and by both theoretical methods. This is in contrast to the prediction of the simple "localization energy" concept in Hückel π-electron theory, according to which localization of a pair of electrons in benzene involves a loss of π-electron energy of -2.536β whereas a comparable calculation on ethylene gives only -2β. Clearly other factors such as the additional σ bonds available for polarization in the larger molecule must be taken into account in discussing proton affinities.

The difference in energy between the benzenium (I) and benzenonium (IV) ions (27.7 kcal/mol for the STO-3G method and 20.6 kcal/mol using the 4-31G basis) is the barrier to proton exchange between carbon centers. Thus while structure 1 is a minimum on the $C_6H_7^+$ potential surface, structure IV actually corresponds to a saddle point, being unstable with respect to movement of the proton away from the exact center of the carbon–carbon bond. The corresponding barriers to proton migration in the ethyl cation have earlier been reported as 11.4 and 6.8 kcal/mol for the STO-3G and 4-31G basis sets, respectively.[7]

Conclusion

We have attempted to elucidate the structure of protonated benzene by theoretical techniques using simple ab initio molecular orbital theory. The general conclusions may be stated as follows.

1. We find the lowest energy structure for protonated benzene to be one in which the proton is attached directly to one of the ring carbons, which in turn has become approximately tetrahedrally coordinated. The form corresponding to the proton bridging a carbon–carbon bond is found to be 20–30 kcal/mol less stable. Edge- and face-protonated structures appear to be energetically very unfavorable.

2. The structures we report here for $C_6H_7^+$ correspond in some detail to those previously published for the ethyl cation.

3. The ptoton affinity of benzene is well described by simple molecular orbital theory (using the extended 4-31G basis) and is noted to be somewhat larger than that of ethylene. This leads to some doubt about localization energy predictions of the stabilities of compounds of this nature.

4. Using the extended 4-31G basis, the barrier to proton migration in $C_6H_7^+$ is found to be 20.6 kcal/mol, significantly larger than the corresponding quantity in the ethyl cation.

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Characterization of Nitrogen-Containing Molecules[1a]

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Abstract: An ab initio procedure for the investigation of large molecules is applied to a series of compounds containing nitrogen as a heteroatom. In particular, the effect of the nitrogen lone pair on geometric and electronic structure predictions is studied. Several descriptions of molecular fragments are tested, in which floating spherical Gaussian orbitals (FSGO) are employed. Applications of the method to methylamine, dimethylamine, hydrazine, methylenimine, diimide, pyridine, pyrazine, and pyrrole are given. When possible, comparisons are made with other theoretical results as well as experimental values. The geometric and electronic structure predictions are, in general, very good and comparable to results obtained earlier for hydrocarbons. Those cases in which exceptions occur are discussed in detail, and suggestions are made for fragment improvements to correct the deficiencies.

In previous studies,[2–8] an ab initio molecular orbital method for application to large molecules has been described, and the characteristics of this method as applied to saturated and unsaturated hydrocarbons have been investigated. In this method, molecular fragments are employed to obtain the basis orbitals for use in an LCAO–MO–SCF procedure on large molecules. If this method is to be applicable in general to molecular systems for the determination of geometric structure, electronic structure, and properties, it is essential that nitrogen-containing single and double bonds also be described adequately.

This investigation emphasizes the study of the electronic and geometric structure of prototype molecules containing nitrogen as the heteroatom, in order to obtain an optimum description for future heteroatom

(1) (a) This work was supported in part by a grant from the National Science Foundation, and a grant from the Upjohn Co., Kalamazoo, Mich.; (b) Phillips Petroleum Fellow, 1970–1971; (c) Alfred P. Sloan Research Fellow, 1971–1973.

(2) R. E. Christoffersen and G. M. Maggiora, Chem. Phys. Lett., 3, 419 (1969).

(3) R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, J. Chem. Phys., 54, 239 (1971).

(4) R. E. Christoffersen, L. L. Shipman, and G. M. Maggiora, Int. J. Quantum Chem., 5S, 143 (1971).

(5) R. E. Christoffersen, J. Amer. Chem. Soc., 93, 4104 (1971).

(6) R. E. Christoffersen, Advan. Quantum Chem., 6, 333 (1972).

(7) G. M. Maggiora, D. W. Genson, R. E. Christoffersen, and B. V. Cheney, Theor. Chim. Acta, 22, 337 (1971).

(8) B. V. Cheney and R. E. Christoffersen, J. Chem. Phys., 56, 3503 (1972).

calculations. In particular, several relatively small polyatomic systems, N_2H_4, CH_3NH_2, $(CH_3)_2NH$, CH_2-NH, N_2H_2, C_4NH_5, C_5NH_5, and $C_4N_2H_4$, have been investigated, in order to delineate the characteristics of the procedure and optimum fragment descriptions before applying it to larger molecules. Specifically, the effect of the lone pair on internuclear distances, bond angles, the shape of rotation barriers, and electronic structure predictions has been examined.

Theoretical Techniques

Since the details of this method have been given previously,[2,3,6] only a brief summary will be presented here. The basis orbitals employed in this procedure, similar to those used by Frost,[9-11] are normalized floating spherical Gaussian orbitals (FSGO), defined as

$$G_i(\mathbf{r}) = (2/\pi\rho_i^2)^{1/4} \exp\{-[(\mathbf{r} - \mathbf{R}_i)/\rho_i]^2\} \quad (1)$$

where ρ_i is known as the orbital radius, and $\mathbf{R}_i$ is the location of the FSGO, relative to an arbitrary origin. If a π-type orbital is employed, it is described by a linear combination of two FSGO, i.e.

$$G_\pi = (G_u - G_d)/[1(1 - \Delta_{ud})]^{1/2} \quad (2)$$

where G_u and G_d are FSGO placed symmetrically above and below the atomic plane, on a line through the central atom, and Δ_{ud} is the value of the overlap integral between them. In the current studies, the optimum description of molecular fragments is obtained by determining the nonlinear parameters of the FSGO variationally with a direct energy minimization. In a few cases, minimization of the energy became insensitive to nonlinear parameter choice, and in these cases the final criterion became the closeness of the scale factor to unity. As in previous studies,[2-8] the fragments examined primarily in this initial investigation are described using the simplest description involving FSGO, i.e., a single FSGO as each basis orbital (except for π-type orbitals).

By suitable combination of the appropriate molecular fragments and associated parameters, ab initio SCF calculations were then carried out. The coordinate systems used in these calculations are shown in Figure 1.

The molecular orbitals for large molecules are taken as linear combinations of fragment FSGO, i.e.

$$\varphi_i = \sum_{A=1}^{p} \sum_{k=1}^{N_A} C_{ki}{}^A G_k{}^A \quad (3)$$

where the $G_k{}^A$ are the previously determined fragment orbitals, and the $C_{ki}{}^A$ are the coefficients which come from the solution of the well-known SCF equations.[12,13]

All calculations have been done employing double precision arithmetic on a Honeywell-635 computer, and convergence was assumed when

$$|P_{rs}{}^{(i+1)} - P_{rs}{}^{(i)}| \leq 0.00002$$

for all r and s, where $P_{rs}{}^{(i)}$ corresponds to the element

(9) A. A. Frost, *J. Chem. Phys.*, **47**, 3707, 3714 (1967); S. Y. Chu and A. A. Frost, *ibid.*, **54**, 764 (1971), and references therein.
(10) A. A. Frost, *J. Amer. Chem. Soc.*, **89**, 3064 (1967); **90**, 1965 (1968).
(11) A. A. Frost, *J. Phys. Chem.*, **72**, 1289 (1968).
(12) G. G. Hall, *Proc. Roy. Soc., Ser. A*, **205**, 541 (1951).
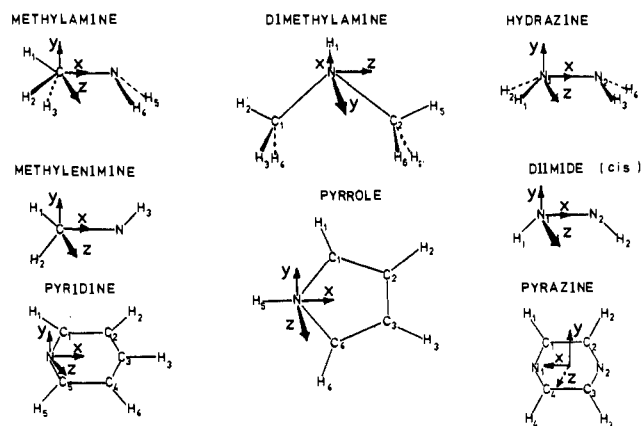(13) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

Figure 1. Coordinate axes and atomic numbering.

of the rth row and sth column in the charge and bond order matrix of the ith iteration, where

$$P_{rs} = 2\sum_{i}^{occ} C_{ir} C_{is} \quad (4)$$

Typically, this corresponds to a root-mean-square error of approximately 10^{-7}.
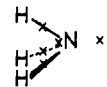
Molecular Fragment Investigations

In each molecular fragment, more than one set of parameters was investigated, and the results of the large molecule calculations were used to determine the relative merit of each description. Throughout these studies the optimum hydrocarbon parameters from previous work[2,3,7] were chosen.

The first molecular fragment of interest is the NH_3 molecule. Assumption of idealized geometry (T_d) has been shown to make only minor differences in studies of other fragments[3,7] and hence was assumed in the current studies. The two NH_3-T_d fragments studied initially differ only in the position of the FSGO describing the lone pair of electrons. In the fragment labeled NH_3-T_d-Max $2p_z$, the distance of the FSGO from the N atom was fixed to correspond to the maximum of one lobe of an exponential $2p_z$ orbital on nitrogen, with the orbital exponent chosen from Slater's rules.[14] The second fragment, labeled NH_3-T_d-Free, was chosen so that the corresponding distance was varied to obtain a minimum energy position. This minimum differs from the previously reported results of Frost[11] because of the fixed tetrahedral nuclear geometry. Frost's parameter values have been essentially reproduced by this procedure when the nuclear geometry is also varied.

In both NH_3 fragment choices, the number of independent nonlinear parameters to be varied is further reduced by the symmetry of the FSGO in the N-H bonding regions. A summary of the optimum parameters for these two fragments appears in Table I. These parameters were used for the N_2H_4, CH_3NH_2, and $(CH_3)_2NH$ molecules.

The second fragment of interest is planar NH_3, where the nitrogen atom has sp^2 hybridization and the lone pair of electrons is in a π-type orbital. Since this fragment does not correspond to a stable molecule, its

(14) For example, see F. M. Pilar, "Elementary Quantum Chemistry," McGraw-Hill, New York, N. Y., 1968, p 194.
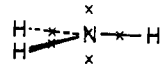
Table I. NH₃-Tetrahedral Fragment[a]

	NH₃-T_d- Max 2p_z	NH₃-T_d-Free
Gaussian distances[b]		
N–Lp	0.51282051	0.25523498
N–H	0.95812500	0.87735349
N–inner shell	0.00099427	0.00099090
Gaussian radii (ρ)		
LP	1.51898438	1.58328000
N–H	1.51490662	1.52791683
N–inner shell	0.27754230	0.27732014
Energy[b] (unscaled)	−47.43710837	−47.46744156
Scale factor	1.00077793	1.00002827

[a] N–H bond distance = 1.012 A (1.91242167 bohrs); see "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. **18**, S7s (1965). [b] All distances and energies are reported in hartree atomic units; see H. Shull and G. G. Hall, *Nature (London)*, **184**, 1559 (1959).

geometry is somewhat arbitrary. Specifically, the N–H bond distance was taken to be 0.99 Å,[15] and the HNH angle was chosen as 120°. Another nonvarying parameter for this fragment is the position of the FSGO describing the π-type orbital. If these Gaussians are allowed to vary freely, they coalesce to the central atom. Therefore, the two functions must be held at a fixed distance above and below the plane of the nuclei. Two different choices were investigated for this distance. The first fragment (NH₃-Planar-0.1) was chosen so that the N π-type orbital is compatible with the "best" ·CH₃ π position,[3] *i.e.*, 0.1 bohr. A second choice for this fragment (NH₃-Planar-Max 2p_z) has the Gaussians which form the π-orbital centered above and below the nuclear plane at a distance which corresponds to the maximum of a Slater 2p_z orbital.

A summary of the optimized parameters for this fragment appears in Table II. These parameters were used in the pyrrole molecule. It is also antic-
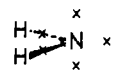
Table II. NH₃-Planar Fragment[a]

	NH₃-Planar-0.1	NH₃-Planar- Max 2p_z
Gaussian distances[b]		
N–H	0.94031372	0.93484009
N–π	0.10000000	0.51282051
Gaussian radii		
N–H	1.47683593	1.47170898
π	1.51198608	1.52089721
N–inner shell	0.27814453	0.27806030
Energy[b] (unscaled)	−47.47519434	−47.46210646
Scale factor	1.00183361	1.00211998

[a] N–H distance = 1.87084729 bohrs (0.99 Å); see ref 15. [b] All distances and energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I.

(15) This value is an average of the N–H bond distances reported for urea and formamide in "Tables of Interatomic Distance and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. **18**, M64S (1965).

ipated that one of these fragments will be used in the future for molecules containing amide groups.

The final nitrogen fragment that is included in this investigation is an ·NH₂ radical. In anticipation of a nitrogen multiple bond, the N atom is given an sp² hybridization, and a single unpaired electron is placed in an orthogonal π-type orbital. Once again the position of the FSGO must be fixed. However, all other nonlinear parameters are optimized. Thus, the two sets of fragment parameters for ·NH₂ correspond to the π-orbital choices in planar NH₃; *i.e.*, ·NH₂-0.1 has a π orbital with Gaussians centered 0.1 bohr above and below the nuclear plane, and ·NH₂-Max 2p_z has the π orbital centered at the distance which corresponds to the maximum of one lobe of a Slater 2p_z orbital. A summary of the optimized parameters for these fragments appears in Table III. These parameters were used to form the CH₂NH, N₂H₂, pyridine, and pyrazine molecules.

Table III. ·NH₂-Fragment[a]

	·NH₂-0.1	·NH₂-Max 2p_z
Gaussian distances[b]		
N–H	0.89803124	0.89566404
N–LP	0.30407714	0.30435156
N–π	0.10000000	0.51282051
Inner shell	0.00088379	0.00089014
Gaussian radii		
N–H	1.43795016	1.43555112
N–LP	1.51400386	1.51151358
π	1.35873044	1.35006653
N–inner shell	0.27698950	0.27697986
Energy[b] (unscaled)	−47.01981688	−47.01500940
Scale factor	0.99418852	0.99441955

[a] N–H distances were chosen according to a "ratio rule," $R_{NH}(\cdot NH_2) = [R_{C-N}(C_4NH_5)/R_{C-N}(CH_3NH_2)]R_{NH}(NH_3)$, and are equal to 1.75153951 bohrs. [b] All distances and energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I.

Applications to Prototype Molecules

As a preface to this section it should be noted that, for molecules of interest to this method, *i.e.*, "large" organic molecules, the geometries will not in general be known. It was shown in a previous study[3] that the assumption of "idealized" geometries about heavy atom nuclei, *e.g.*, tetrahedral or trigonal, affected the calculation only minimally. Therefore, the prototype molecules of this study are formed by bringing "idealized" fragments together at assigned internuclear distances.

1. Methylamine Molecule. The structure of the methylamine molecule was taken to have tetrahedral geometry about the carbon and nitrogen atoms and with the C–H, N–H, and C–N bond distances chosen from microwave data.[16] This particular molecule was employed to aid in the determination of which of the tetrahedral ammonia fragments constitutes the better description for the amine-type nitrogens of larger compounds. Specifically, the barrier to methyl rotation and a predicted C–N single bond distance were investigated in detail.
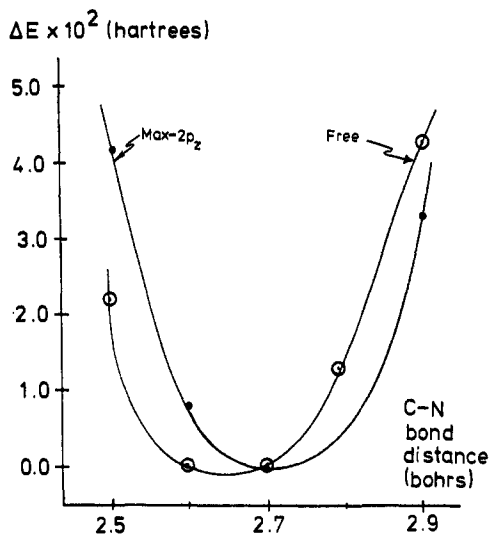
(16) D. R. Lide, Jr., *J. Chem. Phys.*, 27, 343 (1957).

Figure 2. Total energy $vs.$ C–N bond distance for CH_3NH_2.

Figure 3. Total energy $vs.$ C–N–C bond angle for $(CH_3)_2NH$.

Since this particular method has been characterized previously as overestimating rotation barriers in hydrocarbons,[3] the results of Table IV are not espe-

Table IV. Comparison of Rotation Barriers for Methylamine

Con-former	Energy[a]	NH_3–T_d– Max $2p_z$	NH_3–T_d– Free
Stag-gered	Kinetic	78.39810085	78.36271191
	Potential (electron-nuclear)	−271.47723770	−271.53180695
	Potential (electron-electron)	70.41615486	70.46969223
	Potential (nuclear-nuclear)	41.95091152	41.95091152
	Total energy	−80.71206951	−80.74848652
	Scale factor	1.01475780	1.01522262
Eclipsed	Kinetic	78.41469479	78.37932873
	Potential (electron-nuclear)	−271.49441528	−271.54975510
	Potential (electron-electron)	70.42014313	70.47374344
	Potential (nuclear-nuclear)	41.95617819	41.95617819
	Total energy	−80.70339489	−80.74050236
	Scale factor	1.01459356	1.01506247
Barrier to rotation (kcal/mol)		5.50	5.00

[a] All energies are reported as unscaled quantities in hartree atomic units; see Shull and Hall, footnote b, Table I.

cially surprising. On the contrary, the results from the NH_3–T_d–Free fragment, which was anticipated to be the better model here, show a barrier for the CH_3NH_2 barrier height that is smaller than that calculated for C_2H_6, in accord with the experimental trend (CH_3NH_2 barrier 1.97 kcal/mol, ref 16; C_2H_6 barrier 2.98 kcal/mol, ref 17). It should also be noted here that the simplest rigid rotor model was chosen, $i.e.$, one in which the axis of rotation is chosen to be collinear with the C–N bond. If the experimentally observed axis[16] is used instead, the barrier to rotation is lowered by approximately 0.7 kcal/mol in a more extensive Gaussian basis set calculation.[18] It is therefore

anticipated that this change would serve only to increase the quantitative agreement of the current model with experimental evidence.

Not only is it important that this method correctly describe barriers to rotation, but it also should be capable of predicting C–N bond distances. Figure 2 shows the total energy of the methylamine molecule as a function of the C–N bond distance. The minimum value of the curves, 2.70 (NH_3–T_d–Max $2p_z$) and 2.65 bohrs (NH_3–T_d–Free), are well within normal limits of acceptable geometric predictions, 3.1 and 4.8% error, respectively, when compared to the experimental value of 2.78 bohrs.[16] Why this single bond distance prediction is improved over the C–C bond distance is not completely understood. One possibility arises from the special manner in which hydrogen atoms are treated in this procedure. Specifically, the description of the electronic environment near hydrogen atoms is sacrificed in order to obtain a better description of the electrons that participate in "heavy atom–heavy atom" bonds. It might be expected then that the elimination of one X–H bond between C_2H_6 CH_3NH_2 may allow the distance prediction to improve.

2. **Dimethylamine Molecule.** In this particular molecule the torsional rotation is strongly coupled to inversion at the N atom.[19] Since the way in which this method can best treat inversion barriers has not as yet been fully investigated, this molecule was chosen only to investigate the skeletal bending mode. The choice of bending motion is one in which only the CNC bond angle is varied. The tetrahedral symmetry of the methyl groups was not allowed to relax, nor was the H–N–Lone pair angle changed from tetrahedral. The C–H, N–H, and N–C bond distances were taken from the microwave structure.[19] Figure 3 shows the plot of total energy of dimethylamine $vs.$ CNC bond angle for the two choices of nitrogen fragments. Both of these results (approximately 9% error), while considerably poorer than the comparable results in the hydrocarbon study on propane,[3] are still within a 10% limit for geometric predictions on large molecules.

(17) W. J. Lafferty and E. K. Plyler, $J. Chem. Phys.$, **37**, 2688 (1962).
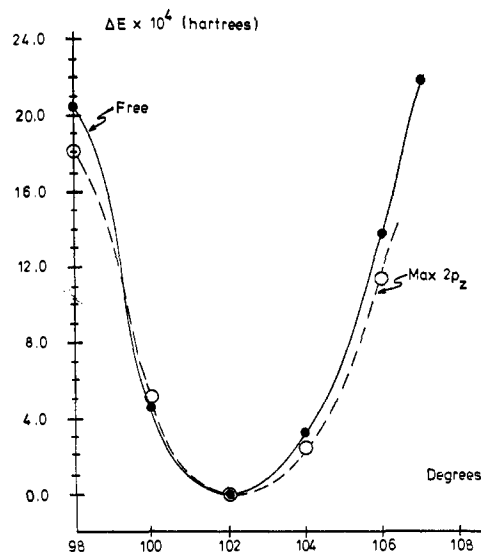(18) L. Pedersen and K. Morokuma, $ibid.$, **46**, 3941 (1967).

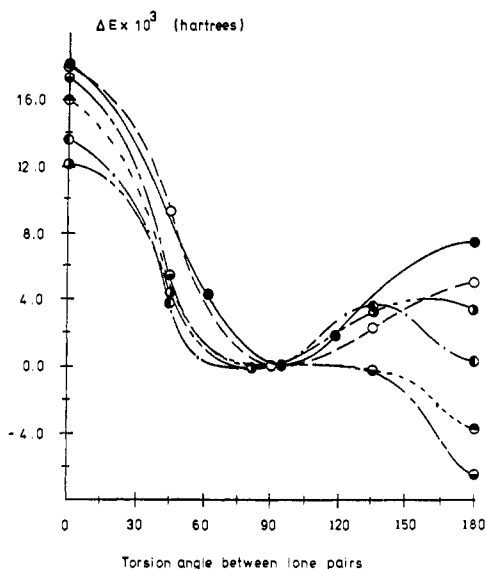(19) J. E. Wollrab and V. W. Laurie, $ibid.$, **48**, 5058 (1968).

Figure 4. Potential energy curve for NH_2 rotation in hydrazine: (—●—) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1966); (—○——) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967); (— ◒ ——) NH_3-T_d-Max $2p_z$; (--- ◒ ---) NH_3-Td-Free; (—◑-·—) NH_3-T_d-Split 1s; (—◐-----) R. P. Lattimer and M. D. Harmony, private communication undergoing current investigation.

3. Hydrazine Molecule. Another molecular system which will aid in making a distinction between the two NH_3-T_d fragments is the hydrazine molecule. Both the shape of the energy surface for rotation of an NH_2 group and the prediction of the N–N single bond distance were investigated.

In calculating the energy curve for NH_2 rotation, the two NH_3-T_d fragments were combined using the N–N and N–H distances as determined by electron diffraction.[20] The best currently available experimental data as well as several other *ab initio* calculations appear in Figure 4 along with the results of the current work. Not only are the curves given for the NH_3-T_d-Max $2p_z$ and NH_3-T_d-Free fragments but also for a new fragment called NH_3T_d-Split 1s. This new fragment, summarized in Table V, consists of more than a minimum description of the 1s electrons on the nitrogen atom. The single Gaussian corresponding to this inner shell orbital is replaced by a linear combination of two FSGO[21] in which the orbital radii and linear coefficients have been taken from the two Gaussian expansion of Hehre, Stewart, and Pople.[22]

Even though this first attempt at improving the description of the hydrazine rotational energy curve is seen to be still not adequate, it is a large step in the right direction. It is anticipated therefore, that further investigation of a fragment similar to this will be sufficiently flexible to describe this rotational curve properly.

Another measure of the relative merit of the two nitrogen fragments is the way in which they describe the NH_2–NH_2 interactions as a function of separation distance. In Figure 5 the total energy of N_2H_4 is

(20) Y. Morino, I. Iijima, and Y. Murata, *Bull. Chem. Soc. Jap.*, **33**, 46 (1960).

(21) A similar approach was previously reported for carbon fragments in ref 3.

(22) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
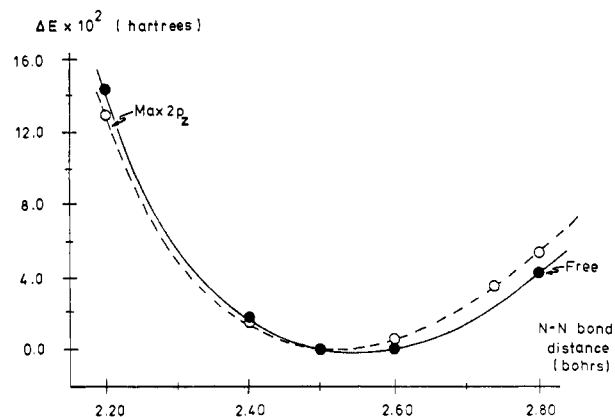
Figure 5. Total energy *vs.* N–N bond distance for N_2H_4.

Table V. NH_3-T_d-Split 1s Fragment[a]

Gaussian distances[b]	
N–LP	0.26990625
N–H	0.88812499
Gaussian radii[c]	
LP	1.60425976
N–H	1.53675000
Inner shell no. 1	0.16244281
Inner shell no. 2	0.38502739
Linear coefficients[c]	
Inner shell no. 1	4.68228734
Inner shell no. 2	2.02529094
Energy[b]	−52.71700001
Scale factor	1.00813542

[a] N–H bond distance of 1.022 Å (1.93131912 bohrs) from hydrazine; see ref 20. [b] All distances and energies are reported in hartree atomic units; see Shull and Hall, footnote *b*, Table I. [c] The ρ values and linear coefficients for the two Gaussian expansion of the inner shell come from the work of Hehre, Stewart, and Pople.[22]

plotted against the N–N bond distance. The minimum energy values are obtained at 2.50 and 2.56 bohrs for the NH_3-T_d-Max $2p_z$ and the NH_3-T_d-Free fragments, respectively, as compared to the experimentally observed value of 2.738 bohrs.[16] Again, the errors in these geometric predictions are less than 10% (8.7 and 6.5%) for both of the fragments.

4. Methylenimine Molecule. In each of the following prototype molecules, the nitrogen heteroatom is usually considered to participate in multiple bonding. Thus, these molecules can be used to determine which of the ·NH_2 fragments constitutes the better description of double bonds containing nitrogen.

The simplest molecule involving a carbon–nitrogen double bond is methylenimine (CH_2NH). Idealized geometry (sp^2 hybridization) was assumed for both "heavy" atoms, and the C–N bond distance for the initial calculations was chosen to be 1.35 Å (2.55115539 bohrs) while the C–H distance was 1.07 Å (2.02202686 bohrs).[23] The N–H bond distance corresponded to the choice made for the NH_3-Planar fragments.[15] Table VI shows that the orderings of molecular energy

(23) These bond distances were taken from "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11, S15, S17 (1958).

Table VI. Molecular Orbital Energy[a] Ordering for Methylenimine (CH₂NH)[b]

· NH₂-Max 2p_z fragment MO symmetry	− Energy	· NH₂-0.1 fragment MO symmetry	− Energy	Lehn, Munsch, and Millie[c] MO symmetry	− Energy	Moffat[d] MO symmetry	− Energy
1a'	3.0184	1a'	13.0016	1a'	15.5824	1a'	15.8223
2a'	9.3745	2a'	9.3535	2a'	11.3031	2a'	11.4012
3a'	1.1900	3a'	1.1792	3a'	1.2191	3a'	1.2874
4a'	0.7885	4a'	0.7805	4a'	0.8565	4a'	0.8874
5a'	0.5660	5a'	0.5576	5a'	0.6839	5a'	0.6780
6a'	0.4964	6a'	0.4880	6a'	0.6113	6a'	0.5951
1a''(π)	0.3136	1a''(π)	0.3174	1a''(π)	0.4450	1a''(π)	0.4370
7a'	0.2260	7a'	0.2183	7a'	0.4253	7a'	0.4063
2a''(π*)	−0.3600	2a''(π*)	−0.3607			2a''(π*)	−0.1551
Total energy	−80.0449		−80.05333		−93.9743		−93.3944

[a] All energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I. [b] The C–N internuclear distance for the first two calculations was taken to be 2.40 bohrs. This corresponds most closely to the minima of the energy vs. bond distance curves. [c] Reference 24. [d] Reference 25

levels which result from both fragments of interest are in complete agreement with the orderings of Lehn, Munsch, and Millie[24] and Moffat.[25]

The geometric feature of concern in methylenimine is the prediction of a C–N double bond distance. Total energy of the molecule vs. the C–N double bond distance is shown in Figure 6. The minima of the curves are obtained at 2.422 and 2.425 bohrs for the ·NH₂-0.1 and ·NH₂-Max 2p_z fragments, respectively. The "experimental" value chosen for this bond was taken from the microwave structure of N-methylmethylenimine of Sastry and Curl[26] and equals 2.46 bohrs. The agreement in the two cases is excellent, with errors of 1.5 and 1.4%, respectively.

5. Diimide Molecule. The diimide molecule is of interest not only as a prototype molecule in this study but also in its own right. It is the simplest possible azo compound, a catalyst for selective hydrogenation of multiple bonds, and is isoelectronic to ethylene. In view of these considerations, a satisfactory electronic structure prediction for diimide is of particular importance.

The geometry chosen for diimide was idealized sp² hybridization at each nitrogen with an N–N double bond distance of 2.30 bohrs[27] and an N–H bond of 1.011 Å (1.91053195 bohrs).[28] Table VII shows the comparative orderings for the molecular orbital energy levels and the energy difference between the cis and the more stable trans forms of diimide. In both of the fragments and for both conformers, it is seen that the molecular orbitals which have major emphasis on the lone pair (4a₁, 3b₂ for cis-diimide and 3b_u, 4a_g for trans-diimide) are too high in energy relative to the other molecular orbitals. However, only in the cis conformer does this create a discrepancy in the order of the molecular orbitals.

In Figures 7 and 8 a plot of the total energy of the trans and cis conformers of diimide vs. N–N double bond distance is shown for each of the fragment

Figure 6. Total energy vs. C–N bond distance for CH₂NH.

descriptions. As far as the minima of the cis- and trans-diimide curves is concerned, there is no difference between the ·NH₂-0.1 and ·NH₂-Max 2p_z fragments. They both gave a cis N=N bond distance of 2.30 bohrs and a trans N=N bond distance of 2.29 bohrs. The absolute magnitude of the trans bond agrees well with an average value of 2.35 bohrs for the N=N double bond as reported by Steinmetz[29] (2.6% error), and the slight lengthening of the predicted cis N=N bond agrees well with chemical intuition and previous calculations.[30,31]

6. Pyridine Molecule. Being the single N-substituted analog to benzene, pyridine contains a more heterogeneous mixture of molecular orbital symmetries than the previous molecules. Therefore it is anticipated that it will be a better overall test of the ability of the two ·NH₂ fragments to predict electronic structures.

(24) J. M. Lehn, B. Munsch, and P. H. Millie, Theor. Chim. Acta, 16, 351 (1970).

(25) J. B. Moffat, Can. J. Chem., 48, 1820 (1970).

(26) K. V. L. N. Sastry and R. F. Curl, Jr., J. Chem. Phys., 41, 77 (1964).

(27) This value is the N–N distance which falls closest to the total energy minimum, although the molecular orbital energy ordering was not particularly sensitive to this parameter.

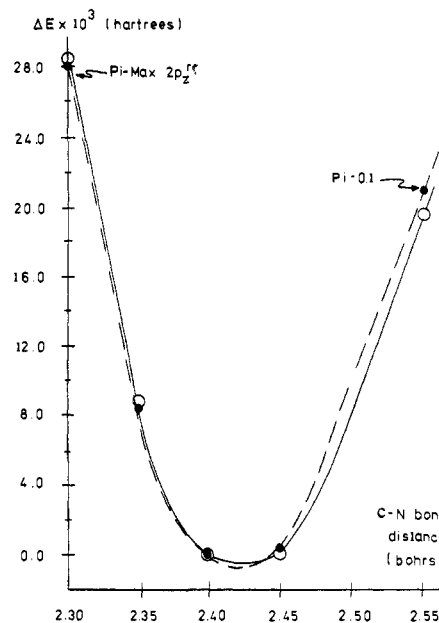(28) This is the value for an N–H bond as reported by Lide in ref 16.

(29) W. Steinmetz, J. Chem. Phys., 52, 2788 (1970).

(30) L. J. Schaad and H. B. Kinser, J. Phys. Chem., 73, 1901 (1969)

(31) D. P. Wong, W. H. Fink, and L. C. Allen, J. Chem. Phys., 52 6291 (1970).

Table VII. Molecular Orbital Energy[a] Ordering for Diimide (N_2H_2)

·NH₂-Max 2p_z fragment MO sym	-Energy	·NH₂-0.1 fragment MO sym	-Energy	Wong, Fink, and Allen[b] MO sym	-Energy	Schaad and Kinser[c] MO sym	-Energy	Lehn and Munsch[d]
				cis-Diimide				
1b₂	13.049	1b₂	13.035			1b₂	15.194	
1a₁	12.900	1a₁	12.886			1a₁	15.187	
2a₁	1.304	2a₁	1.296	2a₁	1.37	2a₁	1.303	
2b₂	0.827	2b₂	0.821	2b₂	0.94	2b₂	0.855	
3a₁	0.582	3a₁	0.576	3a₁	0.76	3a₁	0.665	
1b₁(π)	0.336	1b₁(π)	0.339	4a₁	0.56	4a₁	0.487	
4a₁	0.281	4a₁	0.275	1b₁(π)	0.52	1b₁(π)	0.452	
3b₂	0.156	3b₂	0.151	3b₂	0.40	3b₂	0.332	
1a₂(π*)	−0.419	1a₂(π*)	−0.414	1a₂(π*)	−0.12			
Total energy −93.55385		−93.56048		−109.92913		−106.5243		
E(cis) − E(trans), kcal/mol 4.43		4.52		0.65		5.26		10.50
				trans-Diimide				
1b_u	13.056	1b_u	13.042			1b_u	15.180	
1a_g	12.907	1a_g	12.894			1a_g	15.174	
2a_g	1.301	2a_g	1.293	2a_g	1.41	2a_g	1.300	
2b_u	0.836	2b_u	0.830	2b_u	0.93	2b_u	0.859	
3a_g	0.517	3a_g	0.510	3a_g	0.66	3a_g	0.589	
3b_u	0.386	3b_u	0.380	3b_u	0.65	3b_u	0.562	
1a_u(π)	0.337	1a_u(π)	0.341	1a_u(π)	0.53	1a_u(π)	0.448	
4a_g	0.104	4a_g	0.099	4a_g	0.40	4a_g	0.315	
1b_g(π*)	−0.418	1b_g(π*)	−0.413	1b_g(π*)	−0.15			
Total energy −93.56105		−93.56754		−109.93017		−106.5327		

[a] All energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I. [b] Reference 31. [c] Reference 30. [d] J. M. Lehn and B. Munsch, *Theor. Chim. Acta*, **12**, 91 (1968).
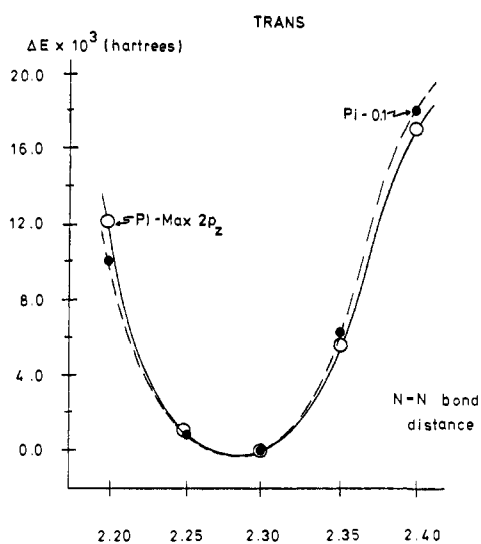
Figure 7. Total energy *vs.* N–N bond distance for N_2H_2 (trans).
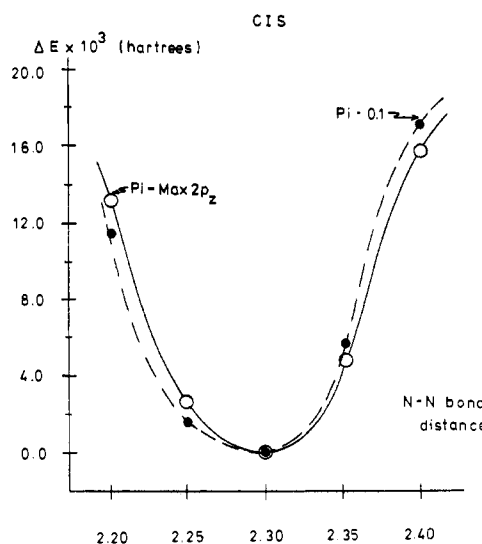
Figure 8. Total energy *vs.* N–N bond distance for N_2H_2 (cis).

The nuclear geometry used was derived from the microwave data of Bak, *et al.*,[32] except that the point group of the molecule was constrained to be C_{2v}.[33] The results of the calculations with the two ·NH₂ fragments appear in Table VIII, along with the corresponding molecular orbital energy orderings predicted by more extensive *ab initio* calculations.[34,35]

The differences between the ordering predicted by this method for both fragment choices and the best available calculation are remarkably small. With the exception of the ordering of the six lowest molecular orbitals, which is expected because the inner-shell description has not been emphasized, only the 11a₁ and 2b₁(π) are interchanged when compared to the calculation of Petke, *et al.*[35] It appears that the same deficiency noted for the electronic structure of diimide

(32) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958).

(33) The bond distances were transferred directly from Bak, *et al.*,[32] but the ring angles that were changed are NC₁C₂ = 123.86958599° and C₁C₂C₃ = 118.54708195° (see Figure 1 for atomic numbering scheme).

(34) E. Clementi, *J. Chem. Phys.*, **46**, 4731, 4737 (1967).

(35) J. D. Petke, J. L. Whitten, and J. A. Ryan, *ibid.*, **48**, 953 (1968).

Table VIII. Molecular Orbital Energy[a] Ordering for Pyridine

·NH₂-Max 2pₓ fragment		·NH₂-0.1 fragment		Clementi[b]		Petke, Whitten, and Ryan[c]	
MO sym	— Energy	MO sym	— Energy	MO sym	— Energy	MO sym	— Energy
$1a_1$	13.112	$1a_1$	13.088	$1a_1$	15.678	$1a_1$	15.639
$2a_1$	9.490	$1b_2$	9.430	$1b_2$	11.461	$1b_2$	11.407
$1b_2$	9.472	$2a_1$	9.427	$2a_1$	11.461	$2a_1$	11.407
$3a_1$	9.437	$2b_2$	9.307	$3a_1$	11.443	$3a_1$	11.388
$2b_2$	9.392	$3a_1$	9.284	$2b_2$	11.434	$2b_2$	11.380
$4a_1$	9.327	$4a_1$	9.228	$4a_1$	11.434	$4a_1$	11.380
$5a_1$	1.257	$5a_1$	1.238	$5a_1$	1.328	$5a_1$	1.295
$6a_1$	1.062	$6a_1$	1.053	$6a_1$	1.158	$6a_1$	1.128
$3b_2$	1.005	$3b_2$	0.983	$3b_2$	1.110	$3b_2$	1.075
$7a_1$	0.816	$7a_1$	0.795	$7a_1$	0.922	$7a_1$	0.891
$4b_2$	0.806	$4b_2$	0.788	$4b_2$	0.904	$4b_2$	0.884
$8a_1$	0.610	$8a_1$	0.595	$8a_1$	0.779	$8a_1$	0.760
$9a_1$	0.575	$9a_1$	0.566	$5b_2$	0.726	$9a_1$	0.694
$5b_2$	0.560	$5b_2$	0.543	$9a_1$	0.701	$5b_2$	0.691
$6b_2$	0.501	$6b_2$	0.485	$6b_2$	0.670	$6b_2$	0.648
$10a_1$	0.476	$10a_1$	0.453	$10a_1$	0.639	$10a_1$	0.619
$1b_1(\pi)$	0.437	$1b_1(\pi)$	0.436	$1b_1(\pi)$	0.622	$1b_1(\pi)$	0.582
$7b_2$	0.423	$7b_2$	0.406	$7b_2$	0.579	$7b_2$	0.556
$2b_1(\pi)$	0.267	$2b_1(\pi)$	0.267	$11a_1$	0.465	$11a_1$	0.443
$11a_1$	0.259	$11a_1$	0.243	$2b_1(\pi)$	0.459	$2b_1(\pi)$	0.426
$1a_2(\pi)$	0.232	$1a_2(\pi)$	0.233	$1a_2(\pi)$	0.447	$1a_2(\pi)$	0.406
$2a_2(\pi^*)$	−0.276	$2a_2(\pi^*)$	−0.278			$2a_2(\pi^*)$	−0.110
Total energy[a]	−210.88630		−210.47950		−245.62194		−246.32653

[a] All energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I. [b] Reference 34. [c] Reference 35.

Table IX. Molecular Orbital Energy[a] Ordering for Pyrazine

·NH₂-Max 2pₓ fragment		·NH₂-0.1 fragment		Clementi[b]		Petke, Whitten, and Ryan[c]	
MO sym	— Energy	MO sym	— Energy	MO sym	— Energy	MO sym	— Energy
$1b_{1u}$	13.169	$1b_{1u}$	13.149	$1b_{1u}$	15.695	$1b_{1u}$	15.685
$1a_g$	13.150	$1a_g$	13.130	$1a_g$	15.695	$1a_g$	15.685
$1b_{3g}$	9.525	$1b_{3g}$	9.502	$1b_{2u}$	11.476	$1b_{2u}$	11.443
$2b_{1u}$	9.521	$2b_{1u}$	9.497	$2a_g$	11.476	$2a_g$	11.443
$1b_{2u}$	9.439	$1b_{2u}$	9.415	$2b_{1u}$	11.475	$1b_{3g}$	11.442
$2a_g$	9.406	$2a_g$	9.383	$1b_{3g}$	11.475	$2b_{1u}$	11.442
$3a_g$	1.335	$3a_g$	1.320	$3a_g$	1.376	$3a_g$	1.371
$3b_{1u}$	1.260	$3b_{1u}$	1.244	$3b_{1u}$	1.273	$3b_{1u}$	1.279
$2b_{2u}$	1.056	$2b_{2u}$	1.041	$2b_{2u}$	1.133	$2b_{2u}$	1.122
$4a_g$	0.896	$4a_g$	0.881	$4a_g$	0.957	$4a_g$	0.957
$2b_{3g}$	0.860	$2b_{3g}$	0.846	$2b_{3g}$	0.931	$2b_{3g}$	0.932
$3b_{2u}$	0.629	$5a_g$	0.617	$5a_g$	0.780	$5a_g$	0.789
$5a_g$	0.629	$3b_{2u}$	0.612	$3b_{2u}$	0.755	$3b_{2u}$	0.746
$4b_{1u}$	0.619	$4b_{1u}$	0.608	$4b_{1u}$	0.723	$4b_{1u}$	0.739
$4b_{2u}$	0.532	$4b_{2u}$	0.519	$4b_{2u}$	0.684	$4b_{2u}$	0.686
$1b_{3u}(\pi)$	0.496	$1b_{3u}(\pi)$	0.497	$1b_{3u}(\pi)$	0.649	$1b_{3u}(\pi)$	0.634
$3b_{3g}$	0.466	$3b_{3g}$	0.453	$3b_{3g}$	0.611	$3b_{3g}$	0.602
$5b_{1u}$	0.353	$1b_{2g}(\pi)$	0.343	$5b_{1u}$	0.533	$5b_{1u}$	0.541
$1b_{2g}(\pi)$	0.342	$5b_{1u}$	0.341	$1b_{2g}(\pi)$	0.494	$1b_{2g}(\pi)$	0.482
$1b_{1g}(\pi)$	0.269	$1b_{1g}(\pi)$	0.272	$1b_{1g}(\pi)$	0.462	$6a_g$	0.447
$6a_g$	0.262	$6a_g$	0.250	$6a_g$	0.441	$1b_{1g}(\pi)$	0.440
$1a_u(\pi^*)$	−0.249	$1a_u(\pi^*)$	−0.248	$2b_{3u}(\pi^*)$		$2b_{3u}(\pi^*)$	−0.079
Total energy[a]	−224.42624		−224.45578		−261.55432		−262.25466

[a] All energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I. [b] Reference 34. [c] Reference 35.

can also be seen in the pyridine calculations. The orbital which has a strong contribution from the lone pair, i.e., the $11a_1$ orbital, is not low enough in energy relative to the other molecular orbitals.

7. Pyrazine Molecule. Substituting a second nitrogen at the fourth position in the benzene ring forms another species isoelectronic to benzene, i.e., pyrazine, thus also making it a suitable prototype molecule for investigation of electronic structure predictions. The molecular geometry was taken as that of Petke, et al.,[35] and corresponds to D_{2h} symmetry. Table IX summarizes the molecular orbital energy ordering for the ·NH₂–0.1 fragment and the ·NH₂–Max 2pₓ fragment and presents for comparison the results of Petke, et al.,[35] and Clementi.[34] Again there is little to differentiate the two fragments. However, two interchanges are noticed. The $3b_{2u}$ and $5a_g$ molecular orbitals, while essentially degenerate, are reversed in order for the

Table X. Molecular Orbital Energy[a] Ordering for Pyrrole

NH$_3$-Planar-Max 2p$_z$ fragment		NH$_3$-Planar-0.1 fragment		Clementi, et al.[b]		Mely and Pullman[c]	
MO sym	−Energy	MO sym	−Energy	MO sym	−Energy	MO sym	−Energy
1a$_1$	13.246	1a$_1$	13.210	1a$_1$	15.710	1a$_1$	15.80
1b$_2$	9.441	1b$_2$	9.415	1b$_2$	11.425	1b$_2$	11.41
2a$_1$	9.424	2a$_1$	9.397	2a$_1$	11.425	2a$_1$	11.41
2b$_2$	9.355	2b$_2$	9.330	3a$_1$	11.379	3a$_1$	11.36
3a$_1$	9.264	3a$_1$	9.240	2b$_2$	11.379	2b$_2$	11.36
4a$_1$	1.291	4a$_1$	1.270	4a$_1$	1.324	4a$_1$	1.346
5a$_1$	0.994	5a$_1$	0.976	5a$_1$	1.095	5a$_1$	1.106
3b$_2$	0.925	3b$_2$	0.908	3b$_2$	1.034	3b$_2$	1.032
6a$_1$	0.726	6a$_1$	0.711	6a$_1$	0.825	6a$_1$	0.830
4b$_2$	0.682	4b$_2$	0.666	4b$_2$	0.797	4b$_2$	0.796
7a$_1$	0.635	7a$_1$	0.621	7a$_1$	0.778	7a$_1$	0.786
8a$_1$	0.485	8a$_1$	0.469	8a$_1$	0.648	8a$_1$	0.647
5b$_2$	0.459	5b$_2$	0.443	1b$_1$(π)	0.631	5b$_2$	0.622
6b$_2$	0.435	6b$_2$	0.418	5b$_2$	0.624	1b$_1$(π)	0.605
1b$_1$(π)	0.418	1b$_1$(π)	0.418	6b$_2$	0.602	6b$_2$	0.596
9a$_1$	0.406	9a$_1$	0.390	9a$_1$	0.577	9a$_1$	0.568
2b$_1$(π)	0.181	2b$_1$(π)	0.182	2b$_1$(π)	0.425	2b$_1$(π)	0.394
1a$_2$(π)	0.146	1a$_2$(π)	0.147	1a$_2$(π)	0.388	1a$_2$(π)	0.280
3b$_1$(π^*)	−0.388	3b$_1$(π^*)	−0.390	3b$_1$(π^*)			
Total energy	−178.32628		−178.36467		−207.93135		

[a] All energies are reported in hartree atomic units; see Shull and Hall, footnote b, Table I. [b] Reference 38. [c] Reference 39.

·NH$_2$–Max 2p$_z$ fragment, but the result for the ·NH$_2$–0.1 fragment agrees with calculations of both Petke, et al., and Clementi. On the contrary, for the other difference, i.e., the 5b$_{1u}$ and 1b$_{2g}$(π) molecular orbitals, the result from the ·NH$_2$–Max 2p$_z$ fragment agrees with the more extensive ab initio calculations, while the ·NH$_2$–0.1 fragment result differs. It should also be noted that in one instance, i.e., for the 1b$_{1g}$(π) and 6a$_g$ molecular orbitals, both of the fragments give an ordering prediction which concurs with that of Clementi, while it disagrees with the order calculated from the energetically superior wave function of Petke, et al.

The ·NH$_2$–0.1 fragment calculation reflects the same incomplete description of the lone pair as noted for diimide and pyridine. The 5b$_{1u}$ and 6a$_g$ molecular orbitals have as their largest contributors the two nitrogen lone-pair FSGO and, as before, these molecular orbitals do not have as negative an energy as they should, relative to the other molecular orbital energies. The interpretation of the ·NH$_2$–Max 2p$_z$ fragment results is considerably less obvious. While the ordering of the highest energy lone-pair orbital, i.e., the 6a$_g$ orbital, is in agreement with the ·NH$_2$–0.1 prediction, both cases give this lone-pair orbital too high an energy relative to the other molecular orbitals. The other orbital which has significant lone-pair contribution, i.e., the 5b$_{1u}$ orbital, however, is predicted by the ·NH$_2$–Max 2p$_z$ fragment to be in the proper sequence. This lack of consistency in the lone-pair description of the ·NH$_2$–Max 2p$_z$ fragment will be discussed in greater detail later. These results on pyridine and pyrazine show the complexity of the nature of the fragment interactions as large molecules are formed and will be brought out in more detail in the Discussion.

8. Pyrrole Molecule. Pyrrole, the five-membered aromatic nitrogen heterocycle, is used to help distinguish which of the NH$_3$–Planar fragments is better. Not only is this fragment type needed to predict the electronic structure of pyrrole, but also it is anticipated

that a planar NH$_3$ fragment will be used when the N–Lone pair is expected to participate in π bonding, e.g., in amides.

The molecular geometry was obtained by fitting the microwave data of Bak, et al.,[36] to C_{2v} symmetry.[37] The molecular orbital energy orderings predicted by both the NH$_3$–Planar-0.1 and NH$_3$–Planar-Max 2p$_z$ fragments appear in Table X along with comparisons made to the ab initio results of Clementi, et al.,[38] and Mely and Pullman.[39]

Again there is essential agreement between the electronic structure predictions of the two fragments in question. The only difference that appears is that, while the 1b$_1$(π) molecular orbital was a significant amount higher in energy than the 6b$_2$ molecular orbital for the NH$_3$–Planar-Max 2p$_z$ results, the two orbitals are effectively degenerate for the NH$_3$–0.1 case. Thus, by making comparisons with more extensive ab initio calculations, the satisfactory predictive capabilities of the current procedure for electronic structure are again verified.

In order to bring the predicted molecular orbital energy order into exact conformity with that of Clementi, et al.,[38] it is necessary to perform two interchanges; first, the 1b$_1$(π) and 6b$_2$ orbital and then with the 5b$_2$ orbital. For the NH$_3$–Planar-0.1 results, only one interchange is actually required, since the 1b$_1$(π) and 6b$_2$ molecular orbitals are effectively degenerate. In comparison with the results of Mely and Pullman,[39] the NH$_3$–Planar-Max 2p$_z$ ordering has one discrepancy, while the NH$_3$–Planar-0.1 is essentially in accord, because of the very small energy differences between the 1b$_1$(π) and 6b$_2$ molecular orbitals in both calculations.

(36) B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, J. Chem. Phys., 24, 720 (1956).

(37) The structural parameters that differed from those of Bak, et al.,[36] were the C$_2$–C$_3$ bond distance of 1.42766373 Å and the C$_1$C$_2$C$_3$ bond angle of 107.76666641° (see Figure 1 for atomic numbering scheme).

(38) E. Clementi, H. Clementi, and D. R. Davis, J. Chem. Phys., 46, 4725 (1967).

(39) B. Mely and A. Pullman, Theor. Chim. Acta, 13, 278 (1969).

Discussion

These studies are concerned primarily with the application of a computational procedure that has already been established for hydrocarbons to a series of nitrogen-containing compounds. Therefore, the discussion will be focused primarily on how these studies compare to the similar ones for hydrocarbons.[2-8]

The first difference of interest between the hydrocarbon and nitrogen heteroatom studies concerns computational considerations. It has been found in the current studies that, for the usual initial guess for the charge and bond order matrix (the unit matrix), the direct substitution SCF procedure sometimes reached a *relative* minimum on the energy hypersurface. In particular, it was found that the converged result for both *cis-* and *trans-*diimide contained a highest occupied molecular orbital (HOMO) with a positive eigenvalue. Upon further examination, the HOMO was found to be an antibonding π molecular orbital, which means that four electrons were placed in π orbitals in the ground state, instead of the expected two electrons. This phenomenon has also been noticed in studies other than those reported here[40] and has been characterized by occupied molecular orbitals with positive eigenvalues, unexpectedly high total energies, and very slow convergence. One solution to this problem, *i.e.*, an improved initial guess, has already been reported[4] for hydrocarbons. Another alternative that was used for N_2H_2 is as follows. Once the SCF procedure has reached a point where it is obvious that an improper minimum will be reached, a matrix of the coefficients of all molecular orbitals, including the current virtual orbitals, can be obtained. The molecular orbitals may then be reordered so that the occupied orbitals correspond to those predicted by chemical intuition or, when available, other calculations. Another technique in which this comparison is regularly carried out is that of Hillier and Saunders.[41] In effect, by forcing the occupied orbitals to be of the expected symmetry, a more nearly correct charge and bond-order matrix is taken as the guess for the next set of iterations. There are, as yet, no examples using the current procedure that have failed to reach the proper convergence point while using this technique.

The next items of interest concern the ability of the specific fragments to describe the interfragment interactions in nitrogen-containing molecules. It appears that the NH_3-T_d-Free fragment supplies basis orbitals better suited for describing both C-N rotation barriers and CNC bond angles, than does the NH_3-T_d-Max $2p_z$ fragment. While both fragments overestimate the magnitude of the methylamine barrier height, only the NH_3-T_d-Free correctly predicts the decreasing trend from C_2H_6 to CH_3NH_2. The C-N-C bond angle, while still in reasonable agreement, was not as close to the value from experiment as was the corresponding value for hydrocarbons. While some of this error is due to the inherent deficiencies of a small basis set, a significant portion can probably be attributed to the nature of the bending mode assumed for the calculation. Having one less positively charged nucleus than pro-

pane, dimethylamine will have a central atom that is more easily distorted during this bend. Therefore, the assumption of fixed tetrahedral geometry during the bending motion is probably not as valid in the current cases. A similar observation has been noted for H_2O_2 by Stevens.[42] For the prediction of C-N single bond distances, the NH_3-T_d-Max $2p_z$ fragment gives a slightly better value. However, since both fragments give results within 5% of the experimental value, there is little to differentiate between them.

The final geometric tests for the amine-type fragments were considerations of the hydrazine molecule. Unfortunately, the N-N barrier also yields little information for determining which is the better NH_3-T_d fragment. For this case, neither of them adequately describes the interactions. As mentioned previously, it is anticipated that a split-inner-shell fragment, in which all parameters are optimized in the usual manner, will be flexible enough to predict properly this rotational curve. The NH_3-T_d-Free fragment furnishes the basis orbitals which more closely predict the N-N single bond distance, with 6.5% error as compared to 8.7% error when the NH_3-T_d-Max $2p_z$ fragment is employed. Since the N-N rotation barrier is not of general interest for large molecule calculations, it is expected the NH_3-T_d-Free fragment will describe the saturated nitrogen portions of most molecules adequately.

Investigation of the nitrogen fragments that anticipate a multiple bond, *i.e.*, the $\cdot NH_2$-Max $2p_z$ and $\cdot NH_2$-0.1 fragments, is also of interest. Even more than in the case for the NH_3-T_d fragments, the geometric considerations on the prototype molecules reveal little to distinguish between the fragments. For example, for both the C-N double bond and the N-N double bond distance predictions, the two sets of basis orbitals performed equally as well, *e.g.*, 1.5 and 1.4% error for CH_2NH, and 2.5 and 2.6% error for N_2H_2, respectively, for $\cdot NH_2$-Max $2p_z$ and $\cdot NH_2$-0.1 fragments.

After considering the electronic structure predictions of these two fragment choices, however, a judgment can be made. As mentioned previously, the most notable deficiency in both fragments for these calculations is that the molecular orbitals containing large contributions from the lone pairs on nitrogen are not low enough in energy relative to the other molecular orbitals. However, the $\cdot NH_2$-0.1 appears to be the better fragment choice for two reasons. First, this fragment has a consistent, but minor deficiency, *i.e.*, all of the molecules treated have the same type of previously mentioned molecular orbital ordering change. On the contrary, the $\cdot NH_2$-Max $2p_z$ fragment for pyrazine predicts the highest lone-pair molecular orbital, $6a_g$, to be too high in energy while correctly positioning the $5b_{1u}$ lone-pair orbital. Second, it has been determined[3,7] previously that the fragment of choice for the $\cdot CH_3$ fragment is one in which the π-type orbital is centered above and below the nuclear plane at 0.1 bohr. Thus, in order to maximize compatibility between fragments, the $\cdot NH_2$ fragment should have the π-type FSGO centered at the same distance from the N nucleus as used in $\cdot CH_3$. It is anticipated that future fragment studies employing both a nonminimum FSGO description of the inner-shell orbital and the use of the fragment N-H bond distance as an adjustable parameter

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will be able to find a flexible enough fragment description in order to predict correctly the last portion of the electronic structure, while preserving the accurate geometric structure predictions for nitrogen double bond containing molecules.

The final fragments studied, the NH_3–Planar fragments, have been evaluated only on the basis of the electronic structure predicted for pyrrole. The better fragment again appears to be a fragment with the π-type FSGO at 0.1 bohr, i.e., NH_3–Planar–0.1. Preliminary studies on simple amides also indicate that this choice of fragment parameters describes quite well the situation where nitrogen contributes its lone pair to an extended π system. However, further studies of the same nature as those mentioned for the NH_2 fragment are contemplated.

In summary, the studies presented here show that the predicted ordering of the chemically interesting molecular orbital energy levels for the nitrogen-containing molecules is in general in very good agreement with more extensive ab initio calculations. The one consistent difficulty that occurs with both types of N–π fragments, i.e., $\cdot NH_3$–Planar and $\cdot NH_2$, is that the molecular orbitals which are primarily lone pair in nature are too high in energy relative to the other molecular orbitals.

These studies further emphasize that, as noted in previous calculations,[2,3,6-8] even the very limited basis sets used in these studies are capable of producing results of a useful qualitative, and often quantitative, nature for several aspects of geometric and electronic structure. In particular, geometric predictions are also quite acceptable. Barriers to rotations are again generally too high. However, this method does appear to be capable of predicting barrier height trends, even as heteroatoms are introduced, with the possible exception of hydrazine. Bond distance predictions, including multiple bonds, average 4.5% from the experimentally accepted values, an improvement over the corresponding results for the hydrocarbons.[3]

Intermolecular Interactions in Nuclear Magnetic Resonance. VII. The Role of the Internal Reference in Aromatic Solvent Induced Shifts

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Abstract: It is shown, both experimentally and theoretically, that the ASIS (aromatic solvent induced shift) of any solute depends very strongly, both in sign and magnitude, on the chosen internal reference compound. It is pointed out that magnitude and sign of ASIS bears little, if any, relation to presumed specific interactions between solute and solvent. It is also found that additivity of ASIS occurs if two conditions are simultaneously fulfilled: if the ASIS of the parent hydrocarbon is zero and if the differential (between the two solvents) substituent medium effects are additive. Several alternative referencing schemes are discussed. A proposal is made for a modified ASIS which is only a function of interaction effects related to the solute, independent of the reference and independent of the solvent bulk susceptibility. The modified ASIS can be related to the common ASIS by means of conversion terms which have been determined for a number of internal references. The advantages of the modified ASIS for solvent effect studies, in particular specific solute–solvent interactions, are pointed out.

It is well known that proton chemical shifts depend not only on the intrinsic shielding properties of the solute molecule (X), but also on the medium (solvent) in which the solute resides. The most widely used solvent effect is known as "aromatic solvent induced shift" or ASIS for short. In this technique the solute is dissolved in two different solvents, usually deuteriochloroform and benzene, and its chemical shift(s) relative to an internal standard, usually TMS, is measured. The ASIS is then simply the difference between these two chemical shifts (eq 1). While progress on

$$ASIS = \Delta = \delta_X^{CDCl_3} - \delta_X^{C_6H_6} \qquad (1)$$

the quantitative and even qualitative understanding of the parameter Δ is slow,[1-5] the empirical use of the above technique has been rather explosive. Laszlo,[1] in reviewing the first three years of ASIS, gave already some 100 references, while at the present there appear approximately 400 papers a year[6] that make a more or less extensive use of ASIS, with applications mainly

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