

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Bond Energy Scheme for Estimating Heats of Formation of Monomers and Polymers. VII. Nitrogen Compounds

R. M. Joshi^a

^a National Chemical Laboratory, Pune, India

To cite this Article Joshi, R. M.(1982) 'Bond Energy Scheme for Estimating Heats of Formation of Monomers and Polymers. VII. Nitrogen Compounds', *Journal of Macromolecular Science, Part A*, 18: 6, 861 — 911

To link to this Article DOI: 10.1080/00222338208077206

URL: <http://dx.doi.org/10.1080/00222338208077206>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Bond Energy Scheme for Estimating Heats of Formation of Monomers and Polymers. VII. Nitrogen Compounds*

R. M. JOSHI

National Chemical Laboratory
Pune 411008, India

ABSTRACT

The bond energy scheme is extended to nitrogen compounds by correlating experimental thermochemical data reviewed to 1980. Heats of formation and atomization energy terms are provided for bonds of nitrogen with other elements: H, C, O, N, S, and halogens. An overall precision of ± 3 kcal/mol was attainable at the best, which is rather low for chemical reaction kinetics purpose. This is attributable mainly to the intrinsically unpredictable bond energies of the nitrogen atom due to the "lone-pair" electrons participation in the valence bonding, rendering nitrogen bonds specific and less transferable. The nearest-neighbor interactions on nitrogen atom are also severe but predictable if sufficient energy terms are generated. The concept of ring strain in five-membered rings (about 5 ± 2 kcal/mol in the background of thermochemical data) has been reviewed and amended by providing a special set of energy terms for the (C, O, N, S)-ring skeleton which is considered strain-free if the hydrogen atom is the only substituent. Heats of formation of some common molecular structures are predicted.

*N.C.L. Communication No. 2904.

Heats of formation of nitrogen-containing polymers and heats of polymer-forming and polymer-modification reactions are estimated and compared with available calorimetric data.

INTRODUCTION

In continuation of previous work on the bond energy scheme [1], nitrogen compounds are dealt with on the basis of bondwise contribution of energy. Thermochemical, structural, and spectroscopic data required for correlation and assignment of bond energies have been taken mostly from Refs. 1 through 15, supplemented by specific new references as cited itemwise in Table 2. The previously adopted criterion of the constancy of kr^2/E (the SEM constant [1e, 1f] had to be abandoned as inapplicable to nitrogen bonds, partly because the true valence-bond force constants are not easily obtainable from the spectroscopic, normal coordinate analysis generally performed on the basis of the Urey-Bradley force fields system by most spectroscopists. On the contrary, the pure valence-bond force constants and bond order are often derived empirically from the bond (length-energy) relationship and employed for molecular orbital calculations such as MINDO 3, MNDO [16, 24], and SINDO [17]. The results emerging from these computer formats are not yet very impressive, at least in respect to the total energy of a molecule, perhaps because the ideal relationship (and equation) to fit bond energy and bond length has not yet been found. (The "tractrix" equation [18], fulfilling a condition that E is finite at $r = 0$ and vanishes as $r \rightarrow \infty$, appears rather unrealistic in relation to the nature of chemical bonding. The internuclear distances seldom fall below, say, 0.9 Å due to nuclear repulsion, and there is no "bond" of any perceivable energy beyond, say, 3 Å. A simple mathematical function giving limiting values of E for r varying between 0.5 and π will be reported in a later publication.)

DERIVATION OF ENERGY TERMS

A literature survey of thermochemical data on nitrogen compounds shows that heats of combustion measurements on a wide variety of compounds in the condensed state (solid or liquid) are ample, but heats of sublimation/vaporization have not been determined or only inaccurately determined [3, p. 300]. This renders good combustion data unsuitable for any correlation purpose, or even for reaction mechanism-kinetics understanding, unless supplemented by heats of mixing/dilution. Prediction schemes [19, 20] for working out phase-change enthalpies in order to convert the combustion data to gas-phase heats of formation are not very successful with nitrogen compounds

which are highly polar and H-bonded. The present bond-energy scheme is generated only on the basis of selected gas-phase data of recent origin coming from established thermochemical laboratories, and a large amount of work on the condensed phase [5] is set aside for the time being, except where obligatory for the sake of estimating a new typical bonding.

Groupwise classification of compounds with similar structural feature is done, followed by determination of weighted-average group contribution energies in terms of $\Delta H_f^0(g)$. Major groups are listed in Table 1, together with standard deviations indicating the level of inter alia agreement of combustion data of nitrogen compounds, which is rather low. All other known bond energy terms of previous work for (C, H, O, S, X) bonds [1] have been eliminated from the group values which then pertain only to nitrogen bonds. Every group energy value has two interlocked bond-energy parameters. With no amount of additional experimental data, the absolute derivation (algebraic) of a single, isolated energy parameter seems possible from the set of equations generated by the group-contribution values, as already experienced and explained by Dewar and Schmeising [18]. The task of bondwise splitting of group energies into a self-consistent set of bond energy terms is performed through repeated, laborious, trial-and-error operations (regression), keeping in view the only constant criterion of the monotonic inverse length-energy relationship of similar bonds. This is depicted by the reasonably smooth curves of Figs. 1 and 2. Occasionally, a few bond energies were fixed by interpolation on these curves when no other solution was possible. Table 2 presents the final $\Delta H_f^0(g)$ terms, with limits of uncertainty, the corresponding atomization energies, bond lengths, vibrational frequencies (ν_{str} symbolic of force constant), and experimental bond dissociation energies if available.

Nitrogen-Hydrogen Bonds

The bond $N-(C^3)'''$ in tertiary amines (see Footnote b, Table 2, for bond symbols) is the first term that could be derived straightway from the $\Delta H_f^0(g)$ of these amines distributed over three identical bonds.

The energy of the bond, however, appears to depend upon the type of C^3 , whether methyl (C_3^3), ethyl (C_2^3), isopropyl (C_1^3), or tertiary butyl (C_0^3). Experimental data on all these types of tertiary amines, including a recent value for triphenyl amine [21], are available. Eliminating respective $N-C^3$ bonds from primary and secondary amines, the energy terms $N-H''$ and $N-H'$ are obtained. The energy of NH bonds follow the order $NH_3 > NH_2 > NH$, in accord with the analysis of vibration spectra and force constants in primary and secondary amines [22, 23]. The $>N-H$ bond bridging five-membered heterocyclics (azoles) ought to have less energy than the acyclic $-NH$,

TABLE 1. $\Delta H_f^0(g)$ Group Contributions with Limits of Uncertainty, Derived from Experimental Thermochemical Data of Nitrogen Compounds

No.	Class of compounds	Group ^a	$\Delta H_f^0(g)$ (kcal./mol.)	Input energy term ^c	Energy term derived ^c	Reference to Table 2 serial number δ
1	Diazines	(C)-N=(N)	+52.9 \pm 0.9(12)	N=N ^b	N ² -C ³	42
2	Imines	(C)-N=C<	+38.7 \pm 1.6(11)	N ² -C ³	N=C	22
3	Oximes	(H)O-N=C	+41.6 \pm 1.5(10)	N=C	N ² -O	52
4	Nitrous acid and esters	O=N-O(H, C)	+6.2 \pm 1.2(4)	N ² -O	N=O	46
5	Nitric acid and esters	O>N-O(H, C)	-6.6 \pm 0.6(5)	N ⁴ -O ^b	N ⁴ -O ¹¹	48
6	Amides and ureas	O=C-N<	-39.0 \pm 2.0(17)	C=O ^d	N-C ² (O)	29
7	Isocyanates	(C)-N=C=O	-26.2 \pm 3(10) ^e	N-C ^b		

8	Azides	(C)-N=N≡N	+63 ± 5(10)	N-C ^s C=O ^d C=S N=N N ² -C	N=C°(O) N=C°(S) N ² ≡N*	20 21 8
9	Nitro compounds ^h	$\begin{array}{c} \text{O} \\ \diagup \\ \text{N}-(\text{C}) \\ \diagdown \\ \text{O} \end{array}$	-10.0 ± 3(15) ^g	N ⁴ ≡O ^h	N ⁴ -(C)	36-39, 61, 64
10	Nitriles ^h	N≡C-(R)	(R + 45.4) ± 2(20)	N≡C ^l	C ^l -(R)	28, 77-90

^aAtom or group in parenthesis indicate the type of nitrogen bond.

^bFigures in parenthesis in this column indicate number of compounds averaged (with appropriate weighting factor).

^cFor bond symbols see Footnote b, Table 2.

^dRevised value of the carboxyl C=O is -28.0 kcal/mol.

^eAromatic.

^fAliphatic.

^gSee text.

^hSingle substitution.

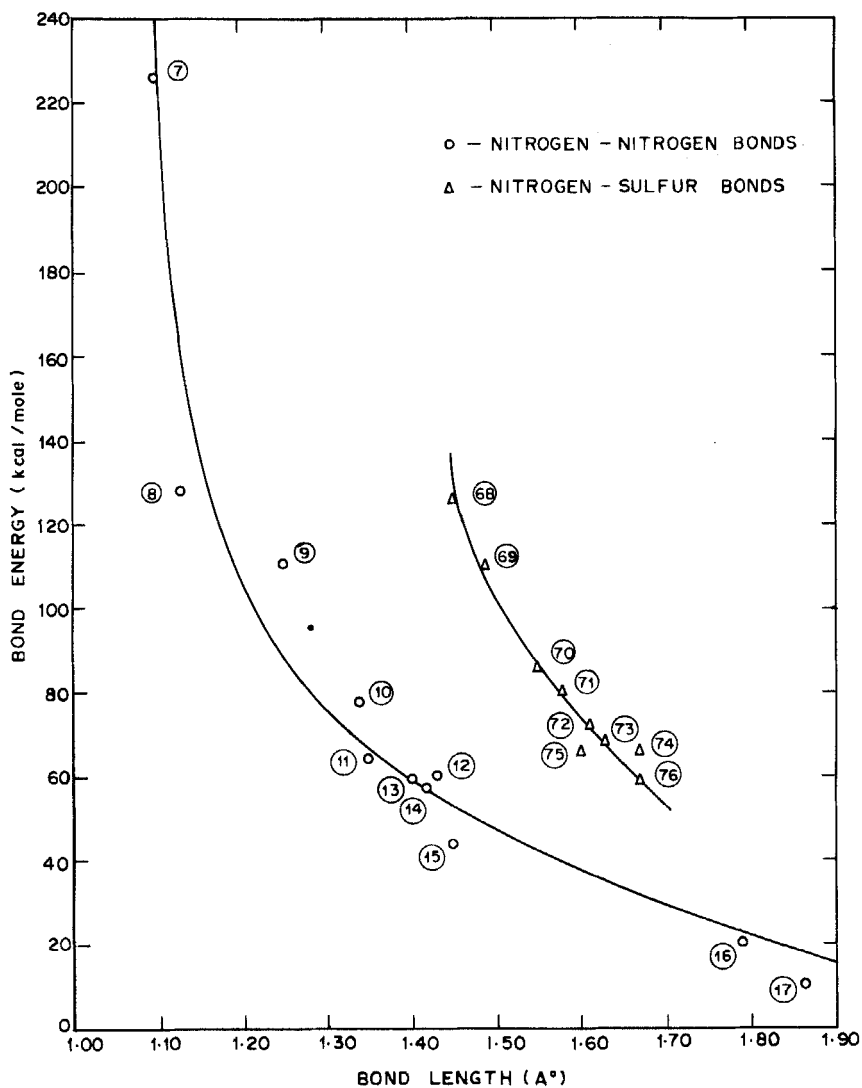


FIG. 1. Bond energy-bond length relationship of nitrogen-nitrogen and nitrogen-sulfur bonds. Encircled numbers correspond to the bond serial numbers in Table 2.

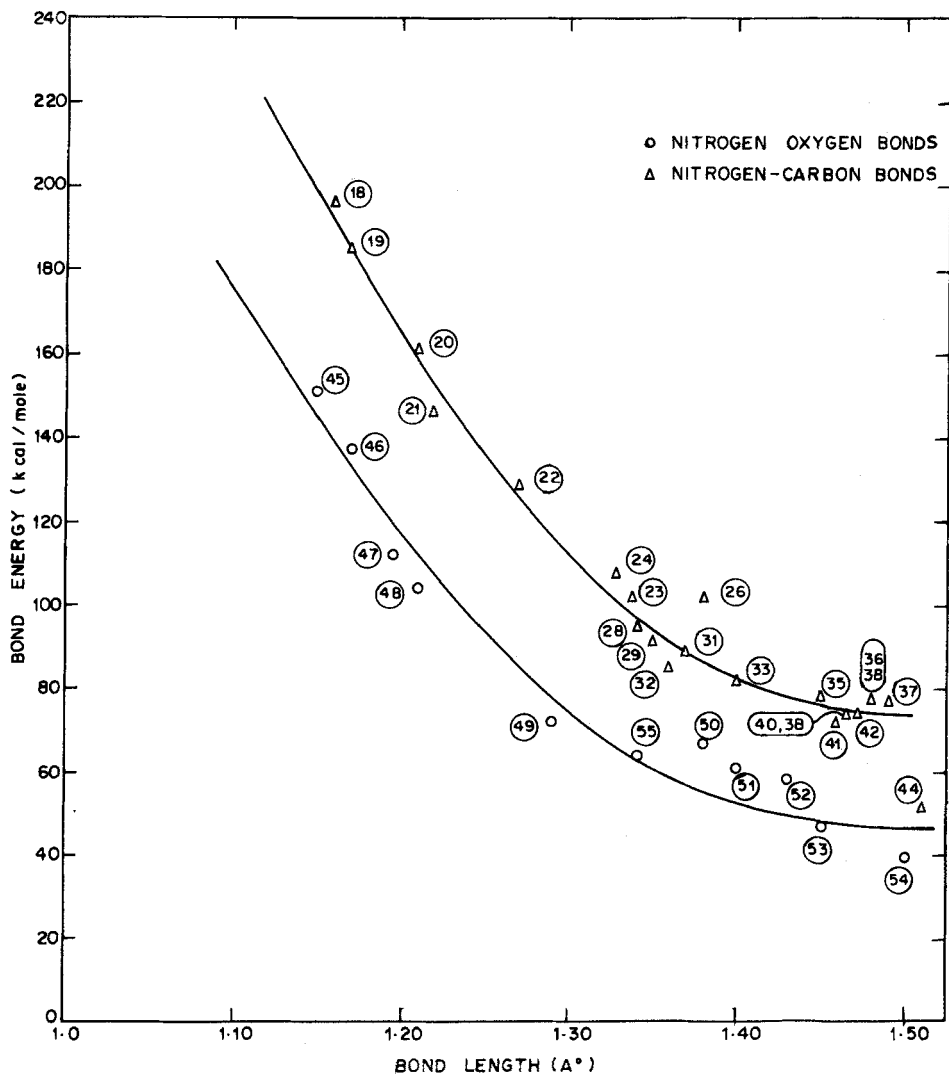


FIG. 2. Bond energy-bond length relationship of nitrogen-oxygen and nitrogen-carbon bonds. Encircled numbers correspond to the bond serial numbers in Table 2.

TABLE 2. Heats of Formation, Thermochemical Bond Energies, and Other Parameters for Nitrogen Bonds

Serial number s^a	Bond ^b	$\Delta H_f^0(g)$ (kcal/mol)	E_a^{25C} (kcal/mol)	Bond length ^d (Å)	Vibrational frequency ^e ν_{str} (cm^{-1})	Dissociation energy DH_f^0 ^f (kcal/mol)	Compounds related or correlated and references
<u>A. Nitrogen-Hydrogen Bonds</u>							
1	N-N ^{'''}		93.4	1.012	3444	110	NH ₃ [15, 32]
2	N-H ^{''}	-2.1 ± 0.3	91.9	1.022	(3427)	103	Amines, primary [15, 22, 23]
3	N-H [']	-1.9 ± 0.3	91.7	1.023		95	Amines, secondary [15, 22, 23]
4	> N-H	0.0 ± 0.5	(89.8) ^g				Azoles/5-membered resonant rings [24]
5	N ² -H	+5.4 ± 1	84.4	1.028	3128	60	HN=NH [25, 33]
6	(O)N ² -H	+26.6 ± 3	(63)	1.063	2854	49	HNO, nitroxyl hydride [8, 15, 66]
<u>B. Nitrogen-Nitrogen Bonds</u>							
7	N≡N	0.0	226.0	1.098	2330	226	N ₂ , ground state [14, 26]
8	N ^{2''} -N [*]	+22.5 ± 3	128.2	1.13	2224		N ₂ O, azides [9, 13, 14, 87]
9	N=N	+40.0 ± 2	110.6	1.25	1583	130	HN=NH [25, 33, 53]

10	$N^{\phi} \equiv N^{\phi}$	+35.3 ± 2	77.7	1.34	Pyridazine, diazophen- anthrene [2, 28, 78]
11	N^2-N	+10.7 ± 1	64.6	1.35	Tetramethyl tetrazene [2]
12	$(OO)N^{\dagger}-N$	+6.1 ± 1	59.8	1.43	Dialkyl nitramines [2, 86]
13	$(O)N^2-N$	+16.0 ± 2	59.3	1.40	N-Nitroso compounds [2, 36]
14	N^2-N^2	+17.8 ± 3	57.5	1.42	Dibenzylideneazine [54, 60]
15	$N-N$	+31.4 ± 1	43.9	1.45	Hydrazines [25, 84]
16	$(OO)N^{\dagger}-N^{\dagger}(O)$		(16.8) ^g	1.78	N_2O_4 [14, 34, 63]
17	$(O)N^{\dagger}-N^2(O)$		(10) ^g	1.86	N_2O_3 [14, 34, 64]
<u>C. Nitrogen-Carbon Bonds</u>					
18	$N \equiv C$	+45.4 ± 4	196.0	1.16	Nitriles [29, 37]
19	$N^2 \equiv C^*$	+61.6 ± 5	(185)	1.17	Isocyanides, fulmi- nates [39, 60, 61]
20	$N=C^{\circ}(O)$	0.0 ± 3	161.0	1.21	Isocyanates [8, 40- 42, 61]
21	$N=C^{\circ}(S,N)$	+15.0 ± 2	146.0	1.22	Isothiocyanates, carbodiimide [43, 61]
22	$N=C$	+32.6 ± 2	128.4	1.27	Imines, guanidines [44]

(continued)

TABLE 2 (continued)

Serial number §a	Bond ^b	ΔH_f^0 (g) (kcal/mol)	E_a^{25C} (kcal/mol)	Bond length ^d (Å)	Vibrational frequency ^e ν_{str} (cm^{-1})	Dissociation energy DH^{0f} (kcal/mol)	Compounds related or correlated and references
23	$N^{\phi} \cdots C^{\phi}$	$+13.5 \pm 0.5$	107.1	1.34			Aromatic nitrogen heterocyclics [1b, 2, 13, 28, 78, 84]
24	$(C^{\phi})N^{\phi} \cdots C^{\phi}(N^{\phi})$	+12.5	108.2	1.32			s-Triazine melamine, cyanuryl chloride
25	$N^{\phi} \cdots C^{\phi}$	+11.5	102.1	1.35			Quinoline, acridine, phenazine [48, 95]
26	$N^{\phi} \cdots C^{\phi}$	0.0	(101.9) ^g	1.38			Aromatic N-oxides, bridgehead-N-aromatics [65, 68-70, 91]
27	$N^{\phi} \cdots C^*$	+63.0	(60.2)	1.40			Pyridinium dicyanomethylide, ylides [2, 99]
28	$N-C^1(N)$	-14.3	94.8	1.34			Cyanamide [2, 3, 9, 30]
29	$N-C^2(O, N)$	-11.0 ± 2	91.5	1.35			Amides, ureas, urethanes, guanidines [58, 60, 93]
30	$N- C^2(O) ''$	-4.1 ± 2	84.6				Thymine, uracil, purines [2, 78]

31	$N-C^2$	-8.9	89.4	1.37	1278	89	Pyrrole, vinyl amine [2]
32	$N-C^2(S)$	-4.6	85.0	1.36			Thioamides, thiourea [59]
33	$N-C^\phi$	-1.0 ± 0.6	81.5	1.40			Aniline, triphenyl- amine and aromatic amines [54]
34	N^2-C^2	+2.5	78.0				Azodicarbamide, cytosine [2, 78c]
35	N^2-C^ϕ	+1.8	78.7	1.45			Diazobenzene [28]
36	$(OO)N^4-C_{0,1}^3$	-8.2	79.3	1.48	851		Nitroalkanes [46]
37	$(OO)N^4-C_{2,3}^2$	-5.6 ± 2	76.6	1.49	(918)	85	Nitroalkanes [46]
38	$(OO)N^4-C^\phi$	-8.4 ± 3	79.5	1.48	1105		Nitrobenzene and nitroaromatics [45, 46]
39	$(OO)N^4-C^2$	-4.7	75.8	1.47	1160		Nitroethylene [47, 62]
40	$N-C_{0,1}^3$	+5.7	74.8	1.46	1160	74	Aliphatic amines (for -CH ₃ group: +8.9) [2, 23]
41	$N-C^3$	$+7.9 + 0.5$	72.6	1.47	(1085)		Diazines, isocyanate link [27, 33]
42	N^2-C^3	$+6.1 \pm 1$	74.4	1.47	(1180)		Aromatic C-nitroso [46]
43	$(O)N^2-C^\phi$	+27.7	52.8				
44	$(O)N^2-C^3$	+30.6	49.9	1.51		40	Aliphatic C-nitroso [37, 46, 69]

(continued)

TABLE 2 (continued)

Serial number §a	Bond ^b	$\Delta H_f^\circ(g)$ (kcal/mol)	E_{25C}^a (kcal/mol)	Bond d length (Å)	Vibrational frequency ^c ν_{str} (cm^{-1})	Dissociation energy DH^{of} (kcal/mol)	Compounds related or correlated and references
D. Nitrogen-Oxygen Bonds							
45	$N \equiv O$		150.9	1.15	1883		NO [34]
46	$N=O$	-2.8 ± 2	137.7	1.17	(1844)		Nitrous acid and esters [34]
47	$N^+ \equiv O''$		112.1	1.19	1618		NO_2 [34]
48	$N^+ \equiv O''$	-1.8 ± 2	103.7	1.22	1516		Nitric acid and esters [34]
49	$N_*^\phi \equiv O$	$+24.6 \pm 5$	(72.6) ^g	1.29	1270		N-Oxide formation of pyridine [65, 68, 70]
50	$N^2 - O$	0.0 ± 8	67.2	1.38			Isoxazoles [68, 69, 76, 95]
51	$(OO)N^1 - O$	-3.0 ± 2	(61) ^g	1.40	(647)	38	Nitrate esters [15, 34]
52	$(O)N^2 - O$	$+9.0 \pm 2$	58.4	1.43	(620)	42	Oximes, nitrite ester bond, hyponitrous acid [7, 8, 34, 94]
53	$N-O$	+19.6	47.8	1.45			NH_2OH , $H_3C-O-NH_2$ [3]
54	$(N^4)'' - O$		(40)	1.50			N_2O_5 [14, 34]

55	$N^* \rightarrow O$	$(-4.8)^E$	(64.3)	1.42	960	Aliphatic amine N-oxide $F_3N \rightarrow O$ radical and ylides [8, 65, 68, 69, 70b]
<u>E. Nitrogen-Halogen Bonds</u>						
56	N^2-F	-10.3	66.8	1.38	989	N_2F_2 [8, 33, 78]
57	$N-F'''$		66.6	1.37	1009	NF_3 [49, 50, 52]
58	$N-F''$	-8.2	64.7	1.40	972	Fluorinated alkane [50, 51, 71]
59	$N-F'$	-6.5	63.0	1.40	58	Fluorinated alkane [72]
60	$(O)N^2-F$	-11.6	68.1	1.47	766	FNO [8, 10, 11, 77]
61	$(OO)N^4-F$	-15.4	71.9	1.47	822	FNO_2 [8, 9, 11]
62	$N-Cl$	+18.3	48.3	1.75	540	NCl_3 [14, 55, 56]
63	$(O)N^2-Cl$	+15.2	51.4	1.98	596	$CINO$ [9, 14]
64	$(OO)N^4-Cl$	+6.8	59.8	1.84	793	$CINO_2$ [14]
65	$N-Br$	+26.7	37.7	2.14	478	NBr_3 [14]
66	$(O)N^2-Br$	+22.3	42.1	2.14	542	$BrNO$ [9, 14]
67	$N-I$		(48) ⁱ	2.53	350	$NH_3 \cdot NI_3$ [57]
<u>F. Nitrogen-Sulfur Bonds</u>						
68	$N \equiv S^4$	+36.5	126.1	1.45	126	NSF [34, 67, 85]
69	$N \equiv S^2$		115.6	1.49	116	NS [6, 8]

(continued)

TABLE 2 (continued)

Serial number	Bond ^b	$\Delta H_f^0(g)$ (kcal/mol)	E_{asC} (kcal/mol)	Bond length (Å)	Vibrational frequency ^e ν_{str} (cm^{-1})	Dissociation energy DH^0_f (kcal/mol)	Compounds related or correlated and references
70	$N \equiv S^6$	+60.6	85.5	1.50		93	NSF_3 [34, 67, 85, 96]
71	$N=S^2$	(+61.5)	(80) ^c	1.58		81	[96, 97]
72	$N^{\phi} \cdots S^{\phi}$	(+16.1)	73.5	1.61		74	S_4N_4 cage [8, 14, 34, 96]
73	$N^2-S^2(N,C)$	(+2.7)	(68) ^c	1.63			1,2,5-Thiadiazole, isothiazole [34]
74	$N-S^2(S,O)$	+4.8	66.0	1.67			N,N' -Dithiadiethyl amine [2, 34, 97]
75	$N-S^6(OO)$	-18.0	66.7	1.60			N,N' -Sulfurylbis(diethyl) amine, sulfamide [2, 14]
76	$N-S^4(O)$	-4.4	58.6	1.67			N,N' -Dithionylbis(diethyl) amine, thionyl diamine [2, 14]
G. Bonds-Supplement to Nitrogen Bonds							
77	$(N)C^1-H$	-14.2	109.1	1.063	3310	120	HCN
78	$(N)C^1-C^3$	-17.6	103.2	1.458	<1000>		Alkane nitriles
79	$(N)C^1-C^2$	-21.8	107.4	1.426			Acrylonitrile

80	(N)C ¹ -C ^ϕ	-20.5	106.1	1.45	846	128	Benzonitrile
81	(N)C ¹ -C ¹	-24.2	109.8	1.369			Dicyanoacetylene
82	(N)C ¹ -C ¹ (N)	-17.0	102.6	1.389	846	128	Cyanogen [73]
83	(N)C ¹ -F	-39.8	101.5	1.262	1077	111	FCN [73]
84	(N)C ¹ -Cl	-13.8	85.6	1.63	694	97	ClCN [73]
85	(N)C ¹ -Br	-2.1	71.7	1.79	600	83	BrCN [73]
86	(N)C ¹ -I	+7.2	61.1	1.99	486	73	ICN [73]
87	(N)C ¹ -S(S)	-5.4	81.3	1.70			NC-SS-CN [2, 9]
88	(N)C ¹ -S(C)	-9.4	85.3	1.68			Thiocyanates [9, 61]
89	(N)C ¹ -O	-14.5	87.1	1.67			Cyanates [9, 23, 61]
90	(N)C ¹ -C ² (O)	-1.8	87.5	1.31			Carbonyl cyanide [2]
91	C=O	-28.0 ^h	173.2	1.23	<1800>		Isocyanates, amide ureas, urethanes, carboxylic acids and esters [1]
92	C=S	+14.0	137.8	1.55	<1523>		S(II) double bond [1]
93	(O)C ² -O	-34.0 ^h	106.6	1.33	<1100>		"Short" bond in car- boxylic acids and esters (revised)
94	O-[C ² (O)] ^h	-26.5 ^h	99.1	1.35	<1200>		Anhydride bond re- vised [1]
95	(C)O-H	-26.4	108.3	0.96	<3650>		Alcohols, phenols, carboxylic acids [1]

(continued)

TABLE 2 (continued)

^aThe symbol \S , followed by the serial number of this column, refers to the particular bond occurring anywhere in the text.

^bBond symbols. Superscript number indicates state of hybridization: $N^2 = sp^2$ -nitrogen, $N^* =$ par-valence canonical structure, $N^0 =$ aromatic, $N =$ tri-covalent nitrogen, $N^0 =$ allene-type nitrogen, $N^4 =$ quadri-covalent nitrogen. The superscripts " and "' mean one of the identical bonds. Type of bonding: arrow (\rightarrow) denotes coordinate bond; \rightarrow , \equiv , \equiv , single, double, triple covalent bond; $\cdot\cdot$ fractional bond order exceeding one but less than two. Subscripts: Small numerical subscripts = number of hydrogens present on the bonding atom; subscript * = atom coupled with two other aromatic bonds or conjugated with two double or triple bonds. Atom placed in parenthesis near the bonding atom denotes its nearest-neighbor association.

^cThermochemical bond energy; parenthesized values in this column denote an estimate obtained by graphical interpolation on (bond-length bond-energy) curve; underlined values are purely arbitrary fixed by rationale/judgment of the author. See text.

^dMostly taken from Refs. 10, 9, 8, 12 in the order of preference.

^eAsymmetric vibrational frequency mostly taken from Ref. 11 as the first choice.

^fDissociation energies mostly taken from Ref. 15.

^gSee text.

^hRevised terms of previous work [1].

ⁱThe N-I bond energy estimate would come to a smaller value if the N^*N bond in the ammonia complex had higher energy than assumed (about 4 kcal/mol) by these authors [57].

on account of the coplanar organization of nitrogen sp -orbitals and the resulting loss of resonance energy of the inversion mode of NH_3 molecule; about 1.9 kcal/mol per bond [24]. The $\Delta H_f^0(g)$ for cyclic $>NH$ in resonant heterocyclic structure is then 0.0 kcal/mol (like bonding in reference-state elements, fortuitously).

The energy term $N=N$ (§9, Table 2)* is derived from a recent, conclusive determination of $\Delta H_f^0(g)$ of diimide, $HN=NH$ [25], as 50.7 \pm 2 kcal/mol at 25°C, which is contributed by two N^2-H and one $N=N$ bonds. The value of $N=N$ bond energy cannot be judged even approximately as interpolation between $N-N$ and $N=N$ in a manner analogous to $C-C$ and $C=C$ bonds. The peculiar nature and unusually high bond energy of $N=N$ has been explained by Pauling [26] who estimated the bond energy of $N=N$ at about 100 kcal/mol. However, the energy for the $N=N$ bond in this work has been determined independently through estimation of the N^2-H bond primarily, and its elimination from the diimide group energy. Since the hydrogen atom has no further electrons other than its valence electron and no electronic repulsion (antibonding) effects of the valence shell type, the bond energies of hydrogen show regularity and smooth dependence on the state of hybridization of the other (bonded) atom. Consequently, $-H$ bonds follow a clean linear pattern of bond (length-energy) relationship, as already observed for $C-H$ bonds in Part II of the earlier work [1b]. The bonds also show reasonable constancy of $kr^2/E = \sigma$, the SFM constant. The valence bond force constant k for the N^2-H bond was calculated as 5.7 mdyne/Å from its observed vibrational frequency (3120 cm^{-1}), in relation to the corresponding established parameters of NH_3 molecule. Assuming for σ a value of 7.1, obtained from $N-H'''$, $N-H''$ and $N-H'$ bonds, $E(N^2-H)$ is found to be 84.4 kcal/mol and the corresponding $\Delta H_f^0(g)$ term (§5) as +5.4 kcal/mol. $\Delta H_f^0(g)$ and E_a^{25} for $N=N$ bond (§9) are then +40.0 and 110.6 kcal/mol, respectively. This estimate of $N=N$ energy is later found to corroborate well with other nitrogen bonds in yielding smooth curves of $NN-$, $NC-$, and $NO-$ bonds as shown in Figs. 1 and 2. The $N=N$ energy estimate, which is higher than Pauling's by 10 kcal/mol, forms the main reference axis of the whole work. The last NH -bond in Table 2 is derived from $\Delta H_f^0(g)$ of the HNO molecule in the ground state as given in the JANAF tables [8], and the weak bond appears reasonable in consideration of its greater bond length.

Bond energy terms of further nitrogen bonds are derived on the basis of $N=N$ term through sequential elimination of known bonds from the group energy aggregates of Table 1, starting from the diazines for which accurate experimental combustion data has become available from Rossini and co-workers [27].

*The symbol § appearing anywhere in the text refers to the serial number of the bond in Table 2.

Nitrogen-Nitrogen Bonds

The energy of the N-N single bond is derived from hydrazines, eliminating the known N-H'', N-H', and other bonds. The aromatic $N^{\phi} \text{---} N^{\phi}$ (§10) and $N^{\phi} \text{---} C^{\phi}$ bonds are derived simultaneously through analysis and correlation of available data on aromatic nitrogen heterocyclics. Recent combustion measurements on diazophenanthrene [28] is of much help in fixing the $N^{\phi} \text{---} N^{\phi}$ bond energy decisively so as to fit mutually with other aromatic bonds and in Fig. 1.

The mutual consistency and harmony of aromatic N^{ϕ} -bonds with the C^{ϕ} -bonds of earlier work [Part II, 1b] show that the nitrogen atom in 6-membered rings forms resonant, aromatic bonds: bond order and bond length intermediate between sp^2 and sp^3 acyclic bonds. The symmetrical s-triazine ring bears an additional resonance energy of about 6 kcal/mol over pyridine- and pyrimidine-type structures. An extra $N^{\phi} \text{---} C^{\phi}$ term (§24) is necessary. The nitrogen atom must adopt a higher oxidation state (IV) if it is to assume the bridge-head position (N_{*}^{ϕ}) without loss of aromaticity. The energy term §26 for this type of $N^{\phi} \text{---} C^{\phi}$ bond is derived from the estimated heat of pyridine N-oxide formation.

The bond $N^2 \rightleftharpoons N^*$ (§8) in azides was identified as the same as in the N_2O or the diazomethane molecule in respect to electronic structure, bond length, and bond energy. Oxides of nitrogen (N_2O_3 and N_2O_4), when the $N=O$ and $N^{\phi} \text{---} O$ energy components of their structures were eliminated from the atomization energies, give rational values for the N-N bonds (§16, 17), though considerably higher than their dissociation energies. Other NN bonds in Table 2 are derived from respective compounds shown in the last column.

Nitrogen-Carbon Bonds

The $C \equiv N$ bond energy is estimated independently by the methodology of Sanderson [29], separately calculating the nonpolar, covalent triple-bond energy and the ionic energy in relation to electronegativities of carbon and nitrogen atoms. The calculated atomization energy of this bond, $E(C \equiv N) = 196.0$ kcal/mol, fitted smoothly with the bond (length-energy) curve of Fig. 2 drawn on the basis of other NC bonds. There seems to be no anomalous, large energy gap between the CN double bond and the triple bond, unlike the nitrogen-nitrogen bonds. Using this value of $C \equiv N$, energies of various other $(N)C^1 \text{---}(X)$ bonds (§77 to 90) are determined, and it is noted that these bonds follow the same energy pattern as the $C^1 \text{---}(X)$ of substituted acetylenes. The data of amides and ureas fitted better when the carboxyl $C=O$ bond was

assigned a $\Delta H_f^0(g)$ value of -28.0 kcal/mol. The term $N-C^2(O)$, the amide linkage (§29), then applies uniformly to amides, ureas, the amido bond in urethanes, and partial amides of polycarboxylic acids. A revision of the $C=O$ in previous work [Part V, 1e] concerning esters, acid halides, etc. seems necessary so as to provide a singular $C=O$ term common to both oxygen and nitrogen compounds. The ester "short" bond and the anhydride bond are revised accordingly, and these new values (§93, 94) are given at the end of Table 2. The experimental $\Delta H_f^0(c)$ of solid cyanamide ($+14.0$ kcal/mol) combined with a reasonable estimate of its heat of sublimation, 12.8 kcal/mol, yield the expected high value for the $N-C^1$ bond ($= 94.8$ kcal/mol) comparable to C^3-C^1 ($= 100.7$ kcal/mol) in acetylenes. The tautomeric carbodiimide structure suspected for this molecule has been ruled out by microwave spectroscopy [30].

The $N-C^\phi$ bond has nearly the same bond energy of 81.5 ± 0.5 kcal/mol in aniline, diphenyl amine, or triphenyl amine [21]. The cyclic bond energy term $N-C^2$ (§31), derived from pyrrole, is adopted for open-chain compounds in the absence of any experimental data on ethylene amines. Using this bond, the $\Delta H_f^0(g)$ for the hypothetical monomer vinyl amine works out to $+7.5$ kcal/mol. Bond energy terms §36 and 37 show that the C^3-NO_2 single bond slightly varies (within 2-3 kcal) with the type of carbon atom depending upon the number of hydrogens resident on it, and this may have some bearing with intramolecular hydrogen bonding in nitro compounds. A similar trend is shown by C^3-NH_2 bonds in amines, §40 and 41. The N^2-C^3 bond (§42), derived from data on diazenes [27], forms an important general link of the type applicable also to isocyanides, isocyanates, isothiocyanates, and nitroso compounds. The energy term §20 for the isocyanate $N=C$ bond was obtained from the isocyanate group contribution, assuming for the carboxyl $C=O$ bond the aforesaid revised value of -28.0 kcal/mol. For the isothiocyanate $N=C$, (§21), the $\Delta H_f^0(g)$ for the $C=S$ bond $= +14.0$ kcal/mol is taken from the carbon disulfide bond of earlier work [1f]. In general, the bond energies of the isocyanate group show considerable disagreement, rendering these bonds specific, as also evidenced by the variety of bond lengths assumed by the same bond in aliphatic and aromatic categories.

Nitrogen-Oxygen Bonds

The energy of the N^2-O bond in oximes and the similar bond in nitrous acid and esters is assumed to be the same from very close bond lengths. Applying this term (§52) to nitrite esters group energy, the value of the $N=O$ bond in trivalent nitrogen compounds is derived as 137.7 kcal/mol (§46). This is apparently lower than the free NO

molecule where the third valence electron contributes an excess binding energy through delocalization or partial ionization, to the extent of about 13 kcal. The bond order of nitric oxide $N\equiv O$ bond exceeds 2, and it is the strongest nitrogen-oxygen bond (§45). However, with only partial delocalization of the valence electron, the nitric oxide molecule, like carbon monoxide, is potentially a reactive free radical. The "short" ester bond $N^{\delta-}-O$ of nitric acid and esters was fixed by interpolation of Fig. 2 as 61.0 kcal/mol for its average bond length of 1.40 Å. This bond is assumed to be slightly stronger (by about 3 kcal) than the N^2-O with bond length of 1.43 Å. The resulting bond energy for the NO_2 group (two identical bonds of the §48 type) is 8.4 kcal less per bond than the bonds of the NO_2 molecule, which is also a free radical structurally, and the N_2O_4 molecule is a result of combination into a covalent $N-N$ bond (§16). The energies of the two coordinate bonds (§49 and 55 of Table 2) $N\rightarrow O$ were derived from the heat of reaction of N -oxide formation of pyridine and aliphatic cyclic amines, respectively.

Nitrogen-Sulfur Bonds

Glemser [96] has characterized SN bonds in respect of their bond lengths, force constants, and bond orders. A revision of these bonds is made with a view to keep consistency with other bond energies of this scheme and also in the light of newer combustion data of the NSF [85] which differ from the earlier value (mass spectrometric) by as much as 46 kcal/mol. Combustion data of some organic molecules, NN' -bis (diethyl) amines of $S-S$, $S=O$, and $O=S=O$ [2], are also not covered by Glemser's review of essentially inorganic nitrogen-sulfur compounds. The bond energy values (§74-76) derived from this data for the $N-S$ single bond are found to be considerably higher and agree more closely with the bond (length-energy) curve of Fig. 1. Tetrasulfur tetranitride S_4N_4 is an eight-membered ring, a "cage" structure formed by two additional, transannular $S-S$ interactions besides the eight regular $N-S$ bonds of bond-order 1.7 assigned to them. The overall bond energy (ignoring $S-S$ interactions) derived from experimental $\Delta H_f^0(g) = 128.8$ kcal/mol [14, 34] for the regular $N-S$ bonds is 73.5 kcal/mol, which falls between a single and a double bond as also does the bond length. The energy term (§72) has therefore been shown as aromatic bonding of $S(IV)$. The bond energies of all NS bonds of Table 2 are consistent with the bond orders assigned to them by Glemser.

The Ring Strain Concept

Ring compounds pose the usual problem of unpredictable strain energy while assigning energies to the bonds. Delocalization of π -electrons or of other nonbonding valence shell electrons such as the

lone pair of nitrogen or oxygen, popularly termed as "resonance," enhances the total binding energy of the molecule. In cyclic compounds, delocalization is more facile due to continuity of the bonded structure ("the ring current" concept [31]), especially when the ring is reasonably planar. Strangely, however, the ring compounds are invariably coupled with (encumbrance of) the ring strain element in the total energy computed bondwise. The paradox seems to arise from first assuming that the usual acyclic bond energies apply to ring bonds and then ascribing the energy deficit to "strain energy" of the ring. The internuclear distances (hence energies) of bonds in the ring skeleton are generally appreciably different from those in the open-chain compounds. The bond lengths, usually slightly larger in ring structure, are indicative of weaker valence bonds (though at times it may be a mere result of geometric adjustment to accommodate bond-angle distortion). For instance, the C-C bond lengths in cyclopentane are 1.546 Å, in cyclobutane 1.558 Å, in cyclopropane 1.512 Å, etc. The Bayer-strain component of the total strain energy can perhaps be eliminated in toto by envisaging and generating a set of special bonds derived from (and for) the ring skeletons with hydrogen atoms as the only substituents of negligible steric factor (i.e., nonbonded interactions or the Pitzer strain [see Part III, 1c]). Adopting these energy terms brings the total ring strain to a higher reference level. The ring strain above this reference line, caused by nonbonded interactions of physically large substituents such as chlorine, -CH₃ groups, etc., may be considered as the true strain energy specific to the particular derivative of the ring skeleton. This idea is similar to the elimination (at least minimization) of the concept of "resonance energy" in favor of stronger hybrid bonds, as advocated and exercised by Dewar and co-workers [18].

A set of special bond energy terms has been provided in Table 3 for five-membered rings which are most often encountered in organic chemistry. The use of these terms would yield exact heats of formation as experimentally observed for five-membered ring compounds with only hydrogens resident on the skeletal atoms. A similar exercise on four- and three-membered rings, with the new energy terms of Table 3, shows that the excess strain in these skeletons due to further bond-angle distortions uniformly amounts to about 22 ± 2 kcal/mol regardless of the composition of the constituent ring-skeletal atoms. Six-membered rings are either essentially strain-free or are "aromatic" [as defined and categorized in Part II, 1b], for which aromatic energy terms superscripted by the symbol ϕ are provided. The application of the new energy terms of Table 3 to polycyclic structures is under study.

DISCUSSION OF RESULTS

The most prominent feature observed regarding the nitrogen bond energies is the active interference of the lone-pair s^2 -electrons with

TABLE 3. Bond Energy Terms for Calculating Strain-free Skeleton of 5-Membered, (C,N,O,S)-Rings, Simple or Fused with Aromatic Moieties

No.	Bond	ΔH_f^0 (g) (kcal/mol)	E_a (kcal/mol)	Compounds related/correlated; references
1	C=C	+39.0	132.3	Cyclopentadiene [2]
2	C ² -C ²	-11.5	97.1	Cyclopentadiene [2]
3	C ² -C ³	-3.3	89.0	Cyclopentane [2]
4	C ³ -C ³	+1.67	84.0	Cyclopentane [2]
5	C ³ - ϕ^{1a}	-4.3	89.9	Fluorene [79]
6	C ³ - ϕ^{1a}	-3.3	89.0	Indane [2]
7	C ² - ϕ^a	-10.5	96.2	Indene [2]
8	ϕ - ϕ^a	-10.0	95.6	Fluorene [2]
9	O-(C ²) ^{1a}	-26.0	98.6	Furan, oxazole [2, 75]
10	O-C ²	-26.0	98.6	Isoxazole [76]
11	O-C ³	-13.8	86.4	Tetrahydrofuran [2]
12	O- ϕ	-19.0	91.6	Benzofuran, dibenzofuran [2]
13	S-(C ²) ^{1a}	-6.8	82.7	Thiophene, methyl thiophenes, 4-methylthiazole [2]
14	S-C ²	-1.8	77.7	2,3-Dihydrothiophene [2]
15	S-C ³	+4.7	71.2	2,5-Dihydrothiophene, thiacyclopentane [2]
16	S- ϕ	+1.2	74.7	Acyclic term [1f]

17	N=N	+38.9	111.7	Terms 17 to 25 are derived simultaneously by solving equations of component energy terms of pyrrole, pyrazole, imidazole, carbazole, indole, benzotriazole, 1,5-diphenyltetrazole, 2,5-diphenyltetrazole, benzopyrrole, etc. (some acyclic terms such as acyclic term §42, §31 were adopted) [2-5]
18	N=C	+33.3	127.6	
19	N ² -N ²	+13.9	61.4	
20	N ² -C ²	-7.0	87.5	
21	N ² -N	+8.5	66.8	
22	N ² -φ	+1.8	78.7	
23	N-φ	-1.6	82.1	
24	N-C ²	-8.9	89.4	§31, Table 2
25	>N-H	0.0	(90)	§4, Table 2 [24]
26	N ² -C ³	+6.1	74.4	Acyclic term §42
27	N-C ³	+8.8	71.7	Pyrrolidine [2]
28	N ² -O	+0.0 ± 3	67.4	Dimethylfuran, 3- and 5-meisoxazole [68, 69, 76]
29	N ² -S	(+2.7)	(68)	Isothiazole, 1,2,5-thiadiazole
30	N-S	+4.8	66.0	Acyclic term §74 adopted
31	S-O	-7.1	70.0	Acyclic term [1f] adopted
32	O-C ² (O) ¹¹	-22.8	95.4	Maleic anhydride; the anhydride bond with C=O = -28.0
33	N ⁴ =C ²	+10.7	132.1	Derived from N-oxide of dimethyl furazan [1a, 69]

^aThe atom connected to -φ indicates its bridged position in the fused ring system.

sp-covalent bonding. The covalent NN single and double bonds are appreciably weakened by the mutual electronic repulsion of the lone pairs and the long nitrogen chain is rarely ever formed, in sharp contrast to the unexcelled CC bonding capacity of carbon. In heteronuclear bonding the lone-pair reserve of electron energy strengthens the bond on account of delocalization of the electron cloud toward the more electronegative atom. Such a polar contribution of varying degree is always involved in the total energy of the heteronuclear bond, causing fractional bond orders. The necessity of calculating separately such polar energy component of the bond energy imposes severe limitations on the transferability of the bond and ultimately on the success of additivity schemes in predicting the total chemical binding energy of a molecule: see Benson's remarks "Pure empiricism thus has come to an impasse" etc. in Ref. 90. Despite these facts, the best possible application of the bond-additivity principle to nitrogen bonds has been attempted here, and prediction capability within ± 3 kcal/mol uncertainty seems to have been attained.

The higher oxidation state N(IV) of the nitrogen atom is caused by promotion of one of the two long-pair s^2 -electrons to sp-orbitals in the tetrahedral orbital structure similar to carbon, while the other unpaired electron is delocalized into partial ionization induced by the more electronegative heteroatom. It is noteworthy, however, that unlike carbon, nitrogen atom rarely forms four independent ligands in a ground-state un-ionized molecule. Only three atoms are generally bonded to nitrogen in either pyramidal N^3 or tetrahedral N^4 symmetry. In the latter, three valence electrons form two bonds of $1\frac{1}{2}$ bond order, like the aromatic bonds of benzene, and the fourth is available for covalent single bonding. Thus the two $N^{\phi}-O$ bonds of the nitro group or nitric acid molecule are aromatic and indistinguishable in respect to energy and bond length, to which the energy term §48 refers. The formation of stable N-oxides from amines provides an example of another kind of N^3-N^4 promotion where the lone pair completely migrates to the oxygen atom octet, forming a coordinate bond according to one view [70b, 70c]. This seems to be the case in aliphatic tertiary amine oxides for which we have assigned the energy term §55 of atomization energy = 64.3 kcal/mol for the purely dative bond, which is to be used without making changes in the energies of other bonds of the aliphatic amine. However, for aromatic amine oxide formation, e.g., pyridine oxide [65], the reaction may be looked upon as a regular N^3-N^4 promotion, since the aromaticity of the pyridine moiety remains essentially the same (perhaps enhanced) according to Chiang [65], who confirms for the oxide the identical aromatic C-C and C-N bond lengths as for pyridine. In pyridine N-oxide the four valence sp-electrons are distributed energywise as three for the two aromatic $N^{\phi}-C^{\phi}$ bonds of pyridine skeleton and one for σ -bonding with oxygen. The ionic energy of the fifth electron of N^4 resides on the $N^{\phi}=O$ bond, making its bond order approach $1\frac{1}{2}$. The two energy terms §26 and §49 are provided for pyridine oxide and other such

aromatic amine oxides. These terms are based on the experimental calorimetric work of Lebedev and co-workers [68, 69].

In some compounds such as isocyanides (RNC), azides (NNN), and fulminates (CNOR) the central nitrogen and the end-atom appear to show unconventional valencies. The nitrogen atom in the IV oxidation state is capable of bonding with a total valence exceeding 4 or approaching 5. These multiple bonds of complexity are shown by superscripts (*) in Table 2, and the $\Delta H_f^0(g)$ terms for such bond, for mere simplicity

and convenience, have been worked out (in relation to E_a^{25}) on the basis of either trivalent (N) or tetravalent (N^4) nitrogen, as shown at the respective places, although it bears $3\frac{1}{2}$ or $4\frac{1}{2}$ or some such fractional total valence. Caution must be exercised if $\Delta H_f^0(g)$ terms are used for calculating the heat of formation that no mix-up of N^3 and N^4 terms is made. As an alternative, atomization energy terms may be used to compute the total atomization energy of a compound, followed by derivation of its heat of formation in the usual manner.

Other miscellaneous, secondary features observed in nitrogen compounds are summarized below.

(1) Like diols and dicarboxylic acids, diamines [83] and dioximes show more negative $\Delta H_f^0(g)$, by about 2 kcal/mol, than predicted.

This may be the result of intramolecular hydrogen bonding [13]. α -Amino acids [78c, 78d] (especially the acyclic ones) show a lower total energy by about 2 to 3 kcal/mol due to the N-C²(O) bond being weaker in the free acid than in the amide or urethane linkage with the same kind of bond.

(2) The bond energy of the C-NO₂ link (§36-39) is considerably higher (30 kcal/mol) than that of the C-NO bond (§43-44), but the bonds N-NO₂ (§12) and N-NO (§13) have equal energies.

(3) The ionic energy component of the C≡N bond (§18) is about 24 kcal/mol as calculated by the procedure of Sanderson [29]. This energy, deducted from the total energy of the bond, yields 172 kcal/mol as the energy of the pure covalent triple bond of nitrogen and carbon, and is identical to C≡C in acetylenes [1b]. Bonds of nitrogen and carbon in different states of hybridization (§29, 30, 32, 39, and 77-80) follow a closely similar pattern as for carbon-carbon bonds in earlier work [1b].

(4) The bond N^2-N (§11) is unexpectedly stronger than N^2-N^2 (§14) by about 7 kcal/mol.

(5) The N-C bond in nitrobenzene (§38) is about 4 kcal/mol stronger than in nitroethylene (§39), attributable to stronger resonance of phenyl conjugation. A similar pattern is followed by the nitroso group (§43, 44).

(6) The ester bond of N-O of nitrite ester (§52) has been assumed to be the same as the one in oximes, purely arbitrarily on the basis of similar bond lengths. Similarly, the energy of the nitrite ester bond (§51) has been judged empirically from its bond length. These

assumptions, if found untenable due to some new experimental or theoretical evidence, may call for a major revision of the scheme.

(7) N-F bonds of all types (§56-61) average to a bond energy of 67 ± 4 kcal/mol, the N-Cl bond to 53 ± 6 kcal/mol, and the N-Br bond to about 40 kcal/mol. The high thermochemical bond energy of 48 kcal/mol experimentally determined [57] for the N-I bond (§67) is not compatible with the above energy pattern of the halogen-nitrogen bonds and the doubtful existence of the bond itself. The energy of the $\text{NH}_3\text{-NI}_3$ complexing bond may be higher than the 5 kcal/mol assumed by these authors.

(8) The scheme is unsuccessful with melamine and cyanuric acid but may yield good predictions in the cases of other derivatives of s-triazine. These compounds exist in dual tautomeric structures with protons shifting from oxygen to nitrogen and vice-versa. The actual experimental heat of formation lies in between the calculated values for these two enol-amide structures. To a lesser extent, these remarks also apply to the unsubstituted oxazoles.

(9) The experimental data on isoxazoles and substituted isoxazoles and isooxadiazoles [68, 69, 75, 76], though of recent origin, grossly disagree. Therefore, the energy term $\text{N}^2\text{-O}$ (§50), which is the mean value of all experimental sources, has a wide limit of uncertainty, ± 8 kcal/mol, and becomes a trivial estimate. More decisive experimental work is needed to determine this term without which oxazoles remain unpredicted.

(10) A comparison of bond energy terms 17 to 25 in Table 3, which relate to bonds in five-membered resonant azole rings, with the corresponding acyclic bonds of Table 2, shows that the bonds in azoles are considerably stronger, contributing all-together an average excess energy of about 20 ± 5 kcal/mol, which may be taken as the net resonance energy in azoles over and above the ring strain conventionally expected with it as a five-membered ring.

(11) In general, the double bonds $\text{C}=\text{O}$, $\text{C}=\text{N}$, and $\text{N}=\text{N}$ seem to assume various unpredictable thermochemical bond energies in different compounds, a fact supported by bond lengths as well as molecular orbital calculations [104]. This gives some justification to the incidence of a large number of redundant energy terms in the additivity scheme.

As specimen calculations, $\Delta H_f^0(g)$, E_a^{25} (atomization energies of some small molecules experimentally yet undetermined or doubtful), and some hypothetical structures have been worked out. These are shown in Table 4, with the fourth column from the left showing the specific new terms of the nitrogen bonds that constitute the compound or structure.

The agreement between calculated and experimental values of heats of formation for a number of compounds in Table 4 (2, 17, 28, 30, 32-35, 45, 46, 53) is quite satisfactory. The experimental data which are compared are of recent origin and conform to modern combustion calorimetry norms and standards, and are complete both in respect


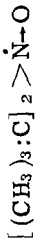

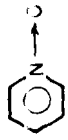

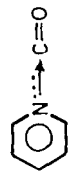
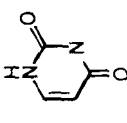
TABLE 4. Heats of Formation and Atomization Energies Predicted for Some Simple Nitrogen Compounds and Hypothetical Structures

No.	Compound	Molecular structure	Relevant energy terms of Tables 2 and 3 ^a	$\Delta H_f^0(g)^b$ (kcal/mol)	E_a^{25} (kcal/mol)	Exptl $\Delta H_f^0(x)$ (kcal/mol), references, remarks ^c
<u>A. Acyclic Compounds</u>						
1	Formimine	$H_2C=NH$	2 (5, 22)	+25.2	415.4	Predicted
2	Diazomethane	$H_2C=N=N$	2 (8, 22)	(+42.2) ^b	459.2	+45.9(g) [9]
3	Formaldazine	$H_2C=N-N=CH_2$	2 (14, 22)	+57.5	719.5	Diazabutadine [54]
4	"Tetrazadiene"	$HN=N-N=NH$	2 (5, 9, 14)	+108.6	447.5	Butadiene analogue
5	Tetrazene	$H_2N-N=N-NH_2$	2 (2, 9, 11)	+53.0	607.4	[92]
6	Tetrazan	$H_2N-NH-NH-NH_2$	2 (2, 3, 15)	+82.0	682.7	[91]
7	Hydrazoic acid	$HN=N=N$	2 (5, 8, 9)	(+67.7) ^b	323.3	
8	Cyanamide	$N=C-NH_2$	2 (2, 18, 28)	+26.9	474.6	+14.1(c) [2], $\Delta H_v^0 = +12.8$
9	Carbodiimide	$HN=C=NH$	2 (5, 21)	+40.8	460.8	[30]
10	Carbamic acid	$H_2N-COOH$	2 (2, 29, 91, 93, 95)	-103.6	663.4	
11	Guanidine	$HN=C(NH_2)_2$	2 (2, 5, 9, 29)	+7.6	763.4	-13.4(c) [44], $\Delta H_v^0 = +21.0$
12	"Cyanofornic" acid	$N\equiv C-COOH$	2 (18, 78, 91, 93, 95)	-64.8	691.5	

(continued)

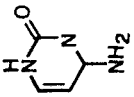
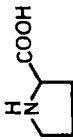
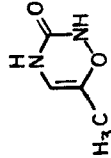
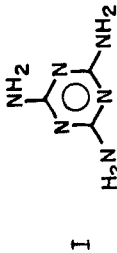
TABLE 4 (continued)

No.	Compound	Molecular structure	Relevant energy terms of Tables 2 and 3 ^a	$\Delta H_f^0(g)^b$ (kcal/mol)	E_a^{25} (kcal/mol)	Exptl $\Delta H_f^0(x)$ (kcal/mol), references, remarks ^c
13	Hydroxylamine	H_2N-OH	2 (2, 53, 95)	-11.0	339.7	-23.5 (aq) [3], -27.3(c) [7]
14	Nitramine	H_2N-NO_2	2 (2, 12, 48)	-1.7	451.0	-21.4(c) [7], $\Delta H_v^0 = +19.7$
15	Formaldehyde	$H_2C=O$	2 (22, 52, 95)	+2.4	497.7	
16	Cyanic acid	$N\equiv C-OH$	2 (18, 88, 95)	+4.0	391.4	
17	Isocyanic acid	$HN=C=O$	2 (5, 20, 91)	-22.6	418.6	-24.3(g) [61]
18	Isotulminic acid	$C\equiv N-OH$	2 (19, 52, 95)	+44.2	351.7	[98]
19	Fulminic acid	$HC\equiv N-O$	2 (19, 55, 77)	(+37.5)	358.4	[98]
20	Thiocyanic acid	$N\equiv C-SH$	2 (18, 88); S-H: -1.3	+34.7	367.8	+41.9(g) [61]
21	Isothiocyanic acid	$HN=C=S$	2 (5, 21); C=S: +14.0	+34.4	368.2	+31.6(g) [61]
22	Hyponitrous acid	$HO-N=N-OH$	2 (9, 52, 95)	+5.2	444.0	-15.4(aq) [7]
23	Dithiocarbamic acid	$S=C(NH_2)-SH$	2 (2, 32); C ² -S: +6.5	+10.4	562.5	
24	Thiourea	$S=C(NH_2)_2$	2 (2, 32); C=S: +14.0	-3.6	675.4	-22.2(c) [2], $\Delta H_v^0 = +18.6$
25	Semicarbazide	$H_2N-CO-NH-NH_2$	2 (2, 3, 15, 29, 91)	-28.9	859.4	

26	Dimethylol urea 	2 (3, 29, 41, 91, 95)	-134.1	1469.6	-174.4(c) [2], $\Delta H_{V,1}^{\circ} = +40$ [80]
27	Ditertiarybutyl N-oxide radical 	2 (40, 55)	-16.1	2496.7	
28	Trifluoramine N-oxide 	2 (55, 57)	-35.1	264.1	-39 ± 5(g) [8]
<u>B. Ring Compounds</u>					
29	Pyridine N-oxide (C ₅ H ₅ NO) 	2 (26, 49)	+31.0	1258.5	Exptl ΔH_f° not reported [65 70]
30	Pyridinium dicyano methylide radical (C ₈ H ₅ N ₃) 	2 (18, 26, 27, 78) ^e	+125.0	1844.5	+125.1(g) [2, 99], singular datum
31	N-isocyanato pyridine (C ₈ H ₅ NO) ^d 	2 (26, 27, 91)	+41.4	1419.3	Predicted ^d
32	Uracil (C ₄ H ₄ N ₂ O ₂) 	2 (3, 29-31, 91); 3 (1, 2)	-70.8	1309.5	-72.4(g) [78a], good agreement

(continued)

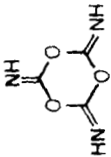
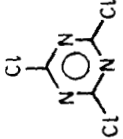
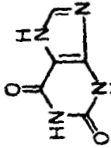
TABLE 2 (continued)

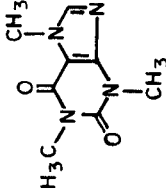
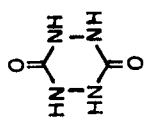
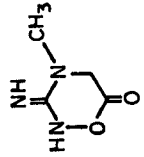
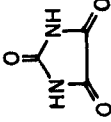
No. Compound	Molecular structure	Relevant energy terms of Tables 2 and 3 ^a	ΔH_f^0 (g) ^b (kcal/mol)	E_a ²⁵ (kcal/mol)	Exptl ΔH_f^0 (x) (kcal/mol), references, remarks ^c
33 Cytosine (C ₄ H ₅ N ₃ O)	 13 bonds	2 (2, 3, 22, 29, 31, 34, 91)	-14.1	1358.5	-14.2(g) [78c], good agreement
34 L-Proline (C ₅ H ₉ NO ₂)	 17 bonds	2 (91, 93, 95); 3 (4, 25, 27)	-88.1	1645.6	-87.5(g) [78d], good agreement
35 Thymine (C ₅ H ₆ N ₂ O ₂)	 15 bonds	2 (3, 29-31, 91)	-80.0	1594.1	-78.6(g) [78a], good agreement
36 Melamine (C ₃ H ₆ N ₆)	 I	2 (2, 24, 33)	+59.4	1445.1	+12.4(g) [2], classical tautomeric structures

II		2 (3, 5, 22, 31)	+54.9	1449.9	See text for Structure III
III		2 (3, 24, 26)	(-0.8) ^b	1505.1	
I		2 (24, 95); C ^φ -O= -23.2	-73.8	1261.5	-165.1(c) [4], classical tautomeric structures, equilibrium at 25°C
II		2 (3, 29, 91)	-155.7	1338.0	
III		2 (3, 30, 91)	-114.3	1302.3	Calc. $\Delta H_v \approx +35$ [20]. H-bonding $\approx +15$ kcal/mol

(continued)


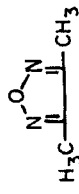
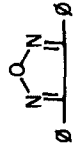

TABLE 4 (continued)






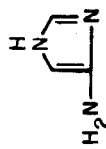
No.	Compound	Molecular structure	Relevant energy terms of Tables 2 and 3 ^a	$\Delta H_f^0(g)^b$ (kcal/mol)	E_a^{28} (kcal/mol)	Exptl $\Delta H_f^0(x)$ (kcal/mol). references, remarks ^c
38	Cyamelide (C ₃ H ₃ N ₃ O ₃)		2 (5, 22); O-C ² = -21.2	-3.2	1201.2	[70a]
39	Cyanuric chloride (C ₃ N ₃ Cl ₃)		2 (23, 24); C -Cl''' = -13.2	+35.4	904.5	+21.9(c) [4], predicted $\Delta H_{V'}^0$ for the two modes is +13.5 or +19.5 kcal/mol ⁶
40	Uric acid (C ₅ H ₄ N ₄ O ₃)		2 (29, 30, 40, 91); 3 (1, 2, 24)	-122.4	1818.1	-147.9(c) [2], $\Delta H_{V'}^0 = +24.5$

41	Caffeine (C ₈ H ₁₀ N ₄ O ₂)		25 bonds	2 (29, 30, 40, 91); 3 (1, 2, 24)	-68.6	2531.5	-76.2(c) [5], old data (1894)
42	Urazine (C ₂ H ₄ N ₄ O ₂)		12 bonds	2 (3, 15, 29, 91)	-44.0	1167.0	-62.4(c) [2], ΔH _v ' = +18.4
43	Creatinine (C ₄ H ₇ N ₃ O ₂)		16 bonds	2 (3, 5, 22, 31, 40, 41, 53, 91, 93)	-30.7	1538.7	-57.0(c) [2, 81], ΔH _v ' = +26.6
44	Parabanic acid (C ₃ H ₂ N ₂ O ₃)		10 bonds	2 (91); 3 (2, 24, 25)	-131.1	1153.9	-138.0(c) [5], old data (1882)

(continued)

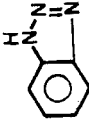


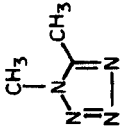
TABLE 4 (continued)

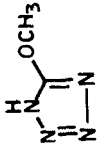
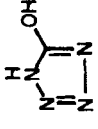

No.	Compound	Molecular structure	Relevant energy terms of Tables 2 and 3 ^a	$\Delta H_f^0(g)$ ^b (kcal/mol)	E_a ²⁵ (kcal/mol)	Exptl $\Delta H_f^0(x)$ (kcal/mol), references, remarks ^c
45	2,1,3-Benzoxadiazole ($C_6H_4N_2O$)		3 (1, 2, 18, 28); ^h $C^\phi-H = -6.8$	+71.4	1449.8	+71.9(g) [95], excellent agreement
		14 bonds				
			<u>C. Azoles</u>			
46	3,4-Dimethylfuran (1,2-5 oxadiazole) ($C_4H_6N_2O$)		3 (2, 18, 28)	+25.4	1257.5	+25.6(g) [69], excellent agreement
		13 bonds				
47	3,4-Diphenyl furazan ($C_{14}H_{10}N_2O$)		3 (2, 18, 28)	+86.6	3117.7	+78.6(c) [2], old data (1931)
		29 bonds				
48	1,3,4-Oxadiazole ($C_2H_2N_2O$)		3 (9, 18, 19)	+17.1	715.0	Prediction
		7 bonds				

49	1,2,4-Thiadiazole (C ₂ H ₂ N ₂ S)		7 bonds	$\underline{3}$ (14, 18, 20, 29)	+49.1	689.6	Prediction
50	Triazoles (C ₂ H ₃ N ₃)	I 		$\underline{3}$ (2, 18, 21, 25)	+60.7	776.9	Structures I and II and Structures III and IV are in tautomeric equilibrium due to annular protonic shift [70a]
		II 		$\underline{3}$ (1, 17, 20, 21, 24, 25)	+59.1	778.7	
		III 		$\underline{3}$ (18, 19, 24, 25)	+51.3	786.4	
		IV 	8 bonds	$\underline{3}$ (18, 20, 21, 24, 25)	+47.8	789.9	
51	3-Amino-1,2,4-triazole (C ₂ H ₄ N ₃)		10 bonds	$\underline{3}$ (18, 20, 21, 24, 25)	+40.4	962.5	+18.4(c) [2], $\Delta H_{\nu}^{\dagger} = +22.0$

(continued)

TABLE 4 (continued)

No. Compound	Molecular structure	Relevant energy terms of Tables 2 and 3 ^a	$\Delta H_f^0(g)^b$ (kcal/mol)	E_a (kcal/mol)	Exptl $\Delta H_f^0(x)$ (kcal/mol), references, remarks ^c
52 Benzotriazole (C ₆ H ₅ N ₃)	 15 bonds	3 (17, 21, 22, 23, 25)	+81.0	1546.3	+59.7(c) [2], $\Delta H_{V'} = +21.3$
53 Tetrazoles (CH ₂ N ₄)	 I	3 (17, 18, 20, 21, 25)	+76.5	650.8	+79.9(g) [2], good agreement
	 II	3 (17, 18, 19, 21, 25)	+80.0	647.3	
54 1,5-Dimethyl tetrazole (C ₃ H ₆ N ₄)	 13 bonds	3 (17, 18, 19, 21, 24); 2 (41)	+68.3	1209.9	+45.1(c) [2], $\Delta H_{V'} = +23.2$, good agreement

55	5-Methoxy tetrazole ($C_3H_4N_4O$)		3 (17, 18, 19, 21, 24, 25)	+40.6	1021.6	+16.5(c) [2], $\Delta H_{V'} =$ +24.1
		11 bonds				
56	5-Hydroxy tetrazole (CH_2N_4O)		3 (17, 18, 19, 21, 24, 25)	+36.1	750.8	+1.5(c) [2], $\Delta H_{V'} =$ +34.6
		8 bonds				
57	2,2'-Azobisiso- butyronitrile ($C_8H_{12}N_4$)	$(CH_3)_2C(CN)-$ $N=N-(CN)C-$ $(CH_3)_2$	2 (9, 18, 42, 78)	+67.8	2379.4	+54.7(c) [2], $\Delta H_{V'} =$ +13.1
		23 bonds				
58	1,2,4,5-sym- Tetrazine ($C_2H_2N_4$)		3 (10, 23)	+111.0	787.2	Prediction
		8 bonds				

^a Together with bond energy terms of previous parts of the scheme [1].

^b Parenthesized value derived via atomization energy; see text.

^c State of compound is shown in parenthesis; (c) = solid, (l) = liquid, (g) = gas, (c') = partly crystalline solid, particularly polymers.

^d A possible reaction between carbon monoxide and pyridine has not been reported.

^e The N atom is taken as promoted to the N^+ state and behaving like aromatic bridge-head nitrogen with 4 valence electrons distributed over three bonds.

(continued)

TABLE 4 (continued)

^fThe enol-type resonant tautomeric structure is ruled out; the carbonodiimide structure II seems to prevail; still the difference. If energy term §30 of Table 2 is used, intramolecular H-bonding as shown may account for about 15 kcal/mol and bring the $\Delta H_v = 35$ kcal/mol in the reasonable range.

^gExperimental heat of sublimation would decide whether the $C^\phi-N^\phi$ bond in cyanuryl chloride has the bond energy of term §23 (pyridine) or §24 (s-triazine).

^hThe aromaticity of the benzo group is destroyed by the two exo bonds; however, the C-H bond is assumed to be of the aromatic (benzene) type, namely -6.8 kcal/mol.

to ΔH_c^0 and the calorimetric sublimation energy. In other cases where reliable combustion data are available but not the heats of sublimation, the predicted values of ΔH_v for sublimation are all very reasonable and in fair conformity with the group-contribution procedures of computing sublimation energies [20]. The two molecules which grossly defy the additivity scheme are melamine and cyanuric acid. In the former, the calculated values for both the classical tautomeric structures, I and II (the aromatic and the amidine), fall short of the experimental atomization energy by some 45 kcal/mol. Structure III is therefore proposed where all the nine C-N bonds in melamine are assumed to be aromatic and intrinsically stronger. The atomization energy computed this way (i.e., assuming $N^3 \rightarrow N^4$ promotion of the NH_2 nitrogen atom) comes closer to the experimental value. In the case of cyanuric acid, the experimental atomization energy is more in favor of the tautomeric, amido structure II (75% amido II + 25% imidol I). Intramolecular hydrogen-bonding in the gas phase may also be a contributing factor in the total energy of the molecule, but experimental sublimation data are not available in the literature for verification. Such measurements would determine whether the strength of the $(O)C^2-N$ amide linkage confirms to \$29 or \$30 as used, respectively, for computing structures II and III of both amido categories.

Polymerization and Polymer Modification Reactions

The results of application of the bond energy scheme to the estimation of heats of reactions leading to polymer formation or modification are presented in Table 5. These typical routes of reactions have been selected from the remarkable compilation of preparative methods in polymer chemistry by Sorenson and Campbell [105]. The estimates of heats of reaction in kcal/mol in the gas phase at 25°C, and pagewise reference to the reaction (underlined numbers) are given. Polymerizations are seldom conducted with gaseous monomer, and gaseous phase for the polymer is hypothetical. However, since the interactions of a common solvent medium with monomer and polymer are essentially the same, and since they cancel out, the calculated energy change for gas-to-gas transformation may be taken as a fair estimate of the heats of reactions in solution, with overall uncertainty of about 2-3 kcal/mol. The real difficulty is nevertheless with polycondensations carried out at higher temperatures in the 250-300°C range such as for heat-resistant polymers (No. 24 or 25 and the oxidative charring of Orlon; No. 19 where the heat of reaction at 25°C has a positive sign). Unless further work on calculating temperature coefficients of all bond energies of this and previous parts of the scheme (i.e., the bondwise ΔC_p^0 assignments) is completed, ΔH_R^0 at the desired temperature cannot be calculated. From a practical viewpoint, merely knowing

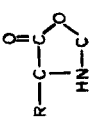

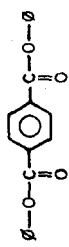
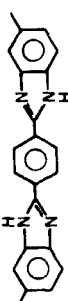
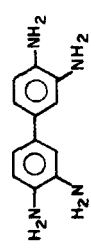
TABLE 5. Heats of Reactions Leading to Polymer Formation or Polymer Modification, Concerning Nitrogen-Containing Monomers and Polymers


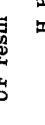
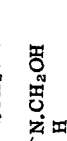
No.	Monomer/ reactants	$\Delta H_f^\circ(g)$: Σ Bond energy terms for bonds broken ^a (kcal/mol)	Polymer/products	$\Delta H_f^\circ(g)$: Σ Bond energy terms for bonds formed ^a (kcal/mol)	Heat of reaction, ^b ΔH_R° (gg) at 25°C (kcal/mol)	Experimental value, ^b reference, remarks
<u>A. Vinyl Polymerization</u>						
1	Vinylamine	+6.46	Poly(vinylamine)	-4.54	-11.0	Predicted
2	Nitroethylene	+11.26	Poly(nitroethylene)	-17.9	-29.1	-21.7(tc) [101, 47]
3	Acrylonitrile	+43.5	Poly(acrylonitrile)	+21.7	-21.8	-18.4(tc) [101]
4	Acrylamide	-35.2	Poly(acrylamide)	-54.7	-19.5	-19.8(ss) [101]
5	Methacrylamide	-44.4	Poly(methacrylamide)	-54.4 ^c	-10.0	-13.9(ss) [101]
6	Maleimide	-69.2	Poly(maleimide)	-87.0	-17.8	-21.2(ss) [101]
7	n-Vinylcarbazole	+64.3	Poly(n-vinylcarbazole)	+41.8	-22.5	-15.2(tc) [101]
8	4-Vinylpyridine	+49.0	Poly(4-vinylpyridine)	+29.8	-19.2	-18.7(ss) [101]
9	n-Vinylpyrrolidone	-40.0	Poly(n-vinylpyrrolidone)	-50.9	-10.9	Predicted
10	Acrylamide	-35.2	Poly(β -alanine) ^d	-47.7	-12.5	Predicted [100, p. 102; 89]
<u>B. Polyaddition (without elimination)</u>						
11	Vinyl polymerization of monoisocyanate: aromatic: $C^\phi-N=C=O$	Σ (20, 35, 42) $\Sigma \Delta H_f^\circ(n) = +1.8$	1-Nylons C^ϕ -N-C- O	Σ (30, 33, 41) $\Sigma \Delta H_f^\circ(n) = -9.9$	-11.7 (aromatic)	[100, p. 411], aromatic iso- cyanates seem to be more reactive
	aliphatic: $C^s-N=C=O$	$\Sigma \Delta H_f^\circ(n) = +6.1$	C^s -N-C- O	$\Sigma \Delta H_f^\circ(n) = -0.4$	-6.5 (aliphatic)	

12	Diamine (active H) + diisocyanate: $\text{OCN}-(\phi)-\text{N}=\text{C}=\text{O}$ $\text{H}_2\text{N}-(\text{R})-\text{NH}_2$	2 (2, 20, 35) $\Sigma \Delta H_f^0(\text{n}) = -2.4$	Polyurea $\text{OCN}(\phi)-\text{N}-\overset{\text{H}}{\underset{\text{O}}{\parallel}}\text{C}-\text{N}-(\text{R})-$	2 (3, 29, 33) $\Sigma \Delta H_f^0(\text{n}) = -26.8$	-24.4 ^e [100, p. 106]
13	Diol (active H) + diisocyanate: $\text{OCN}(\phi)-\text{N}=\text{C}=\text{O}$ $\text{HO}-\text{C}^3(\text{R})-\text{OH}$	2 (20, 35, 95) $\Sigma \Delta H_f^0(\text{n}) = -24.6$	Polyurethane $\text{OCN}(\text{O})-\text{N}-\overset{\text{H}}{\underset{\text{O}}{\parallel}}\text{C}-\text{O}-\text{C}^3$	2 (29, 33, 93) $\Sigma \Delta H_f^0(\text{n}) = -46.0$	-21.4 ^e [100, p. 127] exptl $\Delta H_f^0(\text{ss}) =$ 19.5 to -25.1 [93]
14	Isocyanide polym- erization (carbene- sp^3 -carbon) $\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{N}=\text{C}$	2 (19, 28 ^f) $\Sigma \Delta H_f^0(\text{n}) = +42.6$	Polymer $\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{N} \\ \\ \text{HCH} \\ \\ \text{R} \end{array} \quad \begin{array}{c} \text{N} \\ \\ \text{CH} \\ \\ \text{R} \end{array}$	2 (22, 42); 2 (42, 22) $\Sigma \Delta H_f^0(\text{n}) = +22.9$	-19.7 [100, p. 441; 91]
C. Polyaddition (with elimination)					
15	Inorganic polymer: thioimidodifluoride $\text{HN}=\overset{\text{F}}{\underset{\text{O}}{\text{S}}}-\text{F}$	2 (3, 71); S=O: -35.5 S_4-F^{11} : -46.0 $\Delta H_f^0(\text{g}) = -67.9$	Poly(oxafluoro sulfurtride) $\text{F}-\overset{\text{F}}{\underset{\text{O}}{\text{S}}}-\text{F} + \text{HF}$	2 (71, 76); N-S: -4.4 H-F: -65.0 $\Delta H_f^0(\text{polymer}) = -24.4$ $\Delta H_f^0(\text{HF}, \text{g}) = -65.0$	-21.5 [100, p. 196]
16	Dehydrogenation: $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{C} \equiv \text{N} \end{array} + \frac{1}{2}\text{O}_2$ Polyacrylonitrile (250-275°C)	2 (18, 78) $\Delta H_f^0(\text{g}) = +21.7$	"Black Orlon" + H ₂ O	2 (25); N ^o -C* ^o = +10.0 (non-oxidative) ^g C ^o -C* ^o = +7.0(2) C* ^o -C* ^o = +1.5 C ^o -H = -6.8 $\Delta H_f^0(\text{polymer}) = +31.7$ $\Delta H_f^0(\text{H}_2\text{O}) = -57.8$	+10.0 (non-oxidative) ^g -47.8 (oxida- tive) ^g [100, p. 237]

(continued)

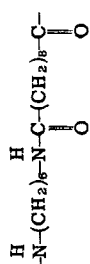

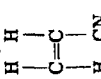
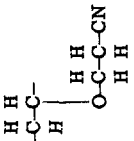
TABLE 5 (continued)

No.	Monomer/ reactants	$\Delta H_f^0(g)$; Σ Bond energy terms for bonds broken ^a (kcal/mol)	Polymer/products	$\Delta H_f^0(g)$; Σ Bond energy terms for bonds formed ^a (kcal/mol)	Heat of reaction, $\Delta H_R^0(gg)$ ^b at 25° C (kcal/mol)	Experimental value, ^b reference, remarks
17	Polypeptides: N-carboanhydride (NCA) of α -amino acids 	2 (2, 29, 91, 94) $\Sigma \Delta H_f^0(n) = -109.0$	Polypeptide 	2 (91) $\Sigma \Delta H_f^0(n) = -28.0$ $\Delta H_f^0(CO_2) = -94.0$	-13.0	[100, p. 352; 88]
18	Diisocyanate (phos- phorane oxide, catalyst): $O=C=N-(R)-$ $N=C=O$	2 (20, 91) $\Sigma \Delta H_f^0(n) = -56.0$	Poly(carbodiimide) $-N=C=N-(R)- + CO_2$	2 (21) $\Sigma \Delta H_f^0(n) = +30.0$ $\Delta H_f^0(CO_2) = -94.0$	-8.0	[100, p. 415]
19	High temperature polymer: conden- sation at 250° C and above: Diphenyl iso- phthalate 	2 (2, 33, 91, 93); $C^{\phi}-O: -23.2$ $\Delta H_f^0(g) = -106.6$	Polybenzimidazole  + 2(phenol) + 2(H ₂ O)	2 (5, 95); 3 (18, 22, 24) +26.9 ^h $C^{\phi}-C^{\phi}: -10.8$ $\phi-\phi: -10.8$ $\Delta H_{f_0}^0(\text{polymer}) = +130.7$ $\Delta H_f^0(\phi-OH) = -23.0(2)$ $\Delta H_f^0(H_2O) = -57.8(2)$	+26.9 ^h	[100, p. 169]
	3,3'-Diaminobenzidine 	$\Delta H_f^0(g) = +48.8$				

20	High temperature polymer: Condensation at 250°C and above: 3,3'-Diaminobenzidine		2 (2,33); Pt, V energy terms	Polybenzimidazole	+15.6 ^h [100, p. 169]
			$\Delta H_f^0(\text{g}) = +48.8$	$\Delta H_f^0(\text{polymer}) = +70.3$	
	Sebacic acid: HOOC-(CH ₂) ₈ -COOH		$\Delta H_f^0(\text{g}) = -225.3$	$\Delta H_f^0(\text{H}_2\text{O}) = -57.8(4)$	
21	Aminoplast resins	Urea/melamine: 	2 (2,29,91)	UF resin	-23.9 ⁱ (dimethyl-ol urea) [100, p. 457]
			$\Delta H_f^0(\text{g}) = -58.4$	C-O: -14.7	
	Formaldehyde: O=CH ₂		$\Delta H_f^0(\text{g}) = -25.9$	$\Delta H_f^0(\text{polymer}) = -93.9$	-17.6 ⁱ (resin)
	Dimethylol urea: 		$\Delta H_f^0(\text{g}) = -134.1$	$\Delta H_f^0(\text{H}_2\text{O}) = -57.8$	

(continued)

TABLE 5 (continued)

No.	Monomer/ reactants	$\Delta H_f^0(g)$; Σ Bond energy terms for bonds broken ^a (kcal/mol)	Polymer/products	$\Delta H_f^0(g)$; Σ Bond energy terms for bonds formed ^a (kcal/mol)	Heat of reaction, $\Delta H_R^0(gg)$ ^b at 25 °C (kcal/mol)	Experimental value, b reference, remarks
22	Interfacial polycon- densation ("nylon rope trick"); Hexamethylene di- amine: $H_2N-(CH_2)_6-NH_2$ Sebacoyl chloride: $Cl-C-(CH_2)_8-C-Cl$	2 (2, 41, 91); C-Cl: -13.3 (O)C ² -C ³ : -4.4 $\Delta H_f^0(g) = -22.1$ $\Delta H_f^0(g) = -131.2$	610 Nylon $H-N(CH_2)_6-N-C(CH_2)_8-C-$  + 2HCl	2 (3, 29, 91) $\Delta H_f^0(\text{polymer}) =$ -160.2 $\Delta H_f^0(HCl, aq) =$ -40.0(2)	-86.9	[100, p. 92]
23	Cyanoethylation of hydroxy polymers; Polyvinyl alcohol:  Acrylonitrile: 	2 (18, 75, 79); C-O: -16.8 $\Delta H_f^0(g) = -49.1$ $\Delta H_f^0(g) = +43.5$	D. Polymer Modification Cyanooethyl PVA 	2 (18, 78) $\Delta H_f^0(\text{polymer}) =$ -19.9	-14.2	[100, p. 243]

24	Nitration of hydroxy polymers (cellulose, PVA, etc.); Polyvinyl alcohol Nitric acid:	2 (48,51,95) $\Delta H_f^0(\text{g}) = -49.1$	Polymer nitrate $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{O}-\text{NO}_2 \end{array}$ + H ₂ O	2 (48,51); -C-O: -16.8 $\Delta H_f^0(\text{polymer}) = -29.3$	-5.0j	For cellulose trinitrate, $\Delta H_R^0 = -15.0$ kcal/mol
	$\begin{array}{c} \text{O} \\ // \\ \text{H}-\text{O}-\text{N} \\ // \quad \backslash \\ \quad \quad \quad \text{O} \end{array}$	$\Delta H_f^0(\text{g}) = -33.0$		$\Delta H_f^0(\text{H}_2\text{O}) = -57.8$		

^a $\sum \Delta H_f^0(n)$ is the summation of energy terms only for those bonds which are formed, broken, or altered during reaction.

^bPhase changes shown in parenthesis: (gg) monomer gas to polymer gas (hypothetically); (lc), liquid monomer to condensed amorphous polymer; (ss), solution to solution.

^cSteric hindrance of about 7 kcal/mol in the polymer chain due to 1, 1-disubstituted alternate carbon (see Part II [1b]) has been taken into account.

^dUnusual ("transition") polymerization route [89].

^eRepresents heat of one single condensation step; for complete reaction ΔH_R^0 will be double the value shown.

^fThe strongest C-N single bond energy (namely §29, Table 2) has been assumed for the isonitrile link.

^gPurely thermal dehydrogenation appears to be endothermic at 25°C; oxidative atmosphere is necessary for the Black-Orlon process. The positive heat of reaction at 25°C does not preclude its occurrence at the substantially elevated temperature of 275-300°C adopted for such condensation; see text for the entropy consideration.

^hMethylol formation and resinification are both strongly exothermic to bring about vigorous reaction. Melamine-formaldehyde condensation is similar but trifunctional.

ⁱMildly exothermic process, dependent strongly upon equilibrium concentration of H₂O, the product of reaction.

the exothermicity of a reaction conducted at such elevated temperatures has little value, especially under the nonequilibrium conditions where one of the products of reaction (HCl, H₂O, CO₂, etc.) is expelled from the reaction site to achieve forward reaction. The free energy must be considered to judge the feasibility of polymerization or condensation reactions. The entropy change ΔS_R^0 for vinyl polymerization of most of the monomers is known to be about 25 ± 5 cal/deg·mol [104], which gives an entropy factor (T ΔS) of about 6-9 kcal/mol at 25°C, unfavorable to the chain-forming process of polymerization. All reactions in Table 5 in which the heat of reaction exceeds about 6 kcal/mol must proceed spontaneously (readily) at room temperature. In a condensation reaction a small molecule is set free and its translational and rotational fraction of the total entropy (H₂O, 45 e.u.; HCl, 44.6 e.u.; CO₂, 51.0 e.u.; H₂, 31.2 e.u.; etc.) may reduce ΔS_R^0 to zero when ΔH_R^0 becomes the sole guiding factor for polymerization reaction. Further, if ΔS_R^0 becomes positive, as is generally the case for condensation reactions [102], higher temperature favors the condensation and esterification or trans-esterification reaction. Besides these thermodynamic considerations (including the usual concentration strategy of removal of the reaction product), the catalysts providing lower (ideally zero) activation energy paths and the pressure are two of the incentives for attempting a new "blackboard" reaction even if it is thermodynamically unfavorable to the extent of 10 kcal/mol in free energy [4]. Such attempts are continuously resulting in novel polymers and breakthroughs in industrial monomer synthesis.

CONCLUDING REMARKS

Large number of parameters (about 90 new energy terms) are necessary to make the bond-additivity concept moderately workable with nitrogen compounds. The bonds of nitrogen are semipolar rather than covalent, and they assume widely differing energies as evidenced by the wide range of bond lengths and vibrational frequencies for similar kind of bonds. In the purely empirical correlation of this level, the only criterion that is preserved is the bond (length-energy) inverse relationship for which an exact mathematical equation must be found. The total chemical energy of a compound may then be predicted, and with acceptable accuracy, merely from the observed bond lengths and a set of these equations, one for each bond between a pair of atoms. The present work and all previous parts (with some revision and integration) hopefully provide a basis for future work in that direction. A noteworthy approach to the prediction of chemical energy is that of Sanderson [29] of calculating separately the covalent and the ionic bonding energies on the basis of electronegativities assigned to the atomic nuclei. Finally, the sophisticated quantum-

mechanical approach: this has recently been analyzed and discussed critically and exhaustively by Dewar [103]. As highlighted by Sander-son [29], the "state-of-the-art" here is still far from satisfactory in spite of computer time and the high costs involved in molecular orbital calculations, even with parameters borrowed from experimental thermochemistry [104].

REFERENCES

- [1] R. M. Joshi, previous work on bond energy scheme. C, H, O, S, and X compounds are published in Parts I to VI in *J. Macromol. Sci.-Chem.*, (a) A4, 1819 (1970); (b) A5, 682 (1971); (c) A6, 595 (1972); (d) A8, 861 (1974); (e) A9, 1309 (1975); (f) A13, 1015 (1979).
- [2] J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic, London, 1970.
- [3] S. W. Benson et al., Chem. Rev., **69**, 279 (1969); **78**, 23 (1978).
- [4] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
- [5] E. S. Domalski, J. Phys. Chem. Data, **1**, 221 (1972).
- [6] B. J. McBride et al., Thermodynamic Properties to 6000°C for 210 Substances Involving the First 18 Elements (NASA-NITS-Publ. N63-23715), U.S. Department of Commerce, Washington, D.C., 1963.
- [7] G. Pilcher, "Specimen Table on Nitrogen Compounds," in CATCH Tables (J. B. Pedley, ed.), University of Sussex, England, 1971.
- [8] D. R. Stull et al. (eds.), JANAF Thermochemical Tables, 2nd ed. (NSRDS-NBS 37), U.S. Department of Commerce-National Bureau of Standards, Washington, D.C., 1970.
- [9] K. H. Hellwege (ed.), Structure of Free Polyatomic Molecules, II/7 (Landolt-Bornstein Compilations: New Series), Springer, Berlin, 1976.
- [10] M. D. Harmony et al., J. Phys. Chem. Data, **8**, 619 (1979).
- [11] T. Shimanouchi, Ibid., **6**, 993 (1977).
- [12] J. Trotter et al. (eds.), Structure Reports, International Union of Crystallography, Oosthoek-Scheltema Publishers, Utrecht, Holland, 1951-1977.
- [13] L. Pauling, The Nature of the Chemical Bonds, 3rd ed., Cornell University Press, Ithaca, New York, 1960.
- [14] C. B. Colburn (ed.), Developments in Inorganic Nitrogen Chemistry, Elsevier, Amsterdam, 1973. Vol. I: M. Green, Chap. 1; A. D. Yoffe, Chap. 2; M. Becke-Goehring, Chap. 3. Vol. II: R. O. Ragsdale, Chap. 1; C. C. Addison and N. Logan, Chap. 2; J. Jander and U. Engelhardt, Chap. 3.
- [15] K. W. Egger and A. T. Cocks, Helv. Chim. Acta, **56**, 1516 (1973).

- [16] M. J. S. Dewar and W. Thiel and T. Morita, J. Am. Chem. Soc. **99**, 4907 (1977); **91**, 796 (1969).
- [17] D. N. Nanda and K. Jug, Theor. Chim. Acta, **57**, 95 (1980).
- [18] M. J. S. Dewar and H. N. Schmeising, Tetrahedron, **11**, 96 (1959).
- [19] A. A. Askadskii et al., Vysokomol. Soedin. (Engl. Transl.), **A19**, 1004 (1977).
- [20] A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968; J. Chem. Eng. Data, **8**, 371 (1963).
- [21] W. V. Steele, J. Chem. Thermodyn., **10**, 441 (1978); Annu. Rep. Prog. Chem., **A**, p. 103 (1974).
- [22] J. E. Stewart, J. Chem. Phys., **30**, 1259 (1959).
- [23] E. M. Layton, Jr., R. D. Cross, and V. A. Fassel, Ibid., **25**, 135 (1956).
- [24] M. J. S. Dewar and G. J. Gleicher, Ibid., **44**, 759 (1966).
- [25] S. N. Foner and R. L. Hudson, Ibid., **68**, 3162 (1978).
- [26] L. Pauling, Tetrahedron, **17**, 229 (1962).
- [27] P. S. Angel, R. A. Melaugh, M. Manson, J. W. Timberlake, A. W. Garner, and F. D. Rossini, J. Chem. Thermodyn., **8**, 607 (1976); **10**, 205 (1978).
- [28] F. W. Schulz, H. J. Petrick, and H. K. Commenga, Z. Phys. Chem. (Frankfurt), **107**, 1 (1977).
- [29] R. T. Sanderson, Chemical Bonds and Bond Energy, 2nd ed., Academic, New York, 1976.
- [30] J. K. Tyler and J. Sheridan, J. Mol. Spectrosc., **43**, 248 (1972).
- [31] J. N. F. Gomes, Theor. Chim. Acta (Berlin), **59**, 333 (1981); cf. Ref. 1.
- [32] C. E. Vanderzee and D. L. King, J. Chem. Thermodyn., **4**, 675 (1972).
- [33] R. A. R. Pearce, I. W. Levin, and W. C. Harris, J. Chem. Phys., **59**, 1209 (1973).
- [34] International Review of Science, Inorganic Chemistry, Ser. 2, Butterworths, London, 1975. Vol. 2: A. J. Vosper, Chap. 4. Vol. 3: A. J. Banister, Chap. 2.
- [35] F. Kaufman, J. Chem. Phys., **46**, 2499 (1967).
- [36] O. F. Golonova et al., Iz. Akad. Nauk SSSR Ser. Khim., No. 7, p. 1495 (1974); Chem. Abstr., **81**, 177814s (1974).
- [37] P. Sellers, G. Stridh, and S. Sunner, J. Chem. Thermodyn., **9**, 1005 (1977).
- [38] G. C. Denault, P. C. Marx, and H. H. Takimoto, J. Chem. Eng. Data, **13**, 514 (1968).
- [39] J. L. Duncan, Spectrochim. Acta, **20**, 1197 (1964).
- [40] V. D. Selinavov et al., Russ. J. Phys. Chem., **49**, 620 (1975).
- [41] A. I. Korovin and L. N. Margolin, Ibid., **50**, 1735 (1976).
- [42] Y. Strepikheev et al., Iz. Vys. Uchebn. Zav. (Khim. Khim., Ch. Tekh.), **5**, 387 (1962); Chem. Abstr., **57**, 14498f (1962).
- [43] S. Sunner, Acta Chim. Scand., **17**, 728 (1962).

- [44] E. P. Kirpichev et al., Russ. J. Phys. Chem., **42**, 269 (1968).
- [45] N. B. Lebedeva et al., Ibid., **45**, 549, 1192 (1971).
- [46] Yu. A. Lebedev and coworkers, Dokl. Akad. Nauk USSR, **221**, 1118 (1975); **190**, 348 (1970).
- [47] D. Vofsi, $\Delta H_{\text{C}}(1) = 292.3$ kcal/mol: Private Communication, 1965; K. R. Loos and H. H. Gunthard, J. Chem. Phys., **46**, 1200 (1967).
- [48] D. M. McEachern, O. Sandoval, and J. C. Imguez, J. Chem. Thermodyn., **7**, 299 (1975).
- [49] G. C. Sinke, J. Chem. Eng. Data, **10**, 295 (1965).
- [50] P. J. Evans and E. Tschuikov-Roux, J. Phys. Chem., **82**, 182 (1978).
- [51] W. D. Good and N. K. Smith, J. Chem. Eng. Data, **15**, 147 (1970).
- [52] A. Allan, J. L. Duncan, J. H. Holloway, and D. C. McKean, J. Mol. Spectrosc., **31**, 368 (1969).
- [53] C. J. Casewit and W. A. Godard III, J. Am. Chem. Soc., **102**, 4057 (1980).
- [54] V. E. Bondybey and J. W. Nibler, Spectrochim. Acta, **29A**, 645 (1973).
- [55] J. Goubeau, Angew. Chem. Int. Ed., **5**, 567 (1965).
- [56] G. Cazzoli, J. Mol. Spectrosc., **53**, 37 (1974).
- [57] M. V. Andrews, J. Shaffer and D. C. McCain, J. Inorg. Nucl. Chem., **33**, 3945 (1971).
- [58] J. L. Duncan, Spectrochim. Acta, **27A**, 1197 (1971).
- [59] G. B. Alken, J. L. Duncan and G. P. McQuillan, J. Chem. Soc., A, p. 2695 (1971).
- [60] Y. Tanaka and K. Machida, J. Mol. Spectrosc., **63**, 306 (1976).
- [61] R. Shaw, "Thermochemistry of Cyanates, Isocyanates and Their Thio Derivatives," in The Chemistry of Functional Groups: Cyanates and Their Thio Derivatives, Part I (S. Patai, ed.), Wiley, New York, 1977.
- [62] H. Hess, A. Bauder, and Hs. H. Gunthard, J. Mol. Spectrosc., **22**, 208 (1967).
- [63] C. H. Bibart and G. E. Ewing, J. Chem. Phys., **61**, 1284 (1974).
- [64] C. H. Bibart and G. E. Ewing, Ibid., **61**, 1293 (1974).
- [65] J. F. Chiang, Ibid., **61**, 1280 (1974).
- [66] J. L. Bancroft, J. M. Hollas, and D. A. Ramsay, Can. J. Phys., **40**, 322 (1962).
- [67] P. A. G. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, J. Chem. Thermodyn., **2**, 71 (1970).
- [68] Yu. A. Lebedev et al., Khim. Geterotsikl. Soedin., p. 963 (1969); Chem. Abstr., **73**, 19191 (1973).
- [69] Yu. A. Lebedev et al., Izvest. Akad. Nauk SSSR, Ser. No. 3, p. 525 Khim., (1967); Chem. Abstr., **75**, 26138 (1967).
- [70] (a) P. A. S. Smith, The Chemistry of Open-Chain Organic Nitrogen Compounds, Vols. I and II, Benjamin, New York, 1966. (b) G. Tsoncaris, J. Chim. Phys., **58**, 619 (1961). (c) C. G. J. Culvenor, Rev. Pure Appl. Chem., **3**, 83 (1953).

- [71] W. D. Good, D. R. Douslin, and J. M. McCullough, J. Phys. Chem., **67**, 1312 (1963).
- [72] H. Richert and O. Glemser, Angew. Chem. Int. Ed., **2**, 530 (1963).
- [73] D. D. Davies and H. Okale, J. Chem. Phys., **49**, 5526 (1968).
- [74] S. N. Ngauv, R. Sabbah, and M. Laffitte, Thermochim. Acta, **20**, 371 (1977).
- [75] D. G. McCormick and W. S. Halinton, J. Chem. Thermodyn., **10**, 275 (1978).
- [76] W. S. Hamilton et al., J. Chem. Eng. Data, **23**, 201 (1978).
- [77] V. I. Chesnokov et al., Russ. J. Phys. Chem. **45**, 1669 (1971).
- [78] R. Sabbah et al., (a) J. Chim. Phys., **74**(1), 115 (1977); (b) Thermochim. Acta, **41**, 33 (1980); (c) Ibid., **35**, 73 (1980); (d) reported under publication in Bull. Soc. Chim. Fr., (1978); Private Communication.
- [79] C. T. Mortimer, Reaction Heats and Bond Energies, Pergamon, 1962, p. 82.
- [80] A. K. Hoffman and A. T. Henderson, J. Am. Chem. Soc., **83**, 4671 (1961).
- [81] W. H. Johnson, J. Res. Natl. Bur. Stand., Sect. A, **79**, 425 (1975).
- [82] N. D. Lebedeva et al., Russ. J. Phys. Chem., **45**, 771 (1971).
- [83] J. F. Messerley, H. L. Finke, A. G. Osborne, and D. R. Douslin, J. Chem. Thermodyn., **7**, 1029 (1975).
- [84] J. R. Durig, S. F. Bush, and E. E. Mercer, J. Chem. Phys., **44**, 4238 (1966).
- [85] J. W. Larson, G. K. Johnson, P. A. G. O'Hare, W. N. Hubbard, and O. Glemser, J. Chem. Thermodyn., **5**, 689 (1973).
- [86] J. K. Tyler, J. Mol. Spectrosc., **11**, 39 (1963).
- [87] W. H. Fletcher and T. P. Garrett, J. Chem. Phys., **25**, 50 (1956).
- [88] M. Goodman and E. Peggion, Pure Appl. Chem., **53**, 699 (1981).
- [89] N. Ogata, J. Polym. Sci., **48**, 271 (1960).
- [90] S. W. Benson, Chem. Technol., **10**, 121 (1980).
- [91] F. Millich, Chem. Rev., **72**, 101 (1972).
- [92] N. Wiberg, H. Bayer, and H. Bachhuber, Angew. Chem. Int. Ed., **14**, 177 (1975).
- [93] E. G. Lovering and K. J. Laidler, Can. J. Chem., **40**, 26 (1962).
- [94] L. Batt, K. Christie, R. T. Milne and A. J. Summers, Int. J. Chem. Kinet., **6**, 877 (1974); Chem. Abstr., **82**, 97460d (1975).
- [95] M. R. Arshadi, J. Chem. Thermodyn., **12**, 903 (1980).
- [96] O. Glemser and R. Mews, Adv. Inorg. Chem. Radiochem., **14**, 333 (1972).
- [97] H. Fleig and M. Becke-Goehring, Z. Anorg. Allgem. Chem., **375**, 8 (1970).
- [98] W. Beck, P. Swoboda, K. Feldl, and R. S. Tobias, Chem. Ber., **104**, 533 (1971).
- [99] R. H. Boyd, K. R. Guhs, and R. Wuthrich, J. Phys. Chem., **71**, 2187 (1967).

- [100] W. R. Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry, 2nd ed., Wiley-Interscience, New York, 1968.
- [101] R. M. Joshi and B. J. Zwolinski, "Heats of Polymerization etc.," in Vinyl Polymerization, Vol. 1, Pt. 1 (G. E. Ham, ed.), Dekker, New York, 1967.
- [102] H. Sawada, Thermodynamics of Polymerization, Dekker, New York, 1976.
- [103] M. J. S. Dewar, Science, 187, 1037 (1975).
- [104] M. J. S. Dewar, The Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, New York, 1969.

Accepted by editor November 25, 1981

Received for publication December 9, 1981