreement is good, given that there is reason to believe that the experimental values may be in error by several tenths of an electron volt (see end of section

Table VII. Heats of Atomization of Derivatives of Pyridine and Pyridazine

Compound	−(Heat of atomization), eV (25°)		
	Calcd	Obsd	Error
Pyridine (I)	51.870	51.79[a]	+0.08
Quinoline (II)	85.322	85.18[b]	+0.14
Isoquinoline (III)	85.316		
Acridine (IV)	118.637		
Pyrimidine (V)	46.864	46.99[c]	−0.13
Pyrazine (VI)	46.272	46.44[c]	−0.17
1,5-Naphthyridine (VII)	79.985		
1,8-Naphthyridine (VIII)	80.162		
Quinoxaline (IX)	79.739		
Quinazoline (X)	80.306		
Phthalazine (XI)	79.215		
Cinnoline (XII)	79.167		
3,4-Benzocinnoline (XIII)	112.727		
Phenazine (XIV)	113.058		
Pyridazine (XV)	45.741	45.59[c]	+0.15

[a] J. D. Cox, A. R. Challoner, and A. R. Meetham, *J. Chem. Soc.*, 265 (1954). [b] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955. [c] J. Tjebbes, *Acta Chem. Scand.*, **16**, 916 (1962).

Table VIII. Heats of Atomization of Pyrroles and Aromatic Amines

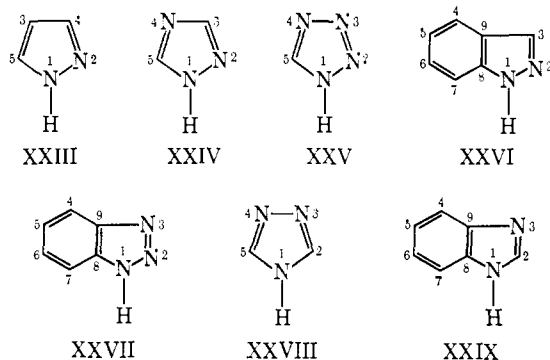| Compound	−(Heat of atomization at 25°), eV		
	Calcd	Obsd	Error
Pyrrole (XVI)	44.768	44.77[a]	0.00
Indole (XVII)	78.438	78.06[a]	+0.38
Carbazole (XVIII)	112.182	111.91[a]	+0.27
Diphenylamine (XIX)	116.624	116.53[b]	+0.09
Aniline (XX)	64.388	64.31[c]	+0.08
α-Naphthylamine (XXI)	97.814	97.79[b]	+0.02
β-Naphthylamine (XXII)	97.811	97.78[b]	+0.03

[a] H. Zimmerman and H. Geisenfelder, Z. Elektrochem., **65**, 368 (1961). [b] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955. [c] Based on heat of formation given by S. W. Benson, J. Chem. Educ., 502 (1965).

Table IX. Calculated Heats of Atomization for Pyrazole and Imidazole Derivatives

Compound	−(Heat of atomization), eV (25°)		
	Calcd	Obsd[a]	Error
Pyrazole (XXIII)	39.322	39.26	+0.06
1,2,4-Triazole (XXIV)	34.541	34.29	+0.25
1,2,3,4-Tetrazole (XXV)	28.006	28.06	−0.05
Benzpyrazole (XXVI)	72.892	72.65	+0.24
Benztriazole (XXVII)	67.145	66.96	+0.18
Imidazole (XXVIII)	39.741	39.66	+0.08
Benzimidazole (XXIX)	73.413	73.24	+0.17

[a] Based on heats of combustion given by H. Zimmerman and H. Geisenfelder, Z. Elektrochem., **65**, 368 (1961).

Table X. Heats of Atomization of Conjugated Compounds Containing Oxygen

Compound	−(Heat of atomization), eV (25°)		
	Calcd	Obsd	Error
Furan (XXX)	41.563	41.52[a]	+0.04
Benzofuran (XXXI)	75.376	...	...
Dibenzofuran (XXXII)	109.224	109.18[b]	+0.04
Diphenyl ether (XXXIII)	113.778	113.84[c]	−0.06
Anisole (XXXIV)	73.279	73.35[c]	−0.07
Benzaldehyde (XXXV)	68.507	68.27[c]	+0.24
Benzophenone (XXXVI)	121.239	120.98[a]	+0.26
p-Benzoquinone (XXXVII)	60.102	59.94[a]	+0.16
o-Benzoquinone (XXXVIII)	59.984	...	...

[a] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955. [b] R. C. Cass, S. E. Fletcher, C. T. Mortimer, H. P. Springall, and T. R. White, J. Chem. Soc., 1406 (1958). [c] S. W. Benson, J. Chem. Educ., 502 (1965).

that our treatment underestimates the charges due to σ polarization in this case. However, our calculations do predict that o-benzoquinone should be less stable than the *para* isomer, which is undoubtedly the case judging by their relative chemical reactivities; unfortunately, there is as yet no good experimental value for the heat of formation of o-benzoquinone.

Bond Lengths. Our procedure[1,4] automatically leads to estimates of bond lengths; unfortunately, there are hardly any experimental values available for comparison. In cases where such data are available (Table XI), the agreement seems reasonably good.

B above). Further evidence for this is provided by comparison of the heats of atomization of pyrrole (XVI), pyrazole (XXIII), and imidazole (XXVIII) with those of their benzo derivatives XVII, XXVI, and XXIX. One might expect the differences to almost be the same for each pair of compounds, and this indeed is the case for our calculated values (33.67, 33.57, 33.67 eV, respectively); however, the differences between the experimental values show a large variation (33.29, 33.39, 33.58 eV, respectively).

Table XI. Calculated and Observed Bond Lengths

Compound	Bond[a]	Bond length, Å	
		Calcd	Obsd
Pyridine (I)[b]	1,2	1.338	1.340
	2,3	1.396	1.395
	3,4	1.397	1.395
Acridine (IV)[c]	1,2	1.365	1.360
	1,13	1.440	1.429
	2,3	1.434	1.428
	3,4	1.366	1.359
	4,14	1.439	1.434
	10,11	1.345	1.348
	11,12	1.417	1.434
	9,12	1.403	1.398
Pyrimidine (V)[d]	1,2	1.341	1.335
	3,4	1.345	1.355
	4,5	1.397	1.395
Pyrazine (VI)[e]	1,2	1.333	1.334
	2,3	1.398	1.388
Pyrrole (XVI)[f]	1,2	1.390	1.383
	2,3	1.358	1.371
	3,4	1.440	1.429
Pyrazole (XXIII)[g]	1,2	1.356	1.361
	2,3	1.309	1.314
	3,4	1.423	1.414
	4,5	1.369	1.335
	1,5	1.367	1.346
Furan (XXX)[h]	1,2	1.381	1.371
	2,3	1.347	1.354
	3,4	1.459	1.440

[a] Structures and numbering found in text. [b] A. Almenningen, O. Bastiansen, and L. Hanson, Acta Chem. Scand., **9**, 1306 (1955). [c] D. C. Phillips, F. R. Almed, and W. H. Barnes, Acta Cryst., **13**, 365 (1960). [d] P. J. Wheatley, ibid., **13**, 80 (1960). [e] P. J. Wheatley, ibid., **10**, 182 (1957). [f] B. Bak, D. Christiansen, L. Hanson, and J. Rastrip-Andersen, J. Chem. Phys., **24**, 720 (1956). [g] H. W. W. Ehrlich, Acta Cryst., **13**, 946 (1960). [h] B. Bak, L. Hansen, and J. Rastrip-Andersen, Discussions Faraday Soc., **19**, 30 (1955).

D. Oxygen Compounds. Table X shows calculated heats of formation for several conjugated compounds containing oxygen. Here again the calculated heats of atomization agree quite well with experiment, although the errors for the carbonyl compounds are somewhat greater than for compounds of other types. Here of course one might expect σ–π interactions to be of especial importance in view of the strong polarity of the C=O bond; it is very possible

Conclusions

The main conclusion from the results described in this paper, and the preceding one,[1] is that the treatment described here provides an astonishingly good account of the heats of formation and geometries of conjugated molecules. Indeed, it seems likely that the calculated heats of formation are subject to smaller errors than any but the most recent thermochemical measurements; the present procedure should therefore provide a satisfactory and very simple substitute for experiment in determining heats of formation of conjugated and aromatic systems. Calculations of this kind should be of especial interest to biochemists, in view of the bio-logical importance of such compounds; the procedures developed here should prove invaluable in interpreting their chemical properties. Previous attempts in this direction have been limited to the HMO method, which is known to be unreliable for molecules containing heteroatoms, or to SCF treatments in which the parameters were chosen by reference to spectroscopic data. The calculations can of course be carried out in a fraction of the time, and at much less cost, than corresponding measurements of heats of combustion: it should be added that an improved version of our computer program, written by Mr. J. A. Hashmall, is available from The Quantum Chemistry Program Exchange (for details see part XI[1]).

Ground States of Conjugated Molecules.[1] XIII. Basicities of Conjugated Carbonyl Compounds[2]

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Abstract: The completely self-consistent treatment of heteroconjugated molecules derived in part XII[1] has been applied to a wide variety of conjugated carbonyl compounds and the conjugated acids derived from them, and the results have been used to account for the pK_a of the carbonyl compounds. The correlation given by the present method is much superior to those derived from the less refined treatments used previously.

Previous papers[1,4] of this series have described an improved SCF–MO treatment of conjugated molecules; our present objective is to test the validity of this approach by applying it to a wide range of chemical problems. Here we describe one such application, an interpretation of the relation between structure and basicity in a series of conjugated carbonyl compounds. This long-standing problem provides a good touchstone for chemical theories for several reasons. First, there are extensive data for the basicities of such compounds, covering a wide range of structural variation. Secondly, the observed dissociation constants cover a wide range. Thirdly, the quantities to be predicted are equilibrium constants rather than rate constants; rate constants are harder to interpret since their prediction involves unavoidable assumptions concerning the geometries of transition states.

The basic strength of a given carbonyl compound, R_2CO, is determined by the difference in free energy between it and its conjugate acid R_2COH^+. Making the usual assumption[5] that the differences in basicity are due to changes in the energy (ΔE) rather than the entropy of reaction, we find that the equilibrium con-stant (K) for a given carbonyl compound should be given by

$$-RT \log K = C + \Delta E \tag{1}$$

where C is a constant. A plot of $\log K$ against ΔE should then be a straight line.

Making the Hückel approximation of treating σ and π electrons independently, we can write ΔE in the form

$$\Delta E = \Delta E_{\sigma b} + \Delta E_{\pi b} \tag{2}$$

where $\Delta E_{\sigma b}$ and $\Delta E_{\pi b}$ are the differences in σ- and π-binding energy, respectively, between the carbonyl compound and its conjugate acid. Previous workers have further assumed that $\Delta E_{\sigma b}$ is the same for different carbonyl compounds, their relative basicities being determined solely by the π-energy term $\Delta E_{\pi b}$; in this case, a plot of $\log K$ vs. $\Delta E_{\pi b}$ should be linear, $\Delta E_{\pi b}$ being calculated by some appropriate theoretical treatment.

Culbertson and Pettit[6] applied this relation to a number of aldehydes (ArCHO), ArH being an alternant aromatic hydrocarbon. They pointed out that in the conjugate acid ArCHOH$^+$, the positive charge should reside mainly on carbon rather than on the electronegative oxygen; the π-MO's of ArCHOH$^+$ should then resemble those of the corresponding arylcarbonium ion ArCH$_2^+$, and $\Delta E_{\pi b}$ should be approximately equal to the difference in π-binding energy between ArH and ArCH$_2^+$. They found an excellent correlation between the measured basic dissociation constants and

(1) Part XII: M. J. S. Dewar and T. Morita, *J. Am. Chem. Soc.*, **91**, 796 (1969).

(2) This work was supported by the Air Force Office of Scientific Research through Grant No. AF·AFOSR·1050-67.

(3) Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Japan.

(4) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

(5) See, e.g., M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 6 5 (1965).

(6) G. Culbertson and R. Pettit, *J. Am. Chem. Soc.*, **85**, 741 (1963).