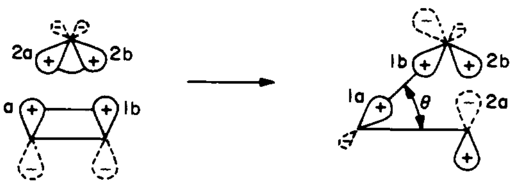

(44)

phase orientation as in (43), thus we expect the energy to decrease monatomically as the molecule opens to diazomethane and hence a predominance of diazomethane, as is observed.

References and Notes

(1) Partially supported by a grant (GP-40783X) from the National Science Foundation.
(2) National Defense Education Act Fellow.
(3) For an interesting example and further references, see J. E. Bercaw, E. Rosenberg, and J. D. Roberts, *J. Am. Chem. Soc.*, **96**, 612 (1974).
(4) See D. J. Cram and G. S. Hammond, "Organic Chemistry", McGraw-Hill, New York, N.Y., 1964.
(5) (a) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973); (b) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972); (c) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Am. Chem. Soc.*, **94**, 8293 (1972); (d) A. P. Mortola and W. A. Goddard, *ibid.*, **96**, 1 (1974).
(6) As an example, consider a four-electron singlet. There are two possible spin couplings: $\chi_1 = 0.5(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)$ and $\chi_2 = (3^{1/2}/6)[2(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha) - (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)]$. We may define a general spin eigenfunction (SEF) by $\chi = \cos\theta\chi_1 + \sin\theta\chi_2$ and then solve for the spin coupling simultaneously with obtaining the optimum orbitals.
(7) In many cases solving for χ as above results in only the χ_1 coupling being important, $\chi = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\ldots(\alpha\beta - \beta\alpha)$. When we force χ to have this form, the wave function is denoted by PP for "perfect pairing". We may then write our GVB wave function as $\mathcal{A}\{\varphi_{1a}\varphi_{1b}\varphi_{2a}\varphi_{2b}\ .\ .\ \varphi_{na}\varphi_{nb}\}\chi_{PP}$, which is equivalent to $\mathcal{A}\{[(\varphi_{1a}\varphi_{1b} + \varphi_{1b}\varphi_{1a})(\varphi_{2a}\varphi_{2b} + \varphi_{2b}\varphi_{2a})\ldots](\alpha\beta\alpha\beta\ldots\alpha\beta)\}$.
(8) A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature* (*London*), 181, 1000 (1958); J. Sheridan, *Adv. Mol. Spectrosc., Proc. Int. Meet., 4th 1959*, 1, 139 (1962).
(9) (a) S. Huzinaga, D. McWilliams, and B. Domsky, *J. Chem. Phys.*, **54**, 2283 (1972); (b) T. H. Dunning, Jr., *ibid.*, **53**, 2823, (1970).
(10) (a) See F. W. Bobrowicz, Ph.D. Thesis, California Institute of Technology, March 1974. (b) Written by F. W. Bobrowicz (vide supra) and N. W. Winter utilizing spin eigenfunction techniques of R. C. Ladner (see Ph.D. Thesis, California Institute of Technology, November 1971). Modifications due to L. A. Harding, S. P. Walch, B. J. Moss, and W. A. Goddard III.
(11) Taking our wave function for the N(^{4}S) state as $\psi = \mathcal{A}(\varphi_{sz}\varphi_{\overline{sz}} + \varphi_{\overline{sz}}\varphi_{sz})2p_x2p_y2p_z\alpha\beta\alpha\alpha\alpha$, where $\varphi_{sz} = \varphi_{2s} + \lambda\varphi_{2p_z}$ and $\varphi_{\overline{sz}} = \varphi_{2s} - \lambda\varphi_{2p_z}$, we see that this is equivalent to $\mathcal{A}[\varphi_{2s}{}^2 - \lambda\varphi_{2p_z}{}^2)2p_x2p_y2p_z\alpha\beta\alpha\alpha\alpha]$, which reduces to $\mathcal{A}[\varphi_{2s}{}^2 2p_x2p_y2p_z\alpha\beta\alpha\alpha\alpha]$ due to the antisymmetrizer.
(12) L. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, in press.
(13) F. Grimaldi, A. Lecourt, and C. Moser, *Int. J. Quantum Chem.*, **15**, 153 (1967).
(14) S. Green. *Chem. Phys. Lett.*, **23**, 115 (1973).
(15) S. P. Walch and W. A. Goddard III, *Chem. Phys. Lett.*, **33**, 18 (1975).
(16) The energy change due to the $\phi_u\phi_u$ configuration is approximately $\Delta E = -(K_{gu})^2/(E_u - E_g)$, and thus the correlation effected by ϕ_u favors maximizing K_{gu}. To maximize K_{gu}, one needs to concentrate ϕ_g and ϕ_u both in the same regions of space.
(17) J.-M. André, M. Cl. André, G. Leroy, and J. Weiler, *Int. J. Quantum Chem.*, **3**, 1013 (1969).
(18) L. Snyder and H. Basch, "Molecular Wave Functions and Properties Tabulated from SCF Calculations in a Gaussian Basis Set", Wiley, New York, N.Y., 1972.
(19) This corresponds to the $^1\Sigma_g{}^+$ state of linear CH_2 or to the MO occupancy $1a_1{}^2 2a_1{}^2 2b_2{}^2 1b_1{}^2$ of bent CH_2.
(20) Using the GVB(3/PP) energy of $CH_2(^1A_1)$ (ref 5c) and estimating the GVB(3/PP) energy of N_2 by adding the pair lowerings for each pair (Table IV) to the HF energy (ref 9b) leads to an H_2C–N_2 bond energy of 0.88 eV for diazomethane in the DZ basis. The best experimental estimate (ref 21) of this quantity is 2.31 eV. Since we did not include d functions in the basis, errors of the order of 1 eV are expected in bond dissociation energies, approximately the value obtained.
(21) A. H. Laufer and H. Okabe, *J. Am. Chem. Soc.*, **93**, 4137 (1971). We use their value relative to $^3B_1$ methylene and add 0.50 eV as the $^1A_1 \leftarrow {}^3B_1$ excitation energy for methylene (ref 5c).
(22) (a) C. W. Wilson, Jr., and W. A. Goddard III, *Theor. Chem. Acta*, **26**, 195 (1972); (b) W. A. Goddard III and C. W. Wilson, Jr., *ibid.*, **26**, 211 (1972); (c) C. W. Wilson, Jr., and W. A. Goddard III, *Chem. Phys. Lett.* **5**, 45 (1970).
(23) T. H. Dunning, Jr., W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969).
(24) G. Herzberg, *Proc. R. Soc. London, Ser. A*, **262**, 291 (1961).
(25) (a) W. J. Hunt and W. A. Goddard III, *Chem. Phys. Lett.*, **3**, 414 (1969); see also W. J. Hunt, Ph.D. Thesis, California Institute of Technology, September 1971. (b) In the IVO procedure it is the ionization potential (IP) of the excited (Rydberg) orbital that is calculated. To obtain excitation energies, this is subtracted from the experimental IP, 8.99 eV for H_2CNN.
(26) A. J. Merer, *Can. J. Phys.*, **42**, 1242 (1964).
(27) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, New York, N.Y., 1966.
(28) J. D. Roberts, private communication.
(29) R. Husigen, *Angew. Chem.*, **2**, 633 (1963).
(30) W. A. Goddard III, *J. Am. Chem. Soc.*, **94**, 793 (1972).
(31) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **41**, 3504 (1964).
(32) W. Braun, A. M. Bass, and M. Pilling, *J. Chem. Phys.*, **52**, 5131 (1970).

Molecular Orbital Theory of the Hydrogen Bond. XIII. Pyridine and Pyrazine as Proton Acceptors

Janet E. Del Bene

Contribution from the Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555. Received January 29, 1975

Abstract: Ab initio SCF calculations with a minimal STO-3G basis set have been performed to determine the equilibrium structures and energies of dimers HF-pyrazine, HF-pyridine, and H_2O-pyridine. The structures of the equilibrium dimers are consistent with structures anticipated from the general hybridization model. The HF-pyridine dimer is more stable than the HF-pyrazine dimer. Its greater stability may be attributed to the presence of a more negatively charged nitrogen atom in pyridine, and to a favorable alignment of molecular dipole moments in the HF-pyridine dimer. An HF-pyridine dimer in which hydrogen bond formation occurs through the π electron system at the nitrogen has also been investigated and found to be a nonequilibrium structure on the intermolecular surface. CI calculations have been performed to determine n → π^* transition energies for the monomers pyrazine and pyridine, the equilibrium dimers, and a 2:1 HF-pyrazine trimer. The results suggest that when pyridine is the proton acceptor molecule, the hydrogen bond is broken upon excitation in the dimer, but when pyrazine is the proton acceptor, the hydrogen-bonded complex remains bound in the excited n → π^* state.

In many chemical and biochemical systems, the aromatic nitrogen atom is an important proton acceptor atom for hydrogen bond formation. It is of interest, therefore, to extend ab initio molecular orbital studies of hydrogen bonding to include dimers in which an aromatic compound is the proton acceptor molecule, with hydrogen bond formation occurring through a lone pair of electrons on a nitrogen atom. While molecular orbital calculations on dimers with proton acceptor nitrogens have previously been reported, the proton acceptor molecules in these dimers have generally been restricted to relatively simple, nonaromatic compounds.[1-4] A notable exception is found in the study of Clementi, Mehl, and von Niessen, where hydrogen bridges in the guanine-cytosine pair were investigated, and potential curves for proton transfer were obtained.[5]

In the present study, ab initio molecular orbital calculations with a minimal STO-3G basis set have been performed on a set of dimers having pyridine and pyrazine as proton acceptor molecules, and either water or hydrogen fluoride as proton donors. Since optimized STO-3G geometries for pyridine and pyrazine were not available, these were first computed, and are compared with experimental geometries below. However, the emphasis in this study is on these molecules as proton acceptor molecules in hydrogen-bonded dimers. Thus, the primary purposes of this work are: (1) to determine the equilibrium structures and energies of the dimers HF-pyrazine, HF-pyridine, and H_2O-pyridine; (2) to analyze the structures and energies of these dimers, and to compare them with other equilibrium dimers in which the proton acceptor atom is a nitrogen atom; (3) to investigate π hydrogen bonding in the HF-pyridine dimer; and (4) to determine the effect of hydrogen bond formation on the n → π^* transition energies of pyrazine and pyridine.

Method of Calculation

Ground States. The closed-shell ground state of each monomer, dimer, and trimer has been described by a single Slater determinant Ψ

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!}$$
$$\equiv |1\bar{1}\,2\bar{2}\ldots n\bar{n}|$$

in which each molecular orbital (MO) is occupied by two electrons. The MO's ψ_i are expressed as linear combinations of atomic basis functions ϕ_μ (the LCAO approximation)

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

with the expansion coefficients $c_{\mu i}$ determined by solving the Roothaan equations.[6] The atomic orbital basis set used for these calculations is the STO-3G basis set with standard scale factors.[7]

Excited States. The wave functions for the excited singlet n → π^* states of the monomers pyridine and pyrazine, of the equilibrium dimers, and of a 2:1 HF-pyrazine trimer have been expressed as linear combinations of functions describing singly excited configurations. The configuration interaction (CI) wave function ${}^1\Phi$ is given as

$${}^1\Phi = \sum_i \sum_l A_{il}\,{}^1\Psi_i^{\,l}$$

where

$${}^1\Psi_i^{\,l} = [|1\bar{1}\ldots i\bar{l}\ldots n\bar{n}| - |1\bar{1}\ldots \bar{i}l\ldots n\bar{n}|]\sqrt{2}$$

with the expansion coefficients A_{il} determined variationally. The function ${}^1\Psi_i^{\,l}$ describes a configuration which arises as an electron is promoted from orbital i, doubly occupied in the ground state, to virtual orbital l. If functions for configurations arising from all possible one-electron excitations are included in the CI expansion, the resulting CI function is a full first-order function. However, because of the large number of singly excited configurations which occur even in the monomers pyridine and pyrazine, it was necessary to truncate the CI expansions, limiting the number of excited configurations to 90. In so doing, symmetry was used to eliminate those configurations which do not interact with the n → π^* transition which gives rise to the dominant configuration in the lowest energy singlet excited state. In addition, high-energy transitions originating from inner-shell orbitals were also omitted. An analysis of the computed monomer spectra indicated that $\pi \rightarrow \sigma^*$ transitions are also quite energetic, and make small contributions to the low-energy n → π^* state, while certain easily identifiable $\sigma \rightarrow \pi^*$ transitions are important for describing this state. These observations were then used as a basis for selecting the configurations which were included in the CI expansions of the singlet n → π^* states in the dimers and trimer. The n → π^* transition energies have been computed at the equilibrium ground state geometries.

Geometry Optimization. Optimized geometries were first computed for pyrazine (D_{2h}) and pyridine (C_{2v}). The intramolecular coordinates were optimized to ±0.01 Å in bond distances, and ±1° in bond angles. The data reported in Table I show that there is good agreement between the computed and experimental geometries of pyrazine and pyridine. The optimized STO-3G geometries of the proton donor H_2O and HF molecules have been reported.[8]

With the optimized monomer geometries held rigid, it is possible to describe the structures of hydrogen-bonded dimers in terms of an intermolecular distance and five intermolecular angles, defined with reference to an intermolecular line and the principal axes of the proton donor and proton acceptor molecules (see Figure 1). For the proton acceptor pyridine molecule, the principal axis is the C_2 symmetry axis, with origin at the nitrogen, and directed toward C_4 (see Figure 2). For pyrazine, the C_2 symmetry axis which passes through the nitrogen atoms is the principal axes, with origin at N_1 and directed toward N_4. For the proton donor molecules, the principal axes are the C_2 and C_∞ axes of H_2O and HF, with origins at the oxygen and fluorine atoms, respectively, and directed toward the hydrogens. In the dimer, the intermolecular distance is the distance between the heavy atom of the proton donor molecule and the proton acceptor nitrogen atom N_1, measured along the intermolecular O-N or F-N line. In the starting orientation, the proton donor and proton acceptor molecules are placed in the intermolecular coordinate system such that their principal axes point inward along the intermolecular line. The angle θ_1 is the angle between the principal axis of the proton donor molecule and the intermolecular line, while the angle χ_1 measures rotation of the proton donor molecule about its principal axis. The angles θ_2 and χ_2 are defined similarly for the proton acceptor molecule. The angle ϕ is a combination of ϕ_1 and ϕ_2 with the rotational sense of ϕ_2, and measures rotation of the principal axis of the proton acceptor molecule about the intermolecular line. Equilibrium dimer structures have been optimized to ±0.01 Å in the intermolecular distance, and ±1° in each intermolecular angle, where possible (see below). The intermolecular (hydrogen bond) energy is computed by subtracting the sum of the energies of the isolated monomers from the total dimer energy. All calculations have been performed in double precision on an IBM 370/145 computer.

Results and Discussion

Dimer Structures and Energies. The structures and intermolecular energies of the equilibrium dimers HF-pyrazine, HF-pyridine, and H_2O-pyridine are reported in Table II. Also reported are the structures and energies of a nonequilibrium HF-pyridine π dimer (B), and of two nonequilibrium H_2O-pyridine dimers (B and C). It is appropriate to discuss the structures of the equilibrium dimers in terms of the general hybridization model for the hydrogen bond (GHM).[4,9,10] GHM describes the hydrogen bond as arising when a directed lone pair of electrons on the proton accep-

Table I. Pyridine and Pyrazine Geometries[a]

	Pyridine (C_{2v})		Pyrazine (D_{2h})	
Distances	Computed	Exptl[b]	Computed	Exptl[b]
N–C	1.35	1.3402 (1.340)	1.35	1.334
C_2–C_3	1.39	1.3945 (1.390)	1.39	1.378
C_3–C_4	1.39	1.3944 (1.400)		
C–H	1.08[c]	1.08[d]	1.09	1.05
Angles				
CNC	116	116.8 (116.7)	114	115.1
NCC	124	123.9 (124.0)		
$C_3C_2H_2$	120	120.2	120	120.3
$C_2C_3H_3$	120	120.2		

[a] Bond distances in Å, bond angles in degrees. See Figure 2 for labeling of atoms. [b] Experimental data from L. E. Sutton, *Chem. Soc. Spec. Publ., Suppl.*, No. 18, (1965). Experimental data in parentheses for pyridine from G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1967. [c] All C–H bonds in pyridine assumed equal. [d] Experimental value for all C–H bonds rounded to 0.01 Å.

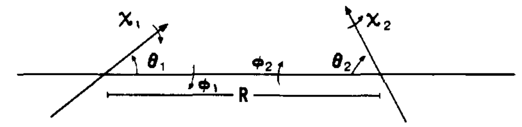

Figure 1. The intermolecular coordinate system. Curved arrows showing rotational senses pass in front of the lines they cross.

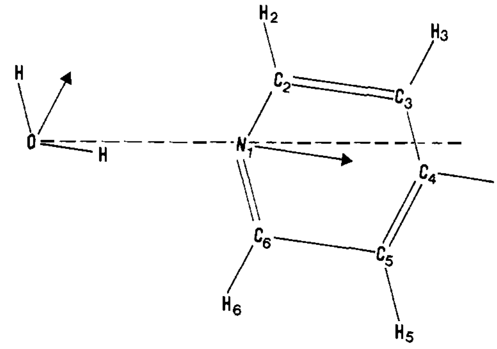

Figure 2. The nonequilibrium H_2O-pyridine dimer B, showing labeling of atoms and principal axes. The equilibrium dimer A is obtained by a 90° rotation of the pyridine molecule about its principal axis.

Table II. Dimer Structures and Energies

	R, Å	θ_1', deg[a]	χ_1, deg	θ_2, deg	χ_2, deg[b]	ϕ, deg	ΔE, au[c]
HF–pyrazine	2.86	0		180	0		−0.00856
HF–pyridine							
A	2.82	0		180	0		−0.01050
B[d]	3.40	0		90	90	0	−0.00147
H_2O–pyridine							
A	2.97	−4	0	175	90	180	−0.00743
B[e]	2.97	−2	0	175	0	180	−0.00725
C[f]	2.97	0	0	180	90		−0.00726

[a] For H_2O, $\theta_1' = \theta_1 - \angle HOH/2$, and is a direct measure of the linearity ($\theta_1' = 0°$) of the hydrogen bond. For HF, $\theta_1' = \theta_1$. [b] In the equilibrium dimers with HF as the proton donor, ΔE as a function of χ_2 is constant. [c] ΔE is the intermolecular (hydrogen bond) energy. 1 au = 627.49 kcal/mol. [d] A nonequilibrium π dimer, optimized with respect to R. [e] Not an equilibrium structure with respect to χ_2. [f] The idealized GHM dimer, with $\theta_1' = 0°$ and $\theta_2 = 180°$.

tor atom takes part in the formation of a linear, or nearly linear, hydrogen bond. In terms of the intermolecular coordinates, the requirement for the directed lone pair of electrons determines the optimized values of the angles θ_2 and χ_2, the latter provided that the lone pair does not lie along the principal axis of the proton acceptor molecule. The formation of a linear X–H···Y hydrogen bond determines the coordinates θ_1 (or θ_1', see Table II) and χ_1, the latter provided that the X–H bond is not coincident with the principal axis of the proton donor. However, these factors do not completely determine the dimer structure, since the ϕ coordinate may not be specified. In previous studies, it was shown that the optimized value of this coordinate is often dependent on such secondary factors as the relative orientation of the permanent dipole moments of the proton donor and proton acceptor molecules, and long-range interactions.

According to GHM, for dimers having pyridine and pyrazine as proton acceptor molecules and HF as the proton donor, a θ_1 value of 0° and a θ_2 value of 180° would be anticipated. Since the proton donor molecule is linear, the χ_1 rotation is not defined. Moreover, with θ_2 equal to 180°, the ϕ rotation is also not defined, and the intermolecular energy is constant with respect to changes in χ_2. As seen in Table II, the equilibrium HF–pyrazine and HF–pyridine dimers have C_{2v} symmetry and the structures anticipated from GHM.

When H_2O is the proton donor molecule in the H_2O-pyridine dimer, the dimer symmetry is reduced to C_s. The equilibrium dimer A with χ_2 equal to 90° has nonplanar C_s symmetry, with the plane of the pyridine molecule perpendicular to the dimer symmetry plane. As evident from Table II, the structure and energy of the equilibrium dimer A are comparable to the structure and energy of an idealized GHM dimer (C), which is only 0.1 kcal/mol less stable than dimer A.

The dimer B (see Figure 2) has planar C_s symmetry, but is not an equilibrium structure with respect to rotation of the proton acceptor molecule about its principal axis. Rather, the χ_2 rotation converts dimer B to the equilibrium dimer A. However, the difference in the stability of dimers A and B is only 0.1 kcal, indicating that the χ_2 potential curve is quite flat. The ϕ potential curve is also flat, as anticipated when θ_2 approaches 180°. Thus, although it has been possible to determine an equilibrium structure (A) for the H_2O-pyridine dimer, it should be recognized that two intermolecular motions, namely, rotation of the proton acceptor molecule about its principal axis, and rotation of this axis about the intermolecular line, are essentially free.

It is important to note that secondary factors have little effect on the structure of the equilibrium H_2O-pyridine dimer. In particular, since the dipole moment vector of pyridine lies along the principal axis, it is nearly colinear with the intermolecular line in the dimer. Hence, changes in the ϕ coordinate produce only small changes in the relative orientation of the dipole moment vectors of H_2O and pyridine. A similar situation was previously encountered in the H_2O-NH_3 dimer in which NH_3 is the proton acceptor molecule.[4]

An HF-pyridine dimer (B) with hydrogen bond formation through the pyridine π electron system at the nitrogen has also been investigated. This dimer was optimized with respect to R, the intermolecular F–N distance, with the angular coordinates fixed at the values shown in Table II. The resulting π dimer is only weakly bound, with an intermolecular energy of less than 1 kcal/mol, and it is not an equilibrium structure on the intermolecular surface. In a previous study of π dimers, it was also found that in those cases where an atom may act as a proton acceptor for hydrogen bond formation through either a lone pair of electrons or its π electrons, bond formation through the lone pair is preferred. In the ground state, it appears that such π dimers do not correspond to equilibrium structures, but convert to equilibrium dimers in which hydrogen bond formation occurs through the lone pair.[11]

It is of interest to examine the energies of the equilibrium dimers which have pyridine and pyrazine as proton acceptor molecules, and to compare the hydrogen bond strengths in these dimers with others which have proton acceptor nitrogen atoms. As evident from Table II, the equilibrium HF-pyridine dimer is more stable than the HF-pyrazine dimer by more than 1 kcal/mol. The greater stability of the HF-pyridine dimer may be attributed in part to a greater electron density at the pyridine nitrogen, as indicated by the Mulliken gross atomic populations[12] of 7.241 and 7.219 electrons for the pyridine and pyrazine nitrogen atoms, respectively. However, because this increased density in pyridine is due to an increased π density, a correlation between increasing charge on the proton acceptor atom and increasing dimer stability may not always occur.[13] It is important to recognize that although the relative orientation of the dipole moment vectors of the proton donor and proton acceptor molecules is not a factor in the determination of the structures of these equilibrium dimers, it most certainly has an influence on the stability of the HF-pyridine dimer in which a favorable head-to-tail alignment of the dipole moments of HF and pyridine occurs. This is probably the major factor contributing to the increased stability of this dimer compared with the equilibrium HF-pyrazine dimer.

A comparison of the intermolecular energies of the equilibrium dimers HF-pyridine (6.6 kcal) and H_2O-pyridine (4.7 kcal) shows that the dimer with HF as the proton donor is more stable. Its increased stability may be associated with the greater positive charge on the HF proton, which tends to make HF a better proton donor that H_2O for hydrogen bond formation.

It is also of interest to compare the stabilities of the equilibrium dimers HF-NH_3 (C_{3v}),[14] HF-pyridine (C_{2v}), and HF-HCN ($C_{\infty v}$),[15] each having HF as the proton donor, and a nitrogen atom as the proton acceptor atom. In a qualitative sense, the nitrogen hybridization changes in these proton acceptor molecules from sp^3 to sp^2 to sp, respectively, and the negative charge on nitrogen decreases simultaneously. The stabilities of these three dimers, each computed using the STO-3G basis set, are 8.3, 6.6, and 3.6 kcal/mol, respectively, decreasing as the p character in the sp hybrid orbital decreases. Thus, for these molecules, the computed order of dimer stability does correspond to the order anticipated from the hybridization of the proton acceptor atom. However, it should also be noted that in each of these proton acceptor molecules the nitrogen lone pair is essentially localized on a single atom, and the monomer dipole moment vectors have the same relative alignment in the dimers, although of course, the dipole moments of the proton acceptor molecules are not equal.[16] Under these conditions, predictions concerning relative dimer stabilities on the basis of the charge on the proton acceptor nitrogen atom or the nature of the hybridization of the proton acceptor atom are most likely to be reliable.

Population Analysis and Force Constants. In previous studies of the hydrogen bond, trends in population changes upon dimer formation have been observed, which are also evident in the dimers with pyridine and pyrazine as proton acceptor molecules. Upon formation of the F-H···N and O-H···N hydrogen bonds in these dimers, the hydrogen-bonded proton loses electron density, while the fluorine and oxygen atoms gain electron density. The hydrogen-bonded nitrogen atom experiences an increase in negative charge even though the proton acceptor pyridine and pyrazine molecules lose electron density in the dimers. It is interesting to note that the increased negative charge on the proton acceptor nitrogen atom is due to polarization of the aromatic π cloud toward nitrogen in the dimer. Thus, electron transfer, which varies from 0.031 electron in H_2O-pyridine to 0.043 electron in HF-pyridine, occurs from the proton acceptor molecule to the proton donor through the σ electron system, and is accompanied by an increased polarization of the π cloud toward the proton acceptor nitrogen atom in the dimer.

Force constants for the H_2O-pyridine dimer have also been estimated by approximating the second derivatives of the intermolecular energy with respect to the intermolecular coordinates, as in previous studies.[4] The force constants for the coordinates R, θ_1, χ_1, and θ_2 are 0.01367, 0.02574, 0.01943, and 0.00904, respectively. These derivatives give some indication of the rigidity of the equilibrium dimer structure to distortions produced by various modes of intermolecular motion. If these constants are compared with the corresponding force constants for H_2O-NH_3,[4] it can be seen that the H_2O-NH_3 dimer, which is more stable, is also more rigid than the H_2O-pyridine dimer with respect to each of these motions. In both dimers, the χ_2 and ϕ rotations are essentially free.

n → π* Transition Energies. The proton acceptor molecules pyrazine and pyridine exhibit n → π^* bands in the uv, which are shifted to higher energies (blue shifted) in hydrogen-bonding solvents. It is of interest, therefore, to examine the effect of hydrogen bond formation on the n → π^* transition energies in the equilibrium dimers which have pyrazine and pyridine as proton acceptor molecules. It is unfortunate, but not surprising, that at this level of treatment, even the singlet n → π^* transition energies of pyrazine and pyridine are overestimated by approximately 1.5 eV when compared with the experimental values.[17] Since the absolute error in the computed monomer transition energy is significantly larger than the magnitude of the blue shift in the dimer, these results for the blue shift could be questioned. However, the computed dimer transition energies relative to the computed monomer n → π^* transition energies are reasonable and consistent with the results of previous studies, in which better agreement between computed and experimental data was found.[18-20] As will be shown below, the interpretation of the data given in this study is also consistent with that proposed previously.

Before analyzing the monomer and dimer transition energies, it is advantageous to consider qualitatively the nature of the one-electron n → π^* transition, since the first excited state of pyrazine and of pyridine is dominated by this configuration, and then to quantitatively examine the nitrogen electron densities in the excited state. In pyridine, the n → π^* transition removes an electron from a somewhat localized nitrogen n orbital, decreasing the nitrogen electron density in the plane of the ring, and increasing the total π density of the molecule by one electron. Part of the increased π density is seen as an increase in the nitrogen π electron density. However, the net effect of this excitation is to leave the nitrogen atom positively charged (6.900 electrons) in the excited state, because of an electron deficiency in the σ system. On this basis, it would appear that pyridine, with a positively charged nitrogen atom, would not be a good proton acceptor molecule for hydrogen bond formation through the σ system in the excited state.

The effect of this transition in pyridine may be compared with its effect in pyrazine. Although the transition still increases the π density in the excited state by one electron, electron density is removed from a σ orbital of a_g symmetry, which is delocalized over both nitrogen atoms. As a result, while both nitrogen atoms lose electron density, they still remain negatively charged (7.168 electrons) in the excited state, and the σ electron deficiency at each nitrogen is not as great as it is in pyridine. Hence, dimer stabilization in

Table III. Hydrogen Bond Energies and Blue Shifts (eV)

	Hydrogen bond energy	Blue shift of the n → π* band[a]
HF–pyrazine	0.23	0.06
2:1 HF–pyrazine	0.44	0.15
HF–pyridine	0.29	0.30
H_2O–pyridine	0.20	0.23

[a] Relative to the n → π* transition energy of the isolated proton acceptor molecule.

the excited state of pyrazine through hydrogen bond formation at the nitrogen may still be possible.

The blue shifts of the n → π* bands in the hydrogen-bonded complexes are reported in Table III along with the hydrogen-bond strengths. It is apparent from these data that when pyridine is the proton acceptor molecule in a hydrogen-bonded dimer, there is a significant increase in the n → π* transition energy. In particular, for both the HF–pyridine and H_2O–pyridine dimers, it is possible to approximate the dimer transition energy as the sum of the monomer n → π* transition energy and the hydrogen bond energy in the ground state. This relationship suggests that the hydrogen bond, formed in the ground state through the nitrogen lone pair, is broken upon excitation in the dimer as the nitrogen atom becomes positively charged. Hence, in these two dimers, the blue shift once again reflects the additional energy required to break the hydrogen bond.[18-20]

The effect of hydrogen-bond formation on the n → π* transition of pyridine may be contrasted to its effect in the HF–pyrazine dimer. As seen in Table III, only a small blue shift of the pyrazine n → π* band in the dimer is predicted. This suggests that the hydrogen bond may become slightly weakened, but that the excited state is stabilized by hydrogen-bond formation at the nitrogen. Although the potential curve for the intermolecular distance has not been computed for this dimer, the similarity between the results obtained for the HF–pyrazine dimer and those reported for the H_2O–glyoxal dimer is apparent. In the latter dimer, such a curve was obtained and found to possess a minimum at a slightly larger intermolecular distance than the ground state equilibrium distance.[20] In these dimers, the n → π* transitions originate in n orbitals which are still delocalized, and the proton acceptor atoms remain negatively charged in the excited state.[21] Thus, the blue shifts and the hydrogen bond energies are no longer comparable, and the dimers apparently remain bound in the excited n → π* state.

A 2:1 HF–pyrazine trimer of D_{2h} symmetry has been constructed with R, the intermolecular distance, fixed at the equilibrium dimer distance. As seen in Table III, the trimer intermolecular energy is slightly less than twice the dimer hydrogen-bond energy. The blue shift of the n → π* band in the trimer has also increased, but is significantly less than the ground state intermolecular energy. This again suggests that while the two hydrogen bonds may become weakened in the excited state, the complex still remains bound.[20]

Although these calculations refer most directly to the gas phase, it is possible to correlate some solution data with these results. In so doing, it must be recognized that some solution effects are being neglected. Nevertheless, it is significant that the data obtained in this work and the interpretations presented are consistent with experimental results obtained from studies of solution effects on n → π* transition energies. Such studies have indicated that (1) the n → π* band of pyridine disappears in a water solution, being blue shifted and masked by the more intense π → π* band;[22] (2) in a hydrogen-bonding solvent, the n → π* band of the ethyl bromide salt of pyrazine (in which only a single nitrogen lone pair exists) shows a larger blue shift than the n → π* band of pyrazine;[22] and (3) the excited state stabilization of pyrazine in a hydrogen-bonding solvent is considerable.[23]

Conclusions

Ab initio SCF calculations have been performed to determine the equilibrium structures and energies of dimers HF–pyrazine, HF–pyridine, and H_2O–pyridine. The structures of these dimers are consistent with structures anticipated from the general hybridization model. A comparison of the hydrogen bond strengths in HF–pyrazine and HF–pyridine shows that the pyridine molecule is the better proton acceptor. This may be attributed to the greater negative charge on the nitrogen in pyridine, and to a favorable head-to-tail alignment of molecular dipole moments in the HF–pyridine dimer. An HF–pyridine dimer in which hydrogen-bond formation occurs through the π electron system at the nitrogen has been investigated and found to be a nonequilibrium structure on the intermolecular surface.

In the equilibrium dimers, charge transfer occurs from the proton acceptor molecule to the proton donor. This transfer takes place through the σ system, and is accompanied by a further polarization of the π cloud toward the hydrogen-bonded nitrogen atom in the dimer. As a result, although the proton acceptor molecule loses electron density, the proton acceptor atom experiences an increase in negative charge. The charge on the nitrogen in the molecules NH_3, pyridine, and HCN decreases in the order $NH_3 >$ pyridine > HCN, as the p character in the sp hybrid orbital decreases. A correlation exists with the decreasing stability of dimers HF–NH_3 > HF–pyridine > HF–HCN.

CI calculations have also been performed to determine the effect of hydrogen-bond formation on n → π* transition energies. When pyridine is the proton acceptor molecule, a blue shift of the pyridine n → π* band is observed which is comparable with the dimer hydrogen-bond strength. This suggests that the hydrogen bond is broken upon excitation in the dimer, and follows as a consequence of the nature of the n → π* transition which produces a positively charged nitrogen atom. In contrast, for the HF–pyrazine dimer, only a small blue shift of the n → π* band is found. In pyrazine, electron excitation occurs from an n orbital which is delocalized over both nitrogens, and these atoms remain negatively charged in the excited state. Both the HF–pyrazine dimer and a 2:1 HF–pyrazine trimer appear to remain bound in the excited state.

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References and Notes

(1) P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 4991 (1971).
(2) L. Piela, *Chem. Phys. Lett.*, **15**, 199 (1972).
(3) A. Johansson, P. Kollman, and S. Rothenberg, *Chem. Phys. Lett.*, **16**, 123 (1972).
(4) J. E. Del Bene, *J. Am. Chem. Soc.*, **95**, 5460 (1973).
(5) E. Clementi, J. Mehl, and W. von Niessen, *J. Chem. Phys.*, **54**, 508 (1971).
(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(7) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(8) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
(9) J. E. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973).
(10) J. E. Del Bene, *J. Chem. Phys.*, **62**, 1961 (1975).

(11) J. E. Del Bene, *Chem. Phys. Lett.*, **24**, 203 (1974).
(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(13) J. E. Del Bene, *J. Chem. Phys.*, **62**, 1314 (1975).
(14) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, in press; the author is grateful to Professor Pople for a preprint of this work.
(15) J. E. Del Bene and F. T. Marchese, *J. Chem. Phys.*, **58**, 926 (1973).
(16) It should also be noted that the order of increasing dipole moment NH_3 < pyridine < HCN is the reversed order of increasing proton accepting ability, again suggesting that the dipole interaction is not the primary factor in dimer stabilization.
(17) J. E. Del Bene, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **55**, 2236 (1971).
(18) J. E. Del Bene, *J. Am. Chem. Soc.*, **95**, 6517 (1973).
(19) J. E. Del Bene, *J. Am. Chem. Soc.*, **96**, 5643 (1974).
(20) J. E. Del Bene, *J. Chem. Phys.*, **62**, 666 (1975).
(21) Hydrogen-bond formation stabilizes the n orbital in the HF–pyrazine dimer. The n orbital remains delocalized, with the LCAO coefficients of N_4 atomic orbitals increasing slightly and those of N_1 atomic orbitals decreasing slightly, in absolute value.
(22) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).
(23) V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **33**, 381 (1960).

A Theoretical Study of the Dodecahedrane Molecule

Jerome M. Schulman,*[1] Thomas Venanzi, and Raymond L. Disch

Contribution from the Department of Chemistry, Queens College, City University of New York, Flushing, New York 11367. *Received February 24, 1975*

Abstract: The molecule dodecahedrane is studied from the viewpoints of group theory, graph theory, and molecular orbital theory. A number of physical properties are considered, among them the multipole moment of the charge density, the molecular force field, and the ordering of the orbital energies. A graph-theoretic procedure for enumerating the substitutional isomers is described, and several particular cases are considered.

I. Introduction

An interesting, though relatively little-studied, class of molecules is the C_nH_n hydrocarbons whose carbon skeletons form convex polyhedra. A subset of these, the regular polyhedral hydrocarbons based upon the perfect solids of antiquity, is composed of three potential members: tetrahedrane ($n = 4$), cubane ($n = 8$), and dodecahedrane ($n = 20$)[2] (Figure 1). As yet, only cubane has been synthesized[3] and geometrically characterized.[4] Tetrahedrane has been the subject of a recent theoretical study[5] which predicted that it would be a bound molecule, detectable and perhaps amenable to isolation at low temperatures. The present paper gives the results of a theoretical study of dodecahedrane.[6,7]

Dodecahedrane is of interest because of its high symmetry, its topology, and, of course, its aesthetic allure.[8] It might well serve as a model system for many physical-organic studies, because of its rigid, though relatively strain-free structure, its limited facility for solvation, and its surface as a potential template for studying various hydrocarbon reactions. In sections II and III respectively we consider various aspects of dodecahedrane's symmetry and topology. Section IV contains the results and interpretation of a molecular orbital calculation, including a plot of the valence-electron charge density.

II. Considerations of Symmetry

One of the most striking of the symmetry properties of dodecahedrane is its sphericality (Figure 1). With CC bond lengths of 1.54 Å (the diamond distance), 20 carbons lie on a sphere of diameter 4.32 Å; the hydrogens at a bond length of 1.09 Å (the ethane value) lie on an outer sphere of 6.50 Å. In fact, dodecahedrane would be the molecule of highest known point group symmetry, I_h,[9] with 120 point group operations leaving the molecule invariant. The dodecahedrane charge density has as its first nonvanishing multipole moment the 2^6-pole moment[10]

$$\int \psi^* \gamma^6 \psi \mathrm{d}^* \tau \qquad (1)$$

where ψ is the ground state vibronic wave function and the multipole operator γ^6 is the sum over electrons and nuclei[11]

$$\gamma^6 = \sum_i q_i r_i{}^6 \left[\sum_{m=-6}^{6} \frac{(6-|m|)!}{(6+|m|)!} P_6{}^m (\cos \Theta_i) e^{im\phi} \right] \qquad (2)$$

where q_i is the charge of particle i and (r_i, Θ_i, ϕ_i) are its polar coordinates referred to some suitably-chosen coordinate system with origin at any point in space; in I_h symmetry only one of the 13 nonvanishing components of the 2^6-pole tensor is unique. By contrast, the two preceding regular polyhedral hydrocarbons tetrahedrane (T_d) and cubane (O_h) have 2^3-pole (octopole) and 2^4-pole (hexadecapole) moments, respectively.

The lack of any low multipole moments in dodecahedrane implies the almost-complete absence of contributions of all but dispersion forces to the long-range interactions, e.g., to the second virial coefficient,[12] suggesting that dodecahedrane in the vapor phase will resemble a large rare gas molecule in its physical properties. For the same reason, dodecahedrane may also be anticipated to sublime more readily than would be expected for a molecule of its molecular weight. An analogous case is cubane which has a heat of sublimation of 19.2 kcal/mol at 298°K, one-fourth the value of its lower-symmetry isomer cyclooctatetraene, 71.1 kcal/mol.[13]

The high symmetry of dodecahedrane serves to simplify the description of its molecular force field. The number of independent harmonic force constants is 74, almost 100-fold fewer than the 6555 which would be necessary to characterize a completely asymmetric 40-atom molecule. This drastic reduction in independent parameters arises from the high degeneracies of the vibrational modes. The 114 normal modes belong to symmetry species: $2A_g$, T_{1g}, $2T_{2g}$, $4G_g$, $6H_g$, $3T_{1u}$, $4T_{2u}$, $4G_u$ and $4H_u$, where the T, G, and H modes are three-, four-, and fivefold degenerate, respectively (there is no twofold degeneracy in I_h symmetry). There are only three infrared active modes (T_{1u}) and eight Raman active modes ($2A_g$ and $6H_g$) and, of course, only single proton and ^{13}C NMR resonances.

It is interesting to note that dodecahedrane is a molecule almost devoid of angle strain. The CC bonds, being edges of