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Atomization Enthalpies of Aliphatic Compounds with Alternately Adjacent Carbonyl Groups and Nitrogen Atoms†

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Hückel MO calculations were made for the title compounds using Hess-Schaad heteroatom parameters. The bond-contribution values were determined for the total π-bonding energies of the acyclic compounds. No resonance stabilization is present for molecules with six-, eight-, and ten-membered rings composed of CO–N linkages. Graph-theoretical calculations gave a similar result. Atomization enthalpies were calculated from the available thermochemical data and analyzed within the framework of the Hess-Schaad theory. The destabilization energies of normal alkanamides and *N,N*-dimethylformamide are close to zero. Diacetamide is not destabilized, while *N*-butyldiacetamide and triacetamide showed small destabilization energies. Trimethyl isocyanurate is not significantly strained. The total strengths of the CO–N bonds are in this order: amide>(urea and diacetamide)>internal bond of acetylurea.

It is well-known that the π-electrons of a carbonyl group in an amide molecule interact with the conjugated lone-pair electrons on the adjacent nitrogen atom to provide the interconnecting C–N bond, which has a significant double bond character. This bond is an important one, since it occurs not only in amides and ureas, but also in proteins, DNA bases, and synthetic polyamides. In another paper,[1] the standard enthalpies of formation, in the gaseous state, of acetylurea and trimethyl isocyanurate [1,3,5-trimethyl-1,3,5-triazine-2,4,6(2*H*,4*H*,6*H*)-trione] were reported, and the estimated stabilization energies of acetamide and urea as well as of these compounds were empirically analyzed in order to study the effect of the elongation and cyclization of an alternating CO–N chain on the stabilization energy. The present study aims at the theoretical interpretation of the extensive thermochemical data for aliphatic compounds containing CO–N linkages, within the framework of the Hess-Schaad theory based on the Hückel MO method.

According to Hess and Schaad,[2,3] the atomization enthalpy of a conjugated alkene is expressed as a sum of the σ-bond contribution terms minus the π-bonding energy, B_π:

$$\Delta_a H = \sum E'(\dot{\mathrm{C}}\text{–H}) + \sum E'(\dot{\mathrm{C}}\text{–}\dot{\mathrm{C}}) - B_\pi, \qquad (1)$$

where $E'(\dot{\mathrm{C}}\text{–H})$ and $E'(\dot{\mathrm{C}}\text{–}\dot{\mathrm{C}})$ are the C–H and C–C σ-bond-contribution terms respectively. In this paper, a 2p electron that takes part in the formation of a π-bond or a lone-pair orbital of a nitrogen atom is denoted by a dot above the atomic symbol. In Method A of Ref. 3, the bond-compression terms were explicitly given, but in Method B they were included in B_π, as is shown in Eq. 1, by treating the resonance integral, β, as a parameter. This treatment was subsequently extended to conjugated amines,[4] ethers,[4] ketones,[5] thiols,[6] thioethers,[6] imines,[7] and fluorides.[8] In addition, Hess and Schaad showed that the difference between a properly calculated π-bonding energy and the corresponding estimated value based on the bond additivity of a cyclic compound is a reasonable measure for the Dewar resonance energy.[2–8]

Calculation

Hückel molecular orbital calculations were carried out for forty cyclic and acyclic molecules with alternating CO–N skeleton, and with or without branching, using the Hess-Schaad heteroatom parameter set.[4,5] The π-electron energy of a single localized carbonyl group was $(2\alpha+2.212\beta)$, while that of a nitrogen atom was $(2\alpha+3\beta)$, where α and β are the Coulomb and resonance integrals of carbon atoms respectively. Dewar-type resonance energies were calculated also by means of Aihara's graph-theoretical method.[9]

Results and Discussion

π-Bond Order and π-Bonding Energy. The calculated π-bond orders are summarized in Table 1, while the classification of bonds is illustrated in Fig. 1. The bond order of a C–N bond that involves a branching nitrogen atom is systematically lower than the value for a C–N bond that does not involve a branching nitrogen atom.

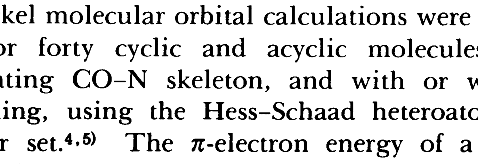

Fig. 1. Classification of bonds and atoms. Hydrogen atoms or alkyl groups bonded to terminal carbon or nitrogen atoms are not shown.

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Table 1. C-N and C=O π-Bond Orders. Upper and Lower Bounds Are Shown. Parenthesized Values Are Those for C-N Bonds That Involve a Branching Nitrogen Atom. For Classification of Bonds, See Fig. 1

Bond	Position		π-Bond order
C-N	Open chain	amide	0.400
		outermost	0.392±0.003(0.374±0.001)
		internal	0.372±0.003(0.356±0.001)
	Ring	$m=2$	0.356(0.338)
	$\lbrack\mathrm{CO{-}N}\rbrack_m$	$m=3$, 4, or 5	0.374(0.356)
C=O	Open chain	amide	0.899
		terminal	0.900±0.010
		internal	0.820±0.015
	Ring	$m=2$	0.837±0.006
	$\lbrack\mathrm{CO{-}N}\rbrack_m$	$m=3$, 4, or 5	0.825±0.006

Table 2. Bond-Contribution Values B_π(C-N) and B_π(C=O) to Total π-Bonding Energy B_π of Acyclic Molecules. Parenthesized Values Are Those for C-N Bonds Involving a Branching Nitrogen Atom. For Classification of Bonds, See Fig. 1

Bond	B_π(bond)/β	Position	B_π(C=O)/β
C-N, amide	0.374	Amide	1.992
C-N, out[a)]	0.367(0.360)	Terminal	1.992
C-N, int[b)]	0.360(0.352)	Internal	1.992

a) Outermost C-N bond. b) Internal C-N bond.

The calculated π-bonding energies of acyclic molecules were empirically analyzed; the bond-contribution values thus derived are shown in Table 2. The bond contribution values were uniquely determined except for amide. It is notable that the value of B_π(C=O), which is the bond-contribution term from a carbonyl group to the π-bonding energy, of acyclic molecules other than amide is constant and equal to the π-bonding energy of a ketone or aldehyde molecule with an isolated carbonyl group. This implies that the delocalization energy of one of the molecules under study is given by the sum of the bond contribution terms of C-N bonds to the π-bonding energy. It was found that the delocalization energy, E_d, of a linear molecule is expressed by this equation:

$$E_d/\beta = 0.360(n_b - 1) + 0.374, \qquad (2)$$

where n_b is the number of C-N bonds in the molecule. It follows that the bond-contribution term from the C-N bond of an amide molecule B_π(C-N,amide) is related to those of the outermost and internal C-N bonds, B_π(C-N,out) and B_π(C-N,int) respectively of other linear molecules by the equation:

$$B_\pi(\text{C-N,amide}) = 2B_\pi(\text{C-N,out}) - B_\pi(\text{C-N,int}). \qquad (3)$$

Thus, the values of B_π(C-N,amide) and B_π(C=O) for amide were determined to be as is shown in Table 2. The latter value is equal to the value of B_π(C=O), which is common to the other acyclic molecules. By using the bond-contribution values given in Table 2, the π-bonding energy of acyclic molecules may be reproduced with deviations less than 0.004β.

Hess-Schaad Resonance Energies. π-bonding energies based on the additivity were calculated for the cyclic molecules without branching by using the bond-contribution values of the internal C-N bonds and that of a C=O bond of acyclic molecules; they were then compared with properly calculated values. As is shown in Table 3, no resonance stabilization was found for six-, eight-, and ten-membered ring molecules, while the four-membered ring molecule is, though quite slightly, destabilized.

Graph-Theoretical Resonance Energies. The total π-electron energies of real cyclic systems are compared with those of the corresponding hypothetical reference molecules in Table 3. The conclusion to be derived from the comparison is the same as that from the Hess-Schaad method.

σ-Bond Contribution Terms. CODATA key values for thermodynamics[10)] were used to calculate the atomization enthalpies of the compounds given in Table 4 from the standard enthalpies of formation in the gaseous state.[11)] The uncertainties for the atomization enthalpies were calculated by combining the related uncertainties by means of the error propagation equation.

The value of β employed in this paper is -128.0 kJ mol^{-1}, which is the mean among the values given by Hess and Schaad for conjugated alkenes (-128.4 kJ mol^{-1}),[3)] imines (-127.1 kJ mol^{-1}),[4)] amines (-128.1 kJ mol^{-1}),[5)] ketones (-130.4 kJ mol^{-1}),[5)] and ethers

Table 3. Resonace Energies E_R of Cyclic Molecules, $\left[\text{CO-}\underset{|}{\text{N}}\right]_n$. B_π Is the Calculated π-Bonding Energy, and B_π(est) Is The Estimated Value Based on the Bond Additivity. E_π and E_π(ref) Are the Toral Total π-Electron Energies of a Real Molecule and the Corresponding Hypothetical Reference Molecule Respectively

(a) Hess-Schaad method

n	2	3	4	5
B_π/β	5.392	8.132	10.846	13.552
$B_\pi(\text{est})/\beta$	5.424	8.136	10.848	13.560
E_R/β	0.032	0.004	0.002	0.008

(b) Aihara's method

n	2	3	4	5
E_π	$8\alpha+11.832\beta$	$12\alpha+17.792\beta$	$16\alpha+23.726\beta$	$20\alpha+29.656\beta$
$E_\pi(\text{ref})$	$8\alpha+11.862\beta$	$12\alpha+17.794\beta$	$16\alpha+23.725\beta$	$20\alpha+29.656\beta$
E_R/β	0.030	0.002	−0.001	0.000

Table 4. Atomization Enthalpies and Its Components According to Eq. 4. B_π: π-Bonding Energy, E(bond): σ-Bond-Contribution Term, and E_{destab}: Destabilization Energy

Compound	Δ_aH(exp)	$-B_\pi$	$\sum E$(bond)	E_{destab}
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
CH_3NH_2	2302.3±0.8	0	2302	0
$(CH_3)_2NH$	3450.6±1.3	0	3460	9
$(CH_3)_3N$	4608.4±1.6	0	4619	11
$(CH_3)_2CO$	3924.5±1.5	254.9	3671	1
CH_3CHO	2720.6±1.0	254.9	2465	−1
H_2CO	1510.4±0.7	254.9	1258	3
CH_3CONH_2	3483.5±1.3	302.8	3181	0
NH_2CONH_2	3029.0±2.3	349.1	2679	−1
$CH_3CONHCONH_2$[a]	5329 ±3	650.0	4680	1
$CH_3CH_2CONH_2$	4656.7±1.5	302.8	4354	0
$CH_3(CH_2)_2CONH_2$	5828.7±2.1	302.8	5528	2
$CH_3(CH_2)_3CONH_2$	6993.7±2.5	302.8	6701	10
$CH_3(CH_2)_4CONH_2$	8180.6±3.2	302.8	7875	−3
$CH_3(CH_2)_6CONH_2$	10523.9±4.7	302.8	10222	0
$HCON(CH_3)_2$	4589.5±2.4	302.8	4291	4
$CH_3CONH(CH_2)_3CH_3$	8160.9±3.4	302.8	7860	2
$(CH_3CO)_2NH$	5787.9±2.2[b]	604.0	5182	−2
$(CH_3CO)_2N(CH_2)_3CH_3$	10448.8±4.0	604.0	9861	16
$(CH_3CO)_3N$	8032.3±2.9	903.2	7146	17
$\left[\text{CO-N(CH}_3)\right]_3$	9017.2±3.3	1040.9	7975	−1
$\left[\text{CO-NH}\right]_3$[c]	5630.0±2.8	1040.9	4497	90
$\text{CO-NH}(\text{CH}_2)_5$	7666.0±3.0	302.8	7382	19

a) Trans-trans conformer. b) Recalculated value.[12] c) Crystalline state.

(−125.9 kJ mol^{-1}).[6]

The atomization enthalpies were analyzed according to the following equation:

$$\Delta_a H = \sum E(\text{bond}) - B_\pi - E_{\text{destab}}, \qquad (4)$$

where E(bond) is the σ-bond contribution term of a bond; the summation extends over all the σ-bonds in the molecule, and E_{destab}(>0) is the destabilization energy.

As was described in the previous paper, the atomization enthalpy of normal alkanes may be expressed by the simplest bond-additivity scheme:

$$\Delta_a H(\mathrm{C}_k\mathrm{H}_{2k+2}) = (2k+2)E(\text{C–H}) + (k-1)E(\text{C–C}), \qquad (5)$$

where E(C–H)=412.9 kJ mol^{-1} and E(C–C)=347.7 kJ mol^{-1}. These σ-bond-contribution values were transferred to the normal alkyl chains of the present compounds.

For σ-bond-contribution terms of the C–N and N–H bonds, E(C–N̈) and E(N̈–H), the values which were found to reproduce the atomization enthalpies of methyl-substituted amines[1] [E(C–N̈)=297.0 kJ mol^{-1} and E(N̈–H)=383.0 kJ mol^{-1}] were transferred to the present compounds. However, these values led to a significantly negative destabilization energy (−22 kJ mol^{-1}) for trimethyl isocyanurate, for which the energetic stabilization should have been fully accounted for by the π-bonding energy. Consequently, only the atomization enthalpy of methylamine was used to define the magnitude of [E(C–N̈)+2E(N̈–H)]. Likewise, initially we attempted to determine E(Ċ–C), E(Ċ–H), and E(Ċ–Ȯ) from the atomization enthalpies of acetone, acetaldehyde, and formaldehyde. However, these terms were not uniquely determined, since the atomization enthalpy of acetaldehyde is expressed as the arithmetic mean of those of acetone and formaldehyde, in terms of the present bond-energy scheme. Cosequently, E(Ċ–C) was chosen as a parameter.

By analogy with the π-bonding energy, the following three assumptions were made to derive CO–N and C–O σ-bond contribution terms from the atomization enthalpies of the open chain compounds: (1) The CO–N bonds of the linear molecules are classified into three kinds by their position in a molecule. E(Ċ–N̈,amide), E(Ċ–N̈,out), and E(Ċ–N̈,int) are the terms for an amidic C–N bond, an outermost C–N bond, and an internal C–N bond respectively. (2) The following equation holds:

$$E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\text{out}) = [E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\text{amide}) + E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\text{int})]/2. \qquad (6)$$

(3) The bond-contribution term of a carbonyl group which is conjugated with lone-pair electrons of an adjacent nitrogen atom, E(Ċ–Ȯ,conj), is a constant, independent of the position of the bond in the molecule.

If the value of E(Ċ–C) can once be tentatively assigned, the terms to be determined are E(N̈–H), E(C–N̈), E(Ċ–N̈,amide), E(Ċ–N̈,out), E(Ċ–N̈,int), and E(Ċ–Ȯ,conj). It seems, at a glance, that these six terms can be determined from the atomization enthalpies of methylamine, acetamide, urea, acetylurea, and diacetamide, together with Eq. 6. However, the atomization enthalpy of diacetamide is equal to the sum of the atomization enthalpies of acetamide and acetylurea, minus that of urea, in the present scheme. Hence, these terms are not uniquely determined. Consequently, the atomization enthalpy of *N*-butylacetamide was used in place of that of diacetamide in the above method.

The derived bond-contribution values are presented in Table 5, and the experimental atomization enthalpies are decomposed into components according to Eq. 4 in Table 4. The values of E(C–N̈) and E(N̈–H) are slightly different from those given above; the present values lead to small destabilization energies for dimethylamine and trimethylamine. The values of E(Ċ–H) and E(Ċ–Ȯ) given in Table 5 were derived by assuming that E(Ċ–C)=347.0 kJ mol^{-1}. A change x in the value of E(Ċ–C) leads to other changes x and $-2x$ in the values of E(Ċ–H) and E(Ċ–Ȯ) respectively. E(Ċ–N̈,amide), E(Ċ–N̈,out), E(Ċ–N̈,int), and E(Ċ–Ȯ,conj) also depend on the value of E(Ċ–C). The values of these terms given in Table 5 are based on the assumption that E(Ċ–C)=347.0 kJ mol^{-1}. By a change x in the value of E(Ċ–C), each of the values of the former three terms changes by x, while that of the latter one changes by $-2x$. It is notable that the sum of the σ-bond-contribution terms for a molecule being studied is not influenced by a change in the value of E(Ċ–C), because a carbonyl C–O σ-bond is always accompanied by two Ċ–C bonds, two CO–N bonds, or a Ċ–C bond and a CO–N bond, which are adjacent to the C–O σ-bond, in the molecules.

The value of E(Ċ–Ȯ,conj) is lower by 29 kJ mol^{-1} than E(Ċ–Ȯ), the difference being independent of x. This shows a weakening of a C–O σ-bond triggered by the π-electron interaction with an adjacent nitrogen atom. Correspondingly, E(Ċ–N̈,amide), E(Ċ–N̈,out),

Table 5. σ-Bond-Contribution Terms. For Classification of the Bonds, See Fig. 1 and the Text

Bond	E(bond) / kJ mol^{-1}	Bond	E(bond) / kJ mol^{-1}
C–N̈	301.0	Ċ–N̈, amide	358.7
N̈–H	381.0	Ċ–N̈, out	340.5
Ċ–C	347.0[a]	Ċ–N̈, out	322.2
Ċ–H	379.0	C–O, conj	474.1
Ċ–Ȯ	500.0		

a) Tentatively assigned.

and $E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\mathrm{int})$ can be expected to be higher than $E(\mathrm{C}\text{–}\ddot{\mathrm{N}})$, which is the case for the values given in Table 5.

The magnitudes of the σ-bond-contribution terms for CO–N bonds are in this order: $E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\mathrm{amide}) > E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\mathrm{out}) > E(\dot{\mathrm{C}}\text{–}\ddot{\mathrm{N}},\mathrm{int})$, which is in accord with the trend of the π-bond contribution terms, the increment being larger in the former. This means that the total strength of a CO–N bond is highest for amide, in the second place for urea and diacetylimide, and in the third place for the internal bond of acetylurea, which, in turn, would be stronger than the C–N bond of methylamine.

Destabilization Energies. For normal alkanamides and *N*,*N*-dimethylformamide, the destabilization energies are close to zero, with the exception of pentanamide.

The destabilization energy of diacetamide with the CO–N–CO skeleton is nearly zero. The agreement between the calculated and experimental atomization enthalpies for diacetamide shows that the present treatment is a reasonable one. The small destabilization energy of *N*-butyldiacetamide is probably due to repulsion between the three groups bonded to the nitrogen atom.[12]

A triacetamide molecule contains three outermost CO–N bonds that involve a common branching nitrogen atom. For this kind of bond, the σ-bond-contribution value has not been determined. Consequently, the σ-bond-contribution value was assumed to be equal to that of the internal CO–N bond which does not involve a branching nitrogen atom, judging from the similarity in the value of π-bond order. The destabilization energy is attributable to repulsion between the three acetyl groups.[12]

Trimethyl isocyanurate is not significantly destabilized by ring strain. The experimental value for isocyanuric acid is not the atomization enthalpy, but the enthalpy difference between the atomic gases and the crystalline state. The value given in the column of destabilization energy seems to be of a reasonable magnitude as a sublimation enthalpy.

The negative of the destabilization energy (due to the ring strain) of 6-hexanlactam corresponds to standard enthalpy change for the following hypothetical gas-phase ring-opening polymerization reaction:

$$\boxed{\text{CO–NH–(CH}_2\text{)}_5} = (1/n)\left[\text{CO–NH–(CH}_2\text{)}_5\right]_n. \tag{7}$$

Thermochemical Stabilization Energies. In Ref. 1, the stabilization energies were evaluated for acetamide, urea, acetylurea(*trans–trans*), and trimethyl isocyanurate as standard enthalpy changes of the following gas-phase isodesmic reactions:

$$\mathrm{CH_3CONH_2 + C_2H_6 = CH_3COCH_3 + CH_3NH_2}, \tag{8}$$

$$\mathrm{NH_2CONH_2 + 2C_2H_6 = CH_3COCH_3 + 2CH_3NH_2}, \tag{9}$$

$$\mathrm{CH_3CONHCONH_2 + 3C_2H_6 = 2CH_3COCH_3 + CH_3NH_2 + (CH_3)_2NH}, \tag{10}$$

$$\boxed{\left[\text{CO–N(CH}_3\text{)}\right]}_3 + \mathrm{6C_2H_6 = 3CH_3COCH_3 + 3(CH_3)_3N}. \tag{11}$$

Enthalpy changes were decomposed into components according to Eq. 4; the results are shown in Table 6. As expected, in every reaction the contribution from π-bonding energies is more dominant than that related to the σ-bonding energies. It is notable that the contribution from the π-bonding energy is underestimated in the present treatment, because the destabilizing effect of bond compression has been included in this energy.[3]

Thus, the atomization enthalpies of the present compounds have been reasonably interpreted within the framework of the Hess–Schaad theory, and new findings have been obtained on the strength of the CO–N bonds of various molecules.

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Table 6. Decomposition of Reaction Enthalpies into Components

Reaction	$\Delta_r H^\circ$	Contribution/kJ mol^{-1}				
	kJ mol^{-1}	π-Bonding energy	σ-Bonding energy			Destabilization energy
			Total	$\dot{\mathrm{C}}$–C and $\dot{\mathrm{C}}$–$\ddot{\mathrm{N}}$	$\dot{\mathrm{C}}$–$\ddot{\mathrm{O}}$	
(8)	81.8	47.9	33	59	−26	1
(9)	150.1	94.2	55	81	−26	1
(10)	202	140.2	50	102	−52	12
(11)	369.5	276.2	53	131	−78	40

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