JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office.

VOLUME 93, NUMBER 2 JANUARY 27, 1971

Physical and Inorganic Chemistry

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. VII. A Systematic Study of Energies, Conformations, and Bond Interactions

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Received July 16, 1970

Abstract: A moderately simple level of *ab initio* molecular orbital theory is uniformly applied to a study of the energies and conformations of the complete set of acyclic molecules containing one, two, or three first-row atoms (C to F) and which can be written as classical valence structures without charges or unpaired electrons. Using the concept of bond separation, the interaction of bonds in these molecules is described, and their heats of formation are estimated (mean absolute error = 3.1 kcal mol^{-1}). Energies of complete hydrogenation for the molecules with two first-row atoms are calculated with a mean absolute error of 7.4 kcal mol^{-1}. Calculated isomerization energies are in good agreement with known experimental values.

Although there have been many *ab initio* molecular orbital calculations of the energies of individual organic molecules, there have been few attempts to study a wide range of compounds at a uniform level of approximation. In this paper, we shall present the results of a systematic study of simple molecules which (1) are acyclic; (2) contain only the atoms H, C, N, O, and F; (3) contain up to three heavy atoms (C, N, O, or F); and (4) may be represented by a classical valence structure (single, double, and triple bonds) with no formal charges or unpaired electrons associated with any atom. Within these limitations, we have attempted a complete study of all distinguishable isomers, including those related by rotation about individual bonds.

The first objective of the work is to make a series of predictions of the relative energies of rotational isomers and, consequently, predictions of the conformations of the lowest energy forms of the various species considered. The second objective is to make a comprehensive study of the relative energies of this complete set of molecules. Although it is widely recognized that single-determinant molecular orbital theory is incapable of describing energies of complete atomization satisfactorily, recent work has suggested that the energies of certain types of reaction may be satisfactorily described at this theoretical level.[1-4] In a previous paper in this series,[4] we suggested that the energy of large molecules should be studied in terms of two consecutive types of formal reactions. In the first (the bond separation reaction), the large molecule is broken down into species with not more than two heavy (nonhydrogenic) atoms, formal bond characters being retained. In the second step, the resulting two-heavy-atom molecules are completely hydrogenated to molecules with one heavy atom (methane, ammonia, water, . . .) by addition of an appropriate number of hydrogen molecules.[1,2] Preliminary studies[3,4] showed that the energies of both sets of reactions were quite well described by relatively simple molecular orbital methods. In this paper we shall examine the energies of the complete set of mole-

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cules specified above from this point of view, comparing with experimental data when possible.

In order to carry out a comprehensive investigation of this kind, it is necessary to use a simple quantum mechanical method together with a systematic scheme for selecting the nuclear geometry for the various molecules. For the quantum mechanical method we have used self-consistent molecular orbital theory with a fairly small extended basis set of contracted Gaussian functions.[5] The geometries are chosen according to a standard model used previously,[6] with some further specifications for rotational isomers. Thus, only a single, relatively simple calculation is performed on each isomer, permitting a broad survey of the energies of this wide range of compounds.

Quantum Mechanical Method

The quantum mechanical method used is single-determinant self-consistent-field molecular orbital theory. Each molecular orbital ψ_i is constructed as a linear combination of atomic orbitals (LCAO)

$$\psi_i = \sum_{\mu} c_{\mu i}\phi_\mu$$

Solution of the Roothaan[7] or Pople–Nesbet[8] equations for closed- and open-shell species, respectively, gives the LCAO coefficients $c_{\mu i}$ and then the total energy, given the coordinates and atomic numbers of each of the nuclei.

For the functions ϕ_μ, we have used the (extended) 4-31G basis set[5] consisting of a set of contracted Gaussian type functions. The 1s atomic orbital for heavy atoms (C, N, O, and F) is a sum of four Gaussian s functions. The valence atomic orbitals (1s for hydrogen; 2s, 2p for heavy atoms) are split into inner and outer parts which are respectively sums of three and one Gaussian functions. Common Gaussian exponents are shared between 2s and 2p functions. The exponents were obtained[5] by minimizing the calculated energy of the atomic ground states and rescaling for molecular use. Full details together with the set of standard molecular scale factors are given in ref 5. Overlap populations and orbital charges reported in this paper were obtained by performing a Mulliken population analysis[9] over the extended basis set and then summing the inner and outer parts.

Geometric Model

In order that a uniform treatment be applied to both known and unknown molecules, a standard geometrical model is used. This has been partly specified in an earlier paper.[6] In this model, the symbol X*m* is used for an atom X bonded to *m* neighboring atoms. Standard bond lengths are then specified (single, double, and triple bonds as appropriate) for all bonded pairs of atoms X*m*–Y*n*. The complete list of standard lengths is given in Table I of ref 6. The orientation of bonds from a single atom was also specified previously and is very simple for the molecules considered in this paper. C4 is always tetrahedral (bond angles 109.47°), C3 is always planar trigonal (bond angles 120°), and C2 is always linear. N3 is taken to be pyramidal (C_{3v} local symmetry and 109.47° bond angles) if it is attached only to saturated atoms. If it is attached to one or more unsaturated atoms, it is taken to be planar trigonal (bond angles 120°). Both N2 and O2 are chosen to be bent (bond angle 109.47°). These local geometries do, in fact, only reflect actual experimental geometries rather crudely. For example, N3 attached to an unsaturated atom is often not completely planar.[10–13] Nevertheless, in the absence of complete experimental data, the use of some such set of simple rules is necessary.

To complete the standard geometrical model, we have to describe dihedral angles, giving rotations about individual bonds. Here we proceed in a similar manner, specifying standard dihedral orientations for each appropriate X*m*–Y*n* bond. We attempt to choose these orientations so that they correspond approximately to local minima in the potential surfaces for the simplest molecules with this particular kind of bond. Each such orientation then corresponds to a rotational isomer.

The set of proposed standard dihedral orientations is given in Table I. This covers all molecules dealt with in this study. In most cases, the choice of standard dihedral geometries is directed by complete experimental structural information on simple species containing the appropriate bond, but it has been supported and supplemented by a theoretical study of potential energy curves not reported in detail here.

Table I. Standard Dihedral Geometries

Bond	Geometry[a]
C4—C4	Staggered
C4—C3	Double bond eclipsed
C3=C3	Planar
C4—N3	Staggered
C4—N2	Double bond eclipsed
C3—N3	Planar
C3=N2	Planar
C4—O2	Staggered
C3—O2	Planar
N3—N3	Orthogonal
N3—N2	Planar
N2=N2	Planar
N3—O2	:NOH planar
N2—O2	Planar
O2—O2	Orthogonal

[a] :N refers to the fourth tetrahedral direction for pyramidal nitrogen.

We shall only comment on a few of the entries in Table I. Microwave studies have shown that a methyl C–H bond eclipses the double bond in propene,[14] acetaldehyde,[15] *N*-methylformaldimine,[16] and nitrosomethane.[17] These results lead to the rules for C4–C3 and C4–N2. Both experiment[18] and calculations[19,20]

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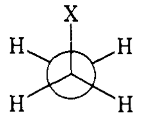
suggest that hydroxylamine has potential minima with :NOH cis and trans,[21] hence the :NOH planar assignment for N3-O2. For some molecules, the potential minima are not determined exactly by symmetry and we have rounded the experimental results in these cases. Thus, for N3-N3 and O2-O2 we have taken the standard conformations, defined by the :NN: and XOOY dihedral angles, respectively, to be orthogonal (dihedral angle 90°) in each case, this being close to the experimental conformations for hydrazine[22] and hydrogen peroxide.[23]

Table I does not define "long-range" (*i.e.*, extending over more than one bond) conformational preferences, as for example in the cumulated systems $CH_2{=}C{=}CH_2$, $CH_2{=}C{=}NH$, and $NH{=}C{=}NH$. By analogy with allene, we might expect the other two molecules to have mutually orthogonal terminal groups. This is indeed supported by calculations (not reported here) on planar and orthogonal forms of these molecules, and so we have taken the standard conformations to be orthogonal.

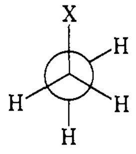
Conformational Isomerism

The standard dihedral geometries so defined lead to a limited number of *standard conformations* for each molecule corresponding, approximately, to local potential minima. We have performed 4-31G calculations on all such standard conformations and the results are shown in Table II. In this table, the molecular conformations are specified only to the extent they are not uniquely determined by the standard rules. For example, ethanol is listed as trans and gauche forms, the fact that all bonds are staggered being omitted because it is already implied by the standard dihedral geometries for C4-C4 and C4-O2 bonds. It is convenient to discuss in turn the conformational isomers arising from rotation about the various bonds.

Let us first consider rotation about the C-N bond in substituted methylamines, XCH_2NH_2. Here, there is the possibility of trans (I) and gauche (II) conformers (as defined by the XCN: dihedral angle). When X = CH_3, the gauche form is calculated to have lower energy while the trans form is favored when X = OH or F. In the intermediate case, $NH_2CH_2NH_2$, there are two C-N bonds, and the favored orientations about them are respectively gauche and trans. Spectroscopic data[24] suggest the presence of both gauche and trans forms for ethylamine (X = CH_3).

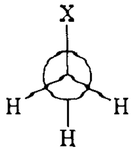


I

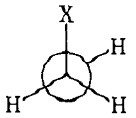


II

Rotation about the C-O bond in substituted methanols, XCH_2OH, also gives rise to trans (III) and gauche (IV) conformers (as defined by the XCOH dihedral angle). When X = CH_3 or NH_2 we find the trans form has lower energy, while the gauche form is favored when X = OH or F. The microwave spectrum of the trans form of ethanol (X = CH_3) has been assigned[25,26] and the spectral results suggest that the gauche conformer is also present.[26,27] Recent theoretical work[28] on fluoromethanol (X = F) has shown the most stable form to be gauche, in agreement with our result and, in addition, has shown that the trans form is a local maximum. A detailed discussion of the potential function for this and related molecules will be presented elsewhere.[29]

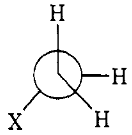


III

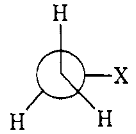


IV

In substituted hydrazines NH_2NHX, rotation about the N-N bond leads to two possible orthogonal forms which we have distinguished by the labels HNNX *external* (V) and HNNX *internal* (VI). When X = CH_3, the *external* form has the lower energy and this agrees with the infrared result[30] that approximately 90% of the molecules exist in the *external* form. For X = OH and F, the *internal* form has the lower energy while in the intermediate case, NH_2NHNH_2, the orientations about the two N-N bonds are, respectively, *internal* and *external.*

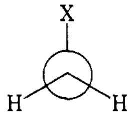


V

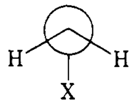


VI

Rotation about the N—O bond in O-substituted hydroxylamines, NH_2OX, leads to cis (VII) and trans (VIII) conformers (as defined by the :NOX dihedral angle). We predict that the cis form is more stable when X = H or CH_3, as suggested by infrared spectral studies.[18,31] The trans form is favored for X = OH and F, while the intermediate case NH_2ONH_2 has cis and trans orientations about the two N-O bonds.

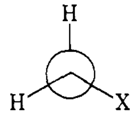


VII

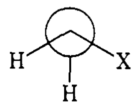


VIII

For N-substituted hydroxylamines, analogous cis (IX) and trans (X) conformers are possible. Here we



IX



X

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Table II. Calculated Total Energies

Stoichiometric formula	Skeleton	Name	Conformation[a]	Total energy, hartrees	Relative energy,[b] kcal mol⁻¹
H_2		Hydrogen		−1.12676	
CH_4		Methane		−40.13955	
NH_3		Ammonia		−56.10452	
OH_2		Water		−75.90841	
FH		Hydrogen fluoride		−99.88728	
C_2H_6	C—C	Ethane		−79.11484	
C_2H_4	C=C	Ethylene		−77.92050	
C_2H_2	C≡C	Acetylene		−76.71105	
CNH_5	C—N	Methylamine		−95.06803	
CNH_3	C=N	Formaldimine		−93.87561	
CNH	C≡N	Hydrogen cyanide		−92.73081	
COH_4	C—O	Methanol		−114.87020	
COH_2	C=O	Formaldehyde		−113.69195	
CFH_3	C—F	Fluoromethane		−138.85648	
N_2H_4	N—N	Hydrazine		−111.00192	
N_2H_2	N=N	Diimide	Trans	−109.81102	0
			Cis	−109.79320	11.18
N_2	N≡N	Nitrogen		−108.75345	
NOH_3	N—O	Hydroxylamine	:NOH cis	−130.78729	0
			:NOH trans	−130.77452	8.01
NOH	N=O	Nitroxyl		−129.57742	
NFH_2	N—F	Fluoramine		−154.75160	
O_2H_2	O—O	Hydrogen peroxide		−150.55257	
O_2	O=O	Oxygen		−149.39267	
OFH	O—F	Hypofluorous acid		−174.51241	
F_2	F—F	Fluorine		−198.45838	
C_3H_8	C—C—C	Propane		−118.09211	
C_3H_6	C—C=C	Propene		−116.90203	
C_3H_4	C—C≡C	Propyne		−115.70061	
	C=C=C	Allene		−115.69753	
C_2NH_7	C—C—N	Ethylamine	CCN: gauche	−134.04904	0
			CCN: trans	−134.04823	0.51
	C—N—C	Dimethylamine		−134.03549	
C_2NH_5	C=C—N	Vinylamine		−132.87015	
	C—C=N	Acetaldimine	HCNH cis	−132.86479	0
			HCNH trans	−132.86128	2.20
	C=N—C	*N*-Methylformaldimine		−132.84406	
C_2NH_3	C—C≡N	Acetonitrile		−131.72711	
	C≡C—N	Ethynylamine		−131.66100	
	C=C=N	Ketenimine		−131.65611	
CN_2H_6	N—C—N	Methylenediamine	:NCN trans, NCN: gauche	−150.00967	0
			:NCN gauche, NCN: gauche	−150.00913	0.34
			:NCN trans, NCN: trans	−150.00872	0.60
			:NCN gauche, NCN: gauche′	−150.00045	5.79
	C—N—N	Methylhydrazine	CNNH external	−149.97197	0
			CNNH internal	−149.97180	0.11
CN_2H_4	N—C=N	Formamidine	HCNH cis	−148.84484	0
			HCNH trans	−148.84016	2.94
	C—N=N	Methyldiimide	Trans	−148.78847	0
			Cis	−148.76758	13.11
	C=N—N	Formaldehyde hydrazone		−148.78528	
CN_2H_2	N—C≡N	Cyanamide		−147.68759	
	N=C=N	Carbodiimide		−147.62058	
C_2OH_6	C—C—O	Ethanol	CCOH trans	−153.85411	0
			CCOH gauche	−153.85306	0.66
	C—O—C	Dimethyl ether		−153.83570	
C_2OH_4	C—C=O	Acetaldehyde		−152.68475	
	C=C—O	Vinyl alcohol	CCOH cis	−152.66422	0
			CCOH trans	−152.66397	0.16
C_2OH_2	C=C=O	Ketene		−151.49451	
	C≡C—O	Ethynol		−151.44137	
CO_2H_4	O—C—O	Methane diol	HOCO gauche, OCOH gauche	−189.62499	0
			HOCO gauche, OCOH trans	−189.61747	4.72
			HOCO gauche, OCOH gauche′	−189.61645	5.36
			HOCO trans, OCOH trans	−189.60717	11.18
	C—O—O	Methyl hydroperoxide		−189.52389	
CO_2H_2	O—C=O	Formic acid	HOCO cis	−188.47060	0
			HOCO trans	−188.46056	6.30
CO_2	O=C=O	Carbon dioxide		−187.32796	
C_2FH_5	C—C—F	Fluoroethane		−177.84154	
C_2FH_3	C=C—F	Fluoroethylene		−176.64601	
C_2FH	C≡C—F	Fluoroacetylene		−175.40948	
CF_2H_2	F—C—F	Difluoromethane		−237.59180	
$CNOH_5$	N—C—O	Aminomethanol	:NCO trans, NCOH trans	−169.81933	0

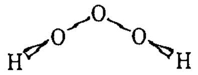
Table II (*Continued*)

Stoichiometric formula	Skeleton	Name	Conformation[a]	Total energy, hartrees	Relative energy,[b] kcal mol^{-1}
			:NCO trans, NCOH gauche	−169.81696	1.49
			:NCO gauche, NCOH gauche′	−169.81600	2.09
			:NCO gauche, NCOH trans	−169.80774	7.27
			:NCO gauche, NCOH gauche	−169.80734	7.52
	C—N—O	*N*-Methylhydroxylamine	:NOH cis	−169.75941	0
			:NOH trans	−169.74833	6.95
	C—O—N	*O*-Methylhydroxylamine	CON: cis	−169.75403	0
			CON: trans	−169.74333	6.71
$CNOH_3$	N—C=O	Formamide		−168.67763	
	N=C—O	Formimidic acid	HNCH cis, NCOH cis	−168.64094	0
			HNCH trans, NCOH trans	−168.63493	3.77
			HNCH trans, NCOH cis	−168.63033	6.66
			HNCH cis, NCOH trans	−168.62767	8.33
	C=N—O	Formaldoxime	CNOH trans	−168.58165	0
			CNOH cis	−168.56453	10.74
	C—N=O	Nitrosomethane		−168.56162	
CNOH	N=C=O	Isocyanic acid		−167.47066	
	O—C≡N	Cyanic acid		−167.45965	
$CNFH_4$	N—C—F	(Fluoromethyl)amine	:NCF trans	−193.80844	0
			:NCF gauche	−193.79752	6.85
	C—N—F	*N*-Fluoro-*N*-methylamine		−193.72640	
$CNFH_2$	N=C—F	Formimidoyl fluoride	HNCH trans	−192.61314	0
			HNCH cis	−192.60762	3.46
	C=N—F	*N*-Fluoroformaldimine		−192.54581	
CNF	F—C≡N	Cyanogen fluoride		−191.42081	
$COFH_3$	O—C—F	Fluoromethanol	HOCF gauche	−213.60830	0
			HOCF trans	−213.59940	5.58
	C—O—F	Methyl hypofluorite		−213.48817	
COFH	O=C—F	Formyl fluoride		−212.43939	
N_3H_5	N—N—N	Triazane	HNNN external, NNNH internal	−165.91159	0
			HNNN internal, NNNH internal	−165.90959	1.26
			HNNN external, NNNH external	−165.89988	7.35
N_3H_3	N—N=N	Triazene	Trans	−164.73792	0
			Cis	−164.72060	10.87
N_2OH_4	N—N—O	*N*-Aminohydroxylamine	HNNO internal, :NOH cis	−185.70176	0
			HNNO external; :NOH cis	−185.69211	6.06
			HNNO internal, :NOH trans	−185.68835	8.41
			HNNO external, :NOH trans	−185.68204	12.37
	N—O—N	*O*-Aminohydroxylamine	:NON cis, NON: trans	−185.66812	0
			:NON cis, NON: cis	−185.66526	1.79
			:NON trans, NON: trans	−185.65437	8.63
N_2OH_2	N—N=O	Nitrosamide		−184.52447	
	N=N—O	Hydroxydiimide	HNNO cis, NNOH trans	−184.52394	0
			HNNO trans, NNOH cis	−184.52353	0.26
			HNNO trans, NNOH trans	−184.52200	1.22
			HNNO cis, NNOH cis	−184.49686	16.99
NO_2H_3	O—N—O	*N*-Hydroxyhydroxylamine	HON: cis :NOH cis	−205.47928	0
			HON: cis :NOH trans	−205.47766	1.02
			HON: trans :NOH trans	−205.46026	11.94
	N—O—O	Hydroperoxyamine	:NOO trans	−205.44393	0
			:NOO cis	−205.44041	2.21
NO_2H	O—N=O	Nitrous acid	HONO trans	−204.30692	0
			HONO cis	−204.30620	0.45
N_2FH_3	N—N—F	Fluorohydrazine	HNNF internal	−207.66950	0
			HNNF external	−207.65765	7.44
N_2FH	N=N—F	Fluorodiimide	Trans	−208.48781	0
			Cis	−208.48595	1.17
NF_2H	F—N—F	Difluoramine		−253.40759	
$NOFH_2$	F—N—O	*N*-Fluorohydroxylamine	:NOH cis	−229.44663	0
			:NOH trans	−229.44085	3.63
	F—O—N	*O*-Fluorohydroxylamine	FON: trans	−229.41193	0
			FON: cis	−229.40459	4.61
NOF	F—N=O	Nitrosyl fluoride		−228.27013	
O_3H_2	O—O—O	Hydrogen sesquioxide	HO---OH anti	−225.21153	0
			HO---OH syn	−225.20512	4.02
O_2FH	O—O—F	Fluorine hydroperoxide		−249.16653	
OF_2	F—O—F	Oxygen difluoride		−273.11712	

[a] The conformations are described from left to right across the molecular skeleton. [b] Energies relative to that of the minimum energy conformation for the particular molecule.

find the cis form has the lower energy in all cases (X = H, CH_3, NH_2, OH, or F).

Hydrogen sesquioxide, HOOOH, has two conformers with HOOO and OOOH dihedral angles both 90°. We have called the form with the plane of symmetry HO---OH syn (XI) and that with the twofold axis HO---OH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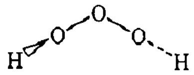
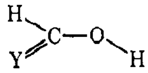
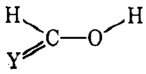

XII

anti (XII). The anti form is found to be more stable.

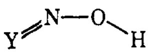
Cis (XIII) and trans (XIV) (as defined by the HOCY dihedral angle) planar forms are possible for molecules of the type HOCH=Y. The cis form has the lower

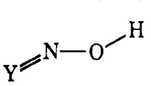

XIII


XIV

energy in each case (Y = CH_2, NH, O). Both experimental[32-35] and other theoretical[36-38] studies have shown the most stable form of formic acid (Y = O) to be cis, but vary in their estimates of the cis–trans energy difference. Infrared work[33] gives this difference as 2.0 kcal mol^{-1}, while the fact that no trans form could be detected in the microwave spectrum suggests[35] an energy difference of at least 4 kcal mol^{-1}. Other theoretical estimates[36-38] range from 8.1 to 9.5 kcal mol^{-1}.

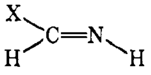
Cis (XV) and trans (XVI) planar forms are also possible for the molecules HON=Y. Here the trans forms

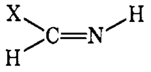

XV


XVI

are predicted to be the more stable for all Y (= CH_2, NH, or O). The microwave spectrum of the trans form of nitrous acid (Y = O) has been assigned,[39] while infrared studies[40,41] show the trans form to be more stable than the cis by 0.5 kcal mol^{-1}, in close agreement with our result. A microwave study on formaldoxime[42] (Y = CH_2) has shown the stable form to be trans, again supporting our calculations.

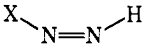
Substituted imines, XCH=NY, may exist as syn (XVII) or anti (XVIII) isomers. We find the syn form

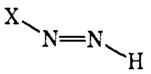

XVII


XVIII

to be more stable for X = CH_3, NH_2, or OH and the anti form to be more stable when X = F.

Finally, cis (XIX) and trans (XX) isomers are possible for substituted diimides, XN=NH. The trans form is calculated to have lower energy in all cases except X = OH. Diimide itself (X = H) has recently been shown[43] to be trans planar.


XIX


XX

Before closing this section, we should point out the notation used to describe the conformations of the molecules $HOCH_2OH$, $NH_2CH_2NH_2$, and NH_2CH_2OH. In these cases, there are two different conformers which may be described as "gauche, gauche" (*e.g.*, for $NH_2CH_2NH_2$ there are two conformations with :NCN gauche and NCN: gauche). We refer to the conformation derived by rotating both terminal methyl groups 120° in the *same* sense from the trans, trans form as gauche, gauche. If the rotations are in opposite senses, we call the conformation gauche, gauche′. Thus in the two molecules above with identical terminal groups, the gauche, gauche form has a C_2 axis while the gauche, gauche′ form has a plane of symmetry.

In the remainder of this paper, we are concerned with the relative stabilities of individual molecules. Since we shall be comparing our calculations with experimental results obtained at temperatures above 0°K when more than one conformation of each molecule is populated, an exact treatment would require consideration of contributions from all such forms. However, only a very small error is involved in using the energy of the conformation of lowest energy, and we have adopted this procedure in the rest of this paper.

Hydrogenation Energies for Molecules with Two Heavy Atoms

We shall now consider the theoretical predictions for the energies of hydrogenation of the molecules with two heavy atoms. A partial study of this was made in ref 4 using experimental geometries. Here we consider the complete set of molecules (for C, N, O, and F) together with standard geometries. There are two main reasons for this study. In the first place, we extend the test of predictions of the 4-31G basis to all the molecules involved. Secondly, since the energies of some of these molecules are unknown experimentally, and since the energies of larger molecules are referred to these by the bond-separation energies, it is necessary to use the theory to help complete the table of hydrogenation energies.

The theoretical hydrogenation energies are for fixed nuclei. They should be compared with experimental heats of hydrogenation at 0°K corrected for zero-point vibrations. To obtain the experimental numbers, the thermodynamic and spectroscopic data shown in Table III are used. These include the zero-point vibrational energy, $H_{vib}(0)$, and observed heats of formation at 0 and 298°. In some cases where heats of formation at 0° were unavailable, they were estimated using the observed heat at 298°, the observed fundamental vibrational frequencies (ν_i), and the formulas

$$H_{trans}(T) = {}^5/_2RT$$

$$H_{rot}(T) = RT \text{ (linear molecule)}$$

$$= {}^3/_2RT \text{ (nonlinear molecule)}$$

$$H_{vib}(T) = H_{vib}(0) + N\sum_i h\nu_i/(e^{h\nu_i/kT} - 1)$$

$$H_{vib}(0) = {}^1/_2Nh\sum_i \nu_i$$

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Table III. Spectroscopic and Thermodynamic Data (kcal mol^{-1}) for Small Molecules

Molecule	Zero-point vibrational energy[a]	$\Delta H_f°$[b] 0°	$\Delta H_f°$[b] 298°
H_2	6.30[c]	0	0
CH_4	27.11	−15.970[d]	−17.889[d]
NH_3	20.63	−9.34	−11.02
H_2O	12.88	−57.102	−57.796
HF	5.92[c]	−64.789	−64.8
$CH_3{-}CH_3$	45.27	−16.523[d]	−20.236[d]
$CH_2{=}CH_2$	30.89	14.515[d]	12.496[d]
$CH{\equiv}CH$	16.18	54.324[d]	54.194[d]
$CH_3{-}NH_2$	39.17	−1.91[e]	−5.49
$CH_2{=}NH$			(26.2 est)[f]
$CH{\equiv}N$	9.77	32.39	32.3
$CH_3{-}OH$	31.13	−45.355	−47.96
$CH_2{=}O$	16.11	−27.1	−27.7
$CH_3{-}F$	23.95	−54.079[g]	−56.000[g]
$NH_2{-}NH_2$	29.79[g]	26.18	22.80
$NH{=}NH$			50.2[g]
$N{\equiv}N$	3.38[c]	0	0
$NH_2{-}OH$			−9.3[h]
$NH{=}O$	8.96[i]	24.5[g]	23.8[g]
$NH_2{-}F$			(−6.6 est)[f]
$HO{-}OH$	15.79[j]	−31.08	−32.58
$O{=}O$	2.26[c]	0	0
$HO{-}F$			(−27.7 est)[f]
$F{-}F$	1.27[c]	0	0

[a] Unless otherwise noted, from T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," NSRDS-NBS 6, 11, and 17, National Bureau of Standards, Washington, D. C., 1967 and 1968. [b] Unless otherwise noted, from D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, W. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968. [c] G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950. [d] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [e] Calculated from $\Delta H_f°(298°)$ and fundamental vibrational frequencies as described in the text. [f] Estimated values; see text. [g] "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Company, Midland, Mich., 1965. [h] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [i] G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1966. [j] R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962).

Table IV. Hydrogenation Energies (kcal mol^{-1}) for Molecules with Two Heavy Atoms

Hydrogenation reaction	Calcd	Exptl Vibrationally corrected, 0°	Exptl 298°
$CH_3CH_3 + H_2 \rightarrow 2CH_4$	−23.5	−18.1	−15.5
$CH_2CH_2 + 2H_2 \rightarrow 2CH_4$	−65.9	−57.2	−48.3
$CHCH + 3H_2 \rightarrow 2CH_4$	−117.8	−105.4	−90.0
$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$	−30.9	−25.7	−23.4
$CH_2NH + 2H_2 \rightarrow CH_4 + NH_3$	−72.1		(−55.1)[a]
$HCN + 3H_2 \rightarrow CH_4 + NH_3$	−83.4	−76.8	−61.2
$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	−32.0	−30.3	−27.7
$CH_2O + 2H_2 \rightarrow CH_4 + H_2O$	−64.3	−57.3	−48.0
$CH_3F + H_2 \rightarrow CH_4 + HF$	−27.4	−29.5	−26.7
$NH_2NH_2 + H_2 \rightarrow 2NH_3$	−50.4	−50.0	−44.8
$NHNH + 2H_2 \rightarrow 2NH_3$	−90.7		−72.2
$N_2 + 3H_2 \rightarrow 2NH_3$	−47.3	−37.7	−22.0
$NH_2OH + H_2 \rightarrow NH_3 + H_2O$	−62.0		−59.5
$HNO + 2H_2 \rightarrow NH_3 + H_2O$	−114.2	−102.9	−92.6
$NH_2F + H_2 \rightarrow NH_3 + HF$	−71.2		(−69.2)[a]
$HOOH + H_2 \rightarrow 2H_2O$	−86.3	−86.8	−83.0
$O_2 + 2H_2 \rightarrow 2H_2O$	−107.1	−125.1	−115.6
$HOF + H_2 \rightarrow H_2O + HF$	−98.2		(−94.9)[a]
$F_2 + H_2 \rightarrow 2HF$	−118.9	−133.8	−129.6

[a] Estimated values, see text.

Calculated and experimental hydrogenation energies are compared in Table IV. The agreement is moderate, the mean absolute error being 7.4 kcal mol^{-1}. In general, the calculated values are too negative, indicating that the theory is handling the one-heavy-atom products better than the larger molecules. Exceptions are CH_3F, H_2O_2, O_2, and F_2. Some of the molecules listed were treated in earlier work.[4] The calculated hydrogenation energies reported here are slightly different because of the change of nuclear geometry. For five of the molecules, complete geometry optimizations have been carried out[5] leading to hydrogenation energies of −23.1 (C_2H_6), −65.1 (C_2H_4), −117.7 (C_2H_2), −84.1 (HCN), and −64.1 (H_2CO). These numbers are almost identical with those in Table IV, indicating that the remaining error is not due to the choice of nuclear geometry.

For the molecules formaldimine, fluoramine, and hypofluorous acid, no thermodynamic data are available and it is not possible to make a comparison. However, since the errors shown in Table IV are fairly regular, it is worthwhile to use the theory to make estimates of the hydrogenation energies (and hence heats of formation) for these compounds.

We first note that the difference between the theoretical hydrogenation energy and the experimental (uncorrected, 298°) is −17.6 for ethylene and −16.3 for formaldehyde. Interpolating between these values, we suggest that the corresponding difference for formaldimine is about −17.0. This leads to a predicted heat of hydrogenation (298°) of −55.1 kcal mol^{-1}. This then gives a value of +26.2 kcal mol^{-1} for the heat of formation (298°) of formaldimine.

For hypofluorous acid, we consider similar differences for the isoelectronic series CH_3OH, NH_2OH, and HOOH. These are −4.3, −2.5, and −3.3. We assume the differences for FOH to be the mean of these (−3.3), leading to a heat of hydrogenation of −94.9 kcal mol^{-1} and a $\Delta H_f°(298°)$ of −27.7 kcal mol^{-1}.

Finally we treat fluoramine as half-way between methyl fluoride and hypofluorous acid, the corresponding difference being −2.0. This gives values of −69.2 kcal mol^{-1} for the heat of hydrogenation and −6.6 kcal mol^{-1} for the heat of formation (298°). A similar value can be obtained by extrapolation along the series NH_2CH_3, NH_2NH_2, NH_2OH, NH_2F.

These estimated energies are included in Tables III and IV for completeness. However, it should be emphasized that they are based on incompletely tested interpolation schemes and may be in error by several kilocalories per mole.

Bond Separation Energies for Molecules with Three Heavy Atoms

In this section we examine the bond separation energies for the larger molecules listed in Table II, comparing with experiment when possible. As introduced in ref 3 and 4, the bond separation energy is the energy of the reaction in which a molecule with three or more heavy atoms is converted into molecules with two heavy atoms and the same types of formal bonds. For ex-

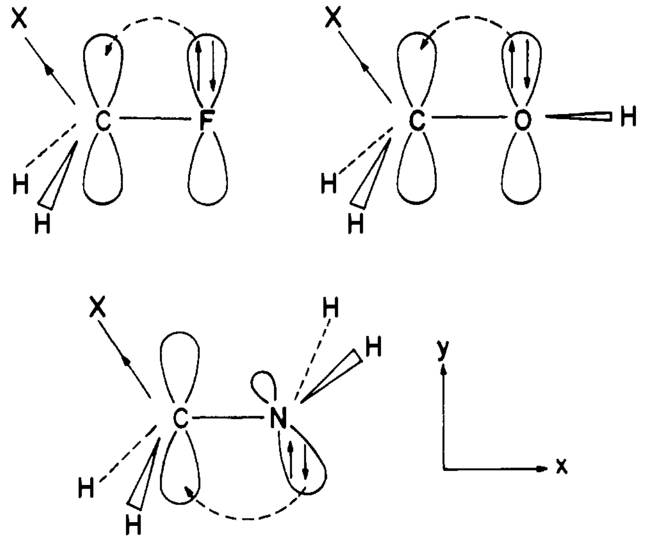


Figure 1. Electron donation from fluorine, hydroxyl, or amino lone pair into C–X bond.

ample, the bond separation reaction for ketene is

$$CH_2{=}C{=}O + CH_4 \longrightarrow CH_2{=}CH_2 + CH_2{=}O$$

The bond separation energies are measures of interactions between bonds and would all be zero if a bond additivity hypothesis were truly valid.

Theoretical bond separation energies can be calculated from the appropriate entries in Table II. As with the hydrogenation energies considered in the last section, these should really be compared with experimental heats of reaction at 0°K corrected for zero-point vibrations. However, we have found that for open-chain systems (for which there are an equal number of molecules on both sides of the bond separation reaction), the contribution of these terms to the bond separation energy at 298° is small, and the calculated correction is often of doubtful value because of errors arising from uncertainties in the vibrational frequencies. We have therefore assumed that the calculated bond separation energies we obtain may be applied without adjustment to reactions at 298°. Experimental bond separation energies listed in Tables V, VII, and IX are derived from the heats of formation listed in Table X.

We now discuss the various types of bond-bond interactions in turn.

(a) **Saturated Molecules.** Bond separation energies of saturated molecules are shown in Table V, where they have been organized into groups to facilitate intercomparisons. In all cases, the theoretical bond separation energies are positive, corresponding to stabilization of the larger molecule. Agreement with experiment is good when comparison is possible.

The bond separation energies of molecules $X{-}CH_2{-}X'$, where X and X′ are CH_3, NH_2, OH, or F, may be rationalized in terms of electron transfer of the type

$$\overset{\curvearrowright}{X{-}}CH_2\overset{\curvearrowright}{{-}X'}$$

Our results suggest that the electron transfer proceeds *via* a π-type donation and a σ-type acceptance. Thus, for example, in XCH_2F (Figure 1) σ withdrawal of electrons from carbon along the C–X bond decreases the occupancy of the carbon $2p_y$ orbital, which is then available to accept more electrons from the $2p_y$ lone pair on F. This corresponds to some double-bond character in the C–F bond and is reflected in a reduced gross population in the fluorine $2p_y$ orbital and an increased π_y-overlap population between C and F. Numerical values for difluoromethane (X = F) compared with fluoromethane (X = H) are given in Table VI and illustrate the effect.

Table V. Interactions of CH_3–, NH_2–, OH–, and F– Groups with Saturated Systems

Molecule	Bond separation energy, kcal mol^{-1} Calcd	Exptl
CH_3-CH_2-CH_3	1.2	2.2
NH_2-CH_2-CH_3	3.6	3.4
OH-CH_2-CH_3	5.4	5.9
F-CH_2-CH_3	6.1	4.2
CH_3-CH_2-NH_2	3.6	3.4
NH_2-CH_2-NH_2	8.3	
OH-CH_2-NH_2	13.0	
F-CH_2-NH_2	14.7	
CH_3-CH_2-OH	5.4	5.9
NH_2-CH_2-OH	13.0	
OH-CH_2-OH	15.2	15.5
F-CH_2-OH	13.3	
CH_3-CH_2-F	6.1	4.2
NH_2-CH_2-F	14.7	
OH-CH_2-F	13.3	
F-CH_2-F	11.5	14.1
CH_3-NH-CH_3	2.5	4.5
NH_2-NH-CH_3	4.1	5.8
OH-NH-CH_3	5.4	
F-NH-CH_3	7.1	
CH_3-NH-NH_2	4.1	5.8
NH_2-NH-NH_2	7.7	
OH-NH-NH_2	10.7	
F-NH-NH_2	12.9	
CH_3-NH-OH	5.4	
NH_2-NH-OH	10.7	
OH-NH-OH	5.8	
F-NH-OH	7.7	
CH_3-NH-F	7.1	
NH_2-NH-F	12.9	
OH-NH-F	7.7	
F-NH-F	5.6	
CH_3-O-CH_3	2.3	5.9
NH_2-O-CH_3	3.1	
OH-O-CH_3	6.0	
F-O-CH_3	8.8	
CH_3-O-NH_2	3.1	
NH_2-O-NH_2	1.2	
OH-O-NH_2	7.8	
F-O-NH_2	13.0	
CH_3-O-OH	6.0	
NH_2-O-OH	7.8	
OH-O-OH	9.3	
F-O-OH	6.3	
CH_3-O-F	8.8	
NH_2-O-F	13.0	
OH-O-F	6.3	
F-O-F	0.5	

Table VI. Orbital and Overlap Populations for Fluoromethane and Difluoromethane

Population[a]	Fluoromethane[b]	Difluoromethane[c]
F($2p_y$) orbital	1.966	1.943
F($2p_z$) orbital	1.966	1.964
C($2p_y$)-F($2p_y$) overlap	0.003	0.078
C($2p_z$)-F($2p_z$) overlap	0.003	0.014

[a] The fluorine atom referred to is the one on the *x* axis in Figure 1. [b] X = H in Figure 1. [c] X = F in Figure 1.

For XCH_2OH compounds, the same feature is operative, but it should be noted (Figure 1) that it will be most effective if the XCO plane is perpendicular to the COH plane (oxygen valence plane). This appears to be an explanation of the preference for gauche arrangements if X = OH or F (see Table II).

For XCH_2NH_2 compounds, there will again be a tendency for lone-pair electrons from nitrogen to move into the carbon $2p_y$ orbital if it is partly emptied by an electron-attracting X group (Figure 1). In this case the lone-pair orbital (which could be crudely represented by an sp^3 hybrid) must have its axis coplanar with the CX bond. Combined with the tendency of the NH_2 bonds to stagger those of the CH_2X group, this would lead to lowest energy in the XCN: trans configuration shown. This is indeed the prediction of the theory for the electron-withdrawing substituents X = OH or F (Table II), in contrast to the gauche form predicted when X = CH_3.

The interaction of the bonds in the X-CH_2-X′ molecules thus depends on both the π-electron-donating properties of X′ and the σ-electron-accepting properties of X. Thus, when X′ is a strong π-electron donor (*e.g.*, NH_2 or OH) and X a strong σ-electron acceptor (*e.g.*, OH or F), the bond separation energy is large (*e.g.*, FCH_2NH_2 or $HOCH_2OH$). On the other hand, bond separation energies for molecules containing methyl groups (X′) are small since the methyl group is only a weak π-electron donor. However, they do increase as the group X becomes a stronger electron acceptor. (See, for example, the series $CH_3CH_2CH_3$, $NH_2CH_2CH_3$, $HOCH_2CH_3$, FCH_2CH_3.)

If the central group is NH or O rather than CH_2, similar trends apply. However, there are some irregularities. The molecule NH_2ONH_2, for example, has only a small theoretical bond separation energy. This may be because the configuration which leads to lowest energy in hydroxylamine (:NOH cis) will lead to an unfavorable orientation of parallel dipoles for the NH_2 groups in NH_2ONH_2. Consequently, the molecule adopts a cis, trans conformation. Also F_2O has a very small theoretical bond separation energy, possibly because the F-O bonds are fairly nonpolar so that the stablizing mechanism discussed is less applicable.

(b) Molecules with One Multiple Bond. We consider first the molecules X—CH=Y, where X is CH_3, NH_2, OH, or F and Y is CH_2, NH, or O. The bond separation energies for these molecules (Table VII) are found (i) to decrease in the sequence X = NH_2, OH, F, CH_3 for a given Y and (ii) to increase in the sequence Y = CH_2, NH, O for a given X.

Analysis of π-electron distributions (Figure 2) shows exactly parallel results. We should note the following points in this connection. (1) As X varies (*i.e.*, looking down a column), π donation by X increases in the order

$$H < CH_3 < F < OH < NH_2$$

(2) As Y varies (*i.e.*, looking across a row), π acceptance by Y increases in the order

$$CH_2 < NH < O$$

(3) As X varies, π acceptance by Y increases as X goes from

$$H < CH_3 < F < OH < NH_2$$

0 1.000 1.000 H—CH=CH_2	0 0.886 1.114 H—CH=NH	0 0.731 1.269 H—CH=O
0.993 0.963 1.044 CH_3—CH=CH_2	0.980 0.857 1.163 CH_3—CH=NH	0.976 0.713 1.311 CH_3—CH=O
1.939 1.006 1.055 F—CH=CH_2	1.929 0.881 1.190 F—CH=NH	1.914 0.736 1.350 F—CH=O
1.914 0.992 1.094 HO—CH=CH_2	1.888 0.832 1.280 HO—CH=NH	1.872 0.709 1.419 HO—CH=O
1.887 0.925 1.188 NH_2—CH=CH_2	1.853 0.834 1.313 NH_2—CH=NH	1.804 0.725 1.471 NH_2—CH=O

Figure 2. π-Electron populations for X—CH=Y molecules.

(4) As Y varies, π donation by X increases as Y goes from

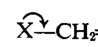
$$CH_2 < NH < O$$

(1) and (2) demonstrate the π-electron donating or accepting properties of X and Y individually. (3) and (4) show how π acceptance by Y depends on X and π donation by X depends on Y; *i.e.*, they are indicative of the *interaction* between X and Y.

Table VII. Interactions of CH_3–, NH_2–, OH–, and F– Groups with Unsaturated Systems

Molecule	Bond separation energy, kcal mol^{-1} Calcd	Exptl
CH_2—CH=CH_2	3.9	5.3
NH_2—CH=CH_2	13.3	
OH—CH=CH_2	8.2	
F—CH=CH_2	5.4	
CH_3—CH=NH	8.7	
NH_2—CH=NH	25.6	
OH—CH=NH	21.8	
F—CH=NH	12.9	
CH_3—CH=O	10.4	9.7
NH_2—CH=O	35.9	29.2
OH—CH=O	30.1	32.7
F—CH=O	19.2	24.2
CH_3—N=CH_2	3.1	
NH_2—N=CH_2	7.7	
OH—N=CH_2	14.6	
F—N=CH_2	14.5	
CH_3—N=NH	8.8	
NH_2—N=NH	18.5	
OH—N=NH	18.9	
F—N=NH	18.6	
CH_3—N=O	13.0	
NH_2—N=O	31.2	
OH—N=O	29.3	44.7
F—N=O	28.6	44.1
CH_3—C≡CH	9.0	7.5
NH_2—C≡CH	13.5	
OH—C≡CH	−0.2	
F—C≡CH	−11.6	
CH_3—C≡N	13.2	9.1
NH_2—C≡N	17.8	
OH—C≡N	−1.1	
F—C≡N	−16.9	−11.3

The sequences in (1) and (3) and (2) and (4) are identical and also agree with the ordering of bond separation energies. Thus the bond separation energies may be rationalized in terms of the π-electron transfer



$X—CH_2=Y$

the ability of X to donate π electrons and the ability of Y to accept them. Highest values of the bond separation energy are found when X is a strong π donor and Y a strong π acceptor (*e.g.*, NH_2CHO), while lowest values are found when X is a weak π donor and Y a weak π acceptor (*e.g.*, $CH_3CH{=}CH_2$). It seems that the increasing σ withdrawal of electrons in the sequence CH_3, NH_2, OH, and F is not a dominant effect for this series of molecules.

In moving from X—CH=NH to X—N=CH_2, π-electron donation by X is reduced, perhaps because X is attached to the negative end of the C=N dipole, and the bond separation energies are smaller. This is particularly marked when X is NH_2 and, in fact, the bond separation energies increase in going from X = NH_2 to X = OH or F. For the set of molecules X—N=NH, the bond separation energies are approximately the same when X is NH_2, OH, and F. Finally, for X—N=O, the results are very similar to those for X—CH=O.

For the triply bonded molecules X—C$\equiv$Z, where Z is CH or N, the σ-electron-withdrawing or -donating property of the group X plays a major role in determining the bond interactions. Acetylene and hydrogen cyanide are both acidic species. Our results suggest that withdrawal of electrons from the C$\equiv$CH or C$\equiv$N groups is an energetically unfavorable interaction. Thus, in moving from X—CH=Y to the corresponding X—C$\equiv$Z, the bond separation energy increases when X is CH_3 but decreases when X is NH_2, OH, or F. These results are in accordance with the σ-donating or -withdrawing properties of the group X. This effect may also be seen in the decrease in electron population of the fluorine 2pσ orbital directed along the F—C bond: 1.528 in CH_3F, 1.493 in FC$\equiv$CH, and 1.455 in FC$\equiv$N.

In the case of the molecules $NH_2C{\equiv}CH$ and NH_2-C$\equiv$N, the bond separation energies are still positive due to the stabilizing π-electron donation of the NH_2 group. However, the increased σ withdrawal for X = OH and F leads to negative bond separation energies for HOC$\equiv$CH, FC$\equiv$CH, HOC$\equiv$N, and FC$\equiv$N. The σ and π populations for the series XC$\equiv$N illustrate these effects and are shown in Table VIII.

Table VIII. π and σ Populations of the CN Group in X—C$\equiv$N Molecules

X	π	σ
CH_3	4.039	9.184
NH_2	4.136	8.736
OH	4.130	8.608
F	4.129	8.517

The molecules with X = CH_3 provide examples of the effect of hyperconjugation. The stabilizing interactions in these cases are larger for triply bonded than for the corresponding doubly bonded systems (compare $CH_3CH{=}CH_2$ and $CH_3C{\equiv}CH$) and are largest when the methyl group is attached to the positive center of a polar bond (*e.g.*, $CH_3N{=}O$, $CH_3C{\equiv}N$).

(c) Molecules with Cumulated Double Bonds. Bond separation energies for molecules Y=C=Y′ (where Y, Y′ are CH_2, NH, or O) with cumulated double bonds are shown in Table IX. Both experimental and calculated values range from small and negative when Y and Y′ are CH_2 to large and positive when Y and Y′ are O. The latter is associated with the strong stabilizing interaction arising from π delocalization over three centers for molecules containing C=O bonds. On the other hand, the terminal groups in the molecules $CH_2{=}C{=}CH_2$, $CH_2{=}C{=}NH$, and NH=C=NH are orthogonal; hence the two π systems are orthogonal and there is reduced three-center delocalization. For a given group Y, the decrease in bond separation energy in going from Y=C=O to Y=C=NH is much greater than the further decrease in going to Y=C=CH_2.

Table IX. Interactions of Cumulated Double Bonds

Molecule	Bond separation energy, kcal mol^{-1}	
	Calcd	Exptl
$CH_2{=}C{=}CH_2$	−2.5	−3.0
$NH{=}C{=}CH_2$	−0.3	
$O{=}C{=}CH_2$	13.6	17.3
$CH_2{=}C{=}NH$	−0.3	
NH=C=NH	5.6	
O=C=NH	26.8	
$CH_2{=}C{=}O$	13.6	17.3
NH=C=O	26.8	
O=C=O	52.5	56.5

Calculation of Heats of Formation

Given the heats of formation of the molecules with one or two heavy atoms (Table III), we may use the theoretical bond separation energies listed in Tables V, VII, and IX to predict heats of formation for all the molecules with three heavy atoms. The complete set of calculated heats of formation is compared with experimental values in Table X. The heats of formation calculated using the estimated heats of formation in Table III (*i.e.*, for $CH_2{=}NH$, HOF, and NH_2F) should be regarded with caution and accordingly are placed in parentheses in Table X. Also, certain of the experimental heats of formation are considered to be less reliable than others, some of these being partially estimated or interpolated quantities. However, we have not attempted a searching evaluation of all the experimental data. The mean absolute error for the 21 molecules for which the more reliable heats of formation are available is 3.1 kcal mol^{-1}. It appears that the best results are obtained for molecules with two or three carbon atoms.

Isomerization Energies

Among the molecules we have studied, there are a number of interesting isomeric pairs. The isomerization energies may be calculated in two ways, either (A) as the difference in the theoretical total energies or (B) from the theoretical heats of formation (Table X) obtained *via* bond separation energies. We have used both methods and the results are presented in Tables XI–XIV. In general, the two calculated isomerization energies (A and B) are in close agreement. In the few cases where there is a significant difference between the two methods, we favor the value obtained as the direct energy difference (A), since (B) incorporates errors due to uncertainties in some of the less precisely known heats of formation in these instances. We now look at the various types of isomerizations in turn.

(a) Saturated Systems. Energy changes for isomerization reactions in saturated systems are shown in Table XI. The calculated isomerization energies compare well with the known experimental values.

Table X. Calculated and Experimental Heats of Formation

Molecule	Heats of formation, kcal mol^{-1} Calcd[a]	Exptl[b,c]	Molecule	Heats of formation, kcal mol^{-1} Calcd[a]	Exptl[b,c]
$CH_3-CH_2-CH_3$	−23.8	−24.82[d]	$CH_3-NH-OH$	−9.2	(−12.0)[e]
$CH_3-CH=CH_2$	6.2	4.88[d]	CH_3-O-NH_2	−2.6	(−6.2)[e]
$CH_3-C\equiv CH$	42.9	44.32[d]	$NH_2-CH=O$	−51.2	−44.5[e]
$CH_2=C=CH_2$	45.3	45.92[d]	$NH=CH-OH$	(−25.6)	
$CH_3-CH_2-NH_2$	−11.4	−11.27	$CH_2=N-OH$	(13.3)	
$CH_3-NH-CH_3$	−2.4	−4.41	$CH_3-N=O$	16.4	(16)[e]
$CH_2=CH-NH_2$	11.6		$HN=C=O$	(−10.4)	(−27.9)[i]
$CH_3-CH=NH$	(15.1)		$HO-C\equiv N$	3.4	
$CH_2=N-CH_3$	(28.6)	(17.3)[e]	NH_2-CH_2-F	−58.3	
$CH_3-C\equiv N$	16.8	20.9	CH_3-NH-F	(−8.2)	
$CH\equiv C-NH_2$	53.1		$NH=CH-F$	(−24.8)	
$CH_2=C=NH$	(56.9)		$CH_2=N-F$	(16.1)	
$NH_2-CH_2-NH_2$	−1.4		$F-C\equiv N$	11.1	5.5[j]
$CH_3-NH-NH_2$	24.2	22.55	$HO-CH_2-F$	−99.4	
$NH_2-CH=NH$	(13.0)		CH_3-O-F	−26.6	
$CH_3-N=NH$	47.0		$O=CH-F$	−85.0	−90.00[i]
$CH_2=N-NH_2$	(52.3)		$NH_2-NH-NH_2$	48.9	
$NH_2-C\equiv N$	26.9		$NH_2-N=NH$	65.5	
$NH=C=NH$	(64.7)		$NH_2-NH-OH$	13.8	
CH_3-CH_2-OH	−55.7	−56.19	NH_2-O-NH_2	38.0	
CH_3-O-CH_3	−40.5	−43.99	$NH=N-OH$	33.0	
$CH_3-CH=O$	−40.4	−39.72	$NH_2-N=O$	26.5	
$CH_2=CH-OH$	−25.8		$HO-NH-OH$	−13.4	
$CH_2=C=O$	−10.9	−14.6	NH_2-O-OH	8.1	
$CH\equiv C-OH$	24.3		$HO-N=O$	−3.8	−19.15
$HO-CH_2-OH$	−93.2	−93.5[e]	NH_2-NH-F	(14.4)	
CH_3-O-OH	−28.7	(−30.9)[e]	$NH=N-F$	(36.0)	
$HO-CH=O$	−87.9	−90.48	$F-NH-F$	(−7.8)	
$O=C=O$	−90.0	−94.05	$F-NH-OH$	(−12.6)	
CH_3-CH_2-F	−64.5	−62.5[f]	$F-O-NH_2$	(7.8)	
$CH_2=CH-F$	−31.0	(−31.6)[g]	$F-N=O$	(−0.4)	−15.9
$CH\equiv C-F$	27.7		$HO-O-OH$	−16.7	
$F-CH_2-F$	−105.7	−108.24[h]	$HO-O-F$	(−8.7)	
NH_2-CH_2-OH	−48.5		$F-O-F$	(1.9)	−5.2

[a] Values in parentheses calculated using estimated $\Delta H_f°(298°)$ values from Table III. [b] Values in parentheses are not pure experimental numbers in most cases and are considered less reliable than the other $\Delta H_f°$'s. [c] Unless otherwise noted, from D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, W. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C. 1968. [d] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa. 1953. [e] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [f] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969. [g] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968. [h] J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968). [i] "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Company, Midland, Mich., 1965. [j] V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, **47**, 4548 (1967).

The first eight reactions involve the transformation of molecules X′-(CH_2-X) to X′-(Y-CH_3), where X is NH_2 or OH, Y is NH or O, and X′ is CH_3, NH_2, OH, or F. In all cases, X′-CH_2-X is found to be more stable than the corresponding X′-Y-CH_3. Thus, for example, ethanol is more stable than dimethyl ether, ethylamine more stable than dimethylamine. The isomerization energies are largest when X and X′ can interact favorably as described earlier in this paper, *i.e.*, when X (or X′) is a good π donor and the other is a good σ acceptor.

Table XI. Isomerization Energies in Saturated Systems

Reaction	Isomerization energy, kcal mol^{-1} Calcd A	B	Exptl
$CH_3CH_2NH_2 \rightarrow CH_3NHCH_3$	8.5	9.0	6.8
$CH_3CH_2OH \rightarrow CH_3OCH_3$	11.6	15.2	12.2
$NH_2CH_2NH_2 \rightarrow NH_2NHCH_3$	23.7	25.6	
$NH_2CH_2OH \rightarrow NH_2OCH_3$	41.0	45.9	
$OHCH_2NH_2 \rightarrow OHNHCH_3$	37.6	39.1	
$OHCH_2OH \rightarrow OHOCH_3$	63.4	64.5	(62.6)
$FCH_2NH_2 \rightarrow FNHCH_3$	51.5	50.1	
$FCH_2OH \rightarrow FOCH_3$	75.4	73.1	
$NH_2NHOH \rightarrow NH_2ONH_2$	21.1	24.2	
$OHNHOH \rightarrow OHONH_2$	22.2	21.5	
$FNHOH \rightarrow FONH_2$	21.8	20.4	

The last three reactions involve the transformations of molecules X′-NH-X to X′-Y-NH_2, where X is OH and Y is O. In each case, X′-NH-X is found to be more stable.

Thus, it appears that saturated molecules with three of the heavy atoms, C, N, O, and F, prefer having a central CH_2 group to having a central NH group which, in turn, is favored over a central O. This generalization is illustrated by the order of stability of the isomeric series: $NH_2CH_2OH > CH_3NHOH > CH_3ONH_2$.

(b) Prototropic Rearrangements in Systems with One Double Bond. Isomerization energies for several potentially tautomeric systems are included in Table XII. There are no direct experimental thermodynamic data for any of these particular isomerizations. However, general experimental observations on larger systems agree with our results in cases where the energy differences are large. Thus keto forms are more stable than enols (1),[44] oximes are favored over nitroso com-

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Table XII. Isomerization Energies for Prototropic Rearrangements in Molecules with One Double Bond

Reaction	Calcd isomerization energy, kcal mol^{-1} A	B
1. $CH_3-CH=O \rightarrow CH_2=CH-OH$	12.9	14.6
2. $CH_3-CH=NH \rightarrow CH_2=CH-NH_2$	−3.4	−3.5
3. $CH_3-N=NH \rightarrow CH_2=N-NH_2$	2.0	5.3
4. $CH_3-N=O \rightarrow CH_2=N-OH$	−12.6	−3.1
5. $NH_2-CH=O \rightarrow NH=CH-OH$	23.0	25.6
6. $NH_2-N=O \rightarrow NH=N-OH$	0.3	6.5

pounds (4),[45] and amides are favored over the tautomeric imidic acids (5).[46] Our predictions for imine–enamine (2) and azo–hydrazone (3) tautomerizations are in apparent disagreement with experiment, where imine and hydrazone forms are believed to be the more stable tautomers.[47–51] However, these generalizations are based on liquid-phase data for larger systems where there is the possibility of substituent and solvent effects altering the equilibrium position. Again, because the calculated numbers are small, the approximations in our theoretical model (such as the assumed geometry) become more important and incomplete cancellation of correlation effects becomes more noticeable. Our results do suggest, however, that the differences in energy for the parent azo and hydrazone tautomers and the imine and enamine tautomers are, respectively, small. Little is known at present in connection with the tautomerization of nitrosamines to their corresponding isonitroso structures (6).[52]

(c) Substituted Imines. Our results for the isomerization of imines (Table XIII) suggest that imines are stabilized to a greater extent by substitution on carbon than on nitrogen. This effect is greatest with NH_2, OH, and F substituents. The result may be compared with the isomerization of saturated systems (Table XI), where an internal CH_2 group is preferred to an internal NH group. Here, there is a preference for the internal group to be CH than N.

Table XIII. Isomerization Energies for Substituted Imines

Reaction	Calcd isomerization energy, kcal mol^{-1} A	B
$CH_3-CH=NH \rightarrow CH_2=N-CH_3$	13.0	13.5
$NH_2-CH=NH \rightarrow CH_2=N-NH_2$	37.4	39.3
$HO-CH=NH \rightarrow CH_2=N-OH$	37.2	38.9
$F-CH=NH \rightarrow CH_2=N-F$	42.2	40.9

(d) Isomerization of Single and Triple Bonds to Cumulated Double Bonds. Isomerization energies for reactions of this type are shown in Table XIV. In general, the singly and triply bonded species are the more stable except when a C=O bond is one of the cumulated double bonds. We should recall the large positive bond separation energies for molecules containing cumulated double bonds including at least one C=O bond (Table IX); this favorable interaction contributes to the stabilization of these molecules. On the other hand, the cumulated species without C=O bonds have negative bond separation energies in some cases.

Table XIV. Isomerization of Single Bond + Triple Bond to Cumulated Double Bonds

Reaction	Isomerization energy, kcal mol^{-1} Calcd A	B	Exptl
7. $CH_3-C\equiv CH \rightarrow CH_2=C=CH_2$	1.9	3.4	1.6
8. $NH_2-C\equiv CH \rightarrow NH=C=CH_2$	3.1	3.8	
9. $HO-C\equiv CH \rightarrow O=C=CH_2$	−33.4	−35.2	
10. $CH_3-C\equiv N \rightarrow CH_2=C=NH$	44.6	40.1	
11. $NH_2-C\equiv N \rightarrow NH=C=NH$	42.1	37.8	
12. $HO-C\equiv N \rightarrow O=C=NH$	−6.9	−13.8	

The theoretical value for the propyne → allene isomerization (7) is in reasonable agreement with experiment. Although there are no direct thermochemical data on the other systems, isocyanic acid is believed to be more stable than cyanic acid (12),[53] cyanamides more stable than carbodiimides (11),[45] and nitriles more stable than ketenimines (10),[45] in agreement with our results.

Acknowledgments. We thank Dr. R. Ditchfield for helpful discussions. This research was supported in part by National Science Foundation Grant No. GP-9338.

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