sine base pair. This broadening is independent of temperature.[54] The interaction causing the polarizability is largely independent of temperature for short unsymmetric hydrogen bonds (Figure 9).

The proton dispersion interaction between neighboring hydrogen bonds, the induced dipole interaction with ions and dipoles of solvate molecules and, in addition, the coupling with intermolecular vibrations are responsible for the widening caused by the polarizability. The band widening caused by polarization corresponds to the band-widening effect which Bratož and Hadži[48] base on the anharmonicity. For, according to this paper, a high degree of anharmonicity always involves high polarizability.

The second band-widening mechanism discussed by these authors[48] is independent of the polarizability and corresponds to the coupling of the stretching vibrations with the bond vibration discussed in section IIE. Maréchal and Witkowski[49] calculated the profile of the wide band of the carboxylic acid dimers in the gaseous state and that of the imidazole in the solid state based on this mechanism.

Symmetric hydrogen bonds with a potential without a barrier should also exhibit a relatively large polarizability, even if this is considerably less than with the double-minimum potential wells. Such a potential well is present in the $(FH\cdots F)^-$ ion.[21,23,61] In this case, an extremely wide intensive band is indeed observed[62] which becomes very much sharper and loses intensity on investigating the $(FH\cdots F)^-$ ions well diluted in KCl. This suggests that the widening is based on the kinds of interaction caused by the polarizability of the hydrogen bond.

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Self-Consistent Field Studies of Glycine and Glycylglycine. The Simplest Example of a Peptide Bond[1a]

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Abstract: *Ab initio* SCF and limited CI treatments of the ground state and certain $\pi \rightarrow \pi^*$ excited states of glycine, $^+NH_3CH_2COO^-$, and glycylglycine, $^+NH_3CH_2CONHCH_2COO^-$, are reported for the two molecules in their equilibrium ground-state geometries. Orbital energies of glycine and glycylglycine are analyzed to elucidate the effect of the charged sites in the molecules, and it is found that certain of these effects can be reproduced by a simple point-charge model. Mulliken population analyses for the two molecules are performed and polarization parameters are obtained for localized orbitals which represent lone pairs, bonds and 1s orbitals in the two molecules. It was found that the description of the peptide bond corresponded to only very weak three-center π bonding and that the highest energy π orbital of the peptide region which is highly localized on the nitrogen is involved in the intense $\pi \rightarrow \pi^*$ absorption band.

In recent years it has become practicable to perform *ab initio* self-consistent-field (SCF) calculations on reasonably large molecules. Therefore, it is appropriate to apply this method, insofar as is possible at the present time, to problems of biological significance. In particular, a study of the peptide linkage is of considerable interest. Eventually it may be possible to extend such calculations to proteins by means of a model in which only a certain section of the protein is treated exactly, the rest of the molecule and other effects such as those due to the solvent and other nearby molecules and ions being represented approximately. In the present work a study is presented of glycine, $^+NH_3CH_2COO^-$, and the simplest dipeptide, glycylglycine, $^+NH_3CH_2CONHCH_2COO^-$, as isolated molecules in the gas phase. The zwitterion form of these molecules is considered since in aqueous solutions at biological pH's the molecules are believed to exist predominately in this form.[2] Although a theoretical treatment which ignores all effects except intramolecular electronic effects must be viewed with a great deal of caution as far as extrapolation to molecular systems in solution is concerned, it is still felt that the results obtained in the present work may be of value to the fundamental understanding of polypeptides. Of specific interest would be the following information: an analysis of the electron distribution in the peptide bond, the nature and energy of electronic transitions originating in the region of the peptide bond, the changes in gross electronic structure (if any) which take place upon formation of glycylglycine from glycine, the effect of the charged regions of the zwitterion upon the gross

(1) (a) Research supported by NSF Grant No. GP-18121; (b) Alfred P. Sloan Fellow.

(2) W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. II, Elsevier, New York, N. Y., 1958, pp 150–157.

electronic structure of the two molecules, and the extent of charge delocalization from the ionic regions.

In this work a basis set of grouped Gaussian functions is employed in an SCF treatment of glycine and glycylglycine to obtain their molecular wave functions. The orbital energies obtained in the SCF process are analyzed to isolate the effects due to a change from the atomic to molecular environment and the effect of the charged sites in the two molecules. The molecular wave functions are analyzed by means of a Mulliken population analysis. Total wave functions also are constructed based on a localized bond orbital formulation, and the results are used for a more chemical interpretation of bonding.

I. Calculations

In Figure 1 the labeling systems for the nuclei in glycine and glycylglycine are given, while the nuclear coordinates used were based on X-ray structural data given in ref 3. Hydrogen bond angles and distances were obtained from the refined X-ray data of Marsh,[3b] and the same bond angles and distances were assumed for glycylglycine. In both glycylglycine and glycine all atoms except the $-NH_3^+$ group and certain of the hydrogens lie in a plane; thus, the z axis for both molecules is chosen perpendicular to this plane with the x and y axes in the plane oriented as shown in Figure 1.

Molecular SCF wave functions were constructed by expansion of molecular orbitals in terms of a basis of grouped Gaussian lobe functions.[4] Basis function parameters for the s orbitals are the same as reported in ref 4 using a scale factor of $\eta = 1.414$ for each hydrogen; p-orbital expansions were reduced to four Gaussian components. The resulting atomic energies differ from Hartree–Fock values by 0.015, 0.024, and 0.045 au for C, N, and O, respectively.[5] The basis itself provides a fairly good approximation of atomic Hartree–Fock orbitals; however, at the molecular level, the small size of the basis set does not allow much flexibility in the expansion of molecular orbitals. Thus, the present level of treatment, while superior to a minimal Slater treatment, is far from molecular Hartree–Fock, and it follows that only the more prominent features of the calculated results clearly have physical significance.

In the present study, two methods are used to construct single-determinant molecular wave functions for the ground state of each molecule. The first method employs a hybrid bond orbital procedure described previously by Petke and Whitten.[6] For each bond, localized orbitals of the form $\phi = \varphi_A + \lambda\varphi_B$ were constructed, where φ_A is a hybrid on atom A pointing in the direction of atom B and λ is a bond polarity parameter related to the distribution of charge in the bond orbital ϕ. Inner-shell 1s orbitals on C, N, and O were taken as localized 1s atomic orbitals. The bond orbitals, lone-pair hybrid orbitals, and 1s orbitals were then orthogonalized and used to construct total molecular wave functions. The value of λ for each ϕ was determined by minimizing the total molecular energy.

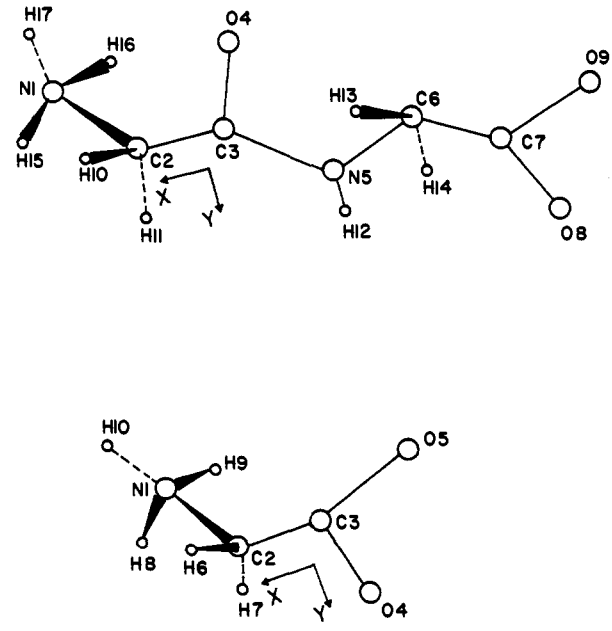

Figure 1. Glycine and glycylglycine showing the atomic labeling. Total electronic charges from a Mulliken population analysis (see text). Glycine: N1, 7.75; C2, 6.46; C3, 5.62; O4, 8.53; O5, 8.57; H6, 0.70; H7, 0.70; H8, 0.58; H9, 0.55; H10, 0.55. Glycylglycine: N1, 7.76; C2, 6.43; C3, 5.85; O4, 8.46; N5, 7.50; C6, 6.47; C7, 5.60; O8, 8.60; O9, 8.58; H10, 0.69; H11, 0.67; H12, 0.62; H13, 0.72; H14, 0.72; H15, 0.55; H16, 0.54; H17, 0.54.

All integrals over basis functions were evaluated accurately; thus, the variational theorem applies rigorously to the calculations. The second method for constructing wave functions utilized closed-shell SCF and CI techniques[7,8] to determine molecular orbital wave functions (Table I). Clearly, the optimum single-determinant wave functions for the present basis set are obtained by means of the latter procedure; however the hybrid bond orbital construction lends itself more readily to a qualitative chemical interpretation of the bonding.

II. Results and Discussion

(A) Total Energy. Table I gives the calculated total, orbital, and binding energies of glycine and glycylglycine. The binding energy values for glycine and glycylglycine are only on the order of one-third of the experimental thermodynamic binding energies estimated by taking the sum of the bond energies for each zwitterion assuming typical single- and double-bond energies.[9] Thus, the calculated binding energies of glycine and glycylglycine are unusually small compared with binding energies calculated for other molecules using a roughly equivalent basis set.[10] However, for the reaction involving the closed-shell species water and the zwitterions glycine (G) and glycylglycine (DG) in the gas phase

$$\Delta H + 2G = DG + H_2O$$

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(10) Compare, for example, the results obtained for pyridine and pyrazine, J. Petke, J. Whitten, and J. Ryan, *J. Chem. Phys.*, **48**, 953 (1968); also butadiene, R. Buenker and J. Whitten, *ibid.*, **49**, 5381 (1968).

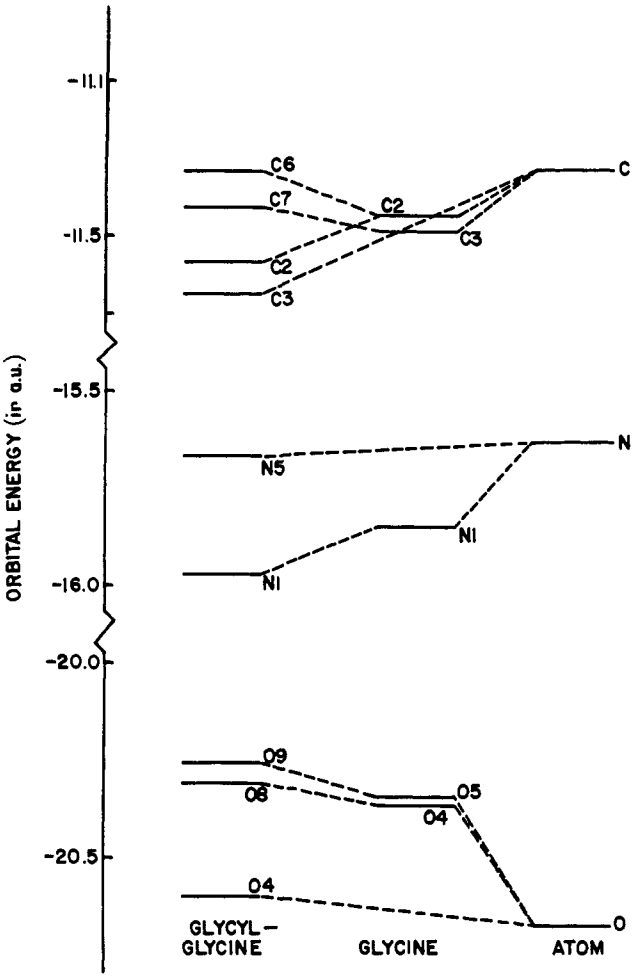

Figure 2. Correlation diagram for the 1s orbital energies of glycylglycine, glycine, and the corresponding atom.

a reasonable value for $\Delta H = +26$ kcal/mol is obtained from an equivalent basis set treatment of water. The binding energy deficiencies mainly are due to the limited basis set and an accumulation of correlation energy errors, and given this situation, it is, of course, necessary to assume that the deficiencies in the theoretical treatment are not excessively localized in any one specific region of the molecules. A secondary effect which contributes to the small calculated binding energies is likely the instability of the zwitterion form relative to the neutral form in an isolated molecule; thus, the zwitterion form probably owes its stability in solutions and in solids to interactions with the surrounding molecules.[11,12]

(B) Orbital Energies. Table I gives the orbital energies of glycine and glycylglycine together with a brief description of the individual molecular orbitals. In Figure 2 a comparison of the 1s orbital energies in the two molecules with atomic orbital energies is presented. It is interesting to note the significant differences in 1s orbital energies for like atoms which reflect differences in the valence-shell charge distribution.[13] The Mulliken population analysis (see Figure 1) indicates that each of the two oxygens in the $-COO^-$ group has gained about 0.5 electron, and this fact leads to the primary destabilization of oxygen 1s orbitals compared to the atomic case. On $-NH_3^+$, the nitrogen (N1) has gained about 0.8 electron according to the population analysis; however, each of the three hydrogens directly bonded to it has a net charge of about +0.5. The latter effect appears to dominate and the N1 1s orbital in both molecules is stabilized with respect to the atom.

The secondary effects are more interesting to consider, however, and these give rise to systematic energy differ-

Table I. Total and Orbital Energies of Glycine and Glycylglycine[a]

Glycine		Glycylglycine	
Orbital description[b]	Orbital energy	Orbital description[b]	Orbital energy
1s (O4)	−20.363	1s (O4)	−20.599
1s (O5)	−20.348	1s (O8)	−20.308
1s (N1)	−15.885	1s (O9)	−20.253
1s (C3)	−11.488	1s (N1)	−15.968
1s (C2)	−11.448	1s (N5)	−15.664
N-H	−1.500	1s (C3)	−11.649
C-O	−1.344	1s (C2)	−11.561
C-O	−1.221	1s (C7)	−11.422
σ	−1.123	1s (C6)	−11.334
N-H	−0.963	N1-H	−1.583
N-H	−0.946	σ	−1.543
σ	−0.807	σ	−1.335
σ	−0.751	C7-O	−1.300
σ	−0.736	σ	−1.213
n_4 (O4, O5)	−0.575	C7-O	−1.154
π_b	−0.523	N1-H	−1.054
n_3 (O4, O5)	−0.504	N1-H	−1.034
n_2 (O4, O5)	−0.358	σ	−1.029
n_1 (O4, O5)	−0.339	σ	−0.905
π_n	−0.289	σ	−0.877
Total energy (SCF)	−282.1205	σ	−0.854
Total energy (CI)	−282.1689	σ	−0.814
Binding energy,[c] kcal/mol	262	σ	−0.713
		n (O4)	−0.706
		σ	−0.676
		σ	−0.647
		$\pi_b + \sigma$ (peptide)	−0.642
		n (O4)	−0.530
		n (O8, O9)	−0.516
		π_n (peptide) + π_b COO^-	−0.475
		π_n (peptide)	−0.449
		n_3 (O8, O9)	−0.445
		n_2 (O8, O9)	−0.290
		n_1 (O8, O9)	−0.265
		π_n (COO^-)	−0.225
		Total energy (SCF)	−488.3172
		Total energy (CI)	−488.3500
		Binding energy,[c] kcal/mol	382

[a] Orbital and total energies are in atomic units; 1 au = 27.21 eV. [b] Because of the delocalized nature of the SCF MO's, this is an approximate description based on the relative magnitudes of atomic orbital coefficients. The notation σ designates a significantly delocalized σ orbital; n denotes a lone-pair orbital; π_b and π_n denote bonding and nonbonding π orbitals, respectively. In subsequent CI calculations, excitations were allowed from subscripted orbitals to the COO^- orbital of glycine and to the amide and COO^- orbitals of glycylglycine. [c] Molecular total energy (CI) − sum of atomic energies.

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ences between essentially equivalent orbitals in the two molecules. Thus, the N1 1s orbital in glycine is destabilized with respect to that in glycylglycine, while the 1s orbitals on C3, O4, and O5 of glycine are stabilized with respect to those on C7, O8, and O9 of glycylglycine. In Table II, similar effects are shown for other orbitals which can be taken as nearly equivalent in the two molecules. It should be noted that the variations which are referred to here are quite large and thus are not attributable to differences in accuracy of the basis set in the two systems; also, while it is expected that larger basis set treatments would yield different values for individual orbital energies,[14] it is highly unlikely that the trends noted here would be eliminated. Instead, since the orbitals under consideration are highly similar in shape in both glycine and glyclyglycine and are also well localized, then the differences in orbital energies can be attributed mainly to differences in proximity to the centers of positive and negative charge in the two molecules. Thus, consider a particular orbital φ_i which is localized in the $-COO^-$ group of glycine, with orbital energy

$$\epsilon_i(\mathrm{G}) = T_1 + T_2 \qquad (1)$$

where T_2 refers to all contributions to the orbital energy which originate from the $-NH_3^+$ group and T_1 combines all the other contributions. Since the orbital φ_i is localized in the $-COO^-$ group, the potential of the $-NH_3^+$ group can be expressed as some effective charge Z separated by the distance R from the center of charge of φ_i

$$\epsilon_i(\mathrm{G}) \cong T_1 + (Z/R) \qquad (2)$$

Similarly, referring to the corresponding localized orbital, φ_i, on glycylglycine

$$\epsilon_i(\mathrm{DG}) \cong T_1^* + (Z^*/R^*) \qquad (3)$$

Now, if it is assumed, insofar as the present analysis of orbital energies is concerned, that the addition of a neutral fragment to glycine to form glycylglycine serves only to lengthen the chain, then, to a first approximation, $T^*_1 = T_1$, $Z^* = Z$, and

$$\Delta\epsilon_i = \epsilon_i(\mathrm{G}) - \epsilon_i(\mathrm{DG}) \simeq (Z/R) - (Z/R^*) \qquad (4)$$

Simple arguments of this type lead immediately to a semiquantitative rationalization of the calculated variations in SCF orbital energies of orbitals localized on either the $-NH_3^+$ or $-COO^-$ group; Table II gives calculated variations based on the model for a choice of $Z = 0.7$ from the population analysis, assuming centers of positive and negative charge on N1 and midway between the oxygens of the $-COO^-$ group, respectively.[15]

The relatively large effects on orbital energies due to charged sites, and the simplicity of the interpretation, suggest the interesting possibility that experimental ionization potential studies could potentially be applied to study the proximity of charged sites to the electron distribution (localized) involved in the ionization, *i.e.*, to observe secondary shifts in ionization potentials in addition to shifts caused by valence-shell effects.

(C) Bond Orbital Analysis. As described in section I, total wave functions were also constructed in terms of localized bond orbitals $\phi = \varphi_A + \lambda_{AB}\varphi_B$, where φ_A and φ_B are hybrid orbitals on atoms A and B and λ_{AB} describes the polarization of the electron distribution in the bond. In Table III λ_{AB} values are reported, and here it is found that many of the values differ significantly from λ_{AB} values reported for smaller molecules.[6]

λ_{NH} in both glycine and glycylglycine is low compared to the value 0.62 found for ammonia, as is λ_{N1C2} compared to that found for HCN; thus the electrons in these bonds are unusually polarized toward N1. This is evidently the response of the system to the bonding of a proton to N1 to form the zwitterion. The effect of the charged sites diminishes as bonds further removed from the nitrogen are considered. Thus λ_{C2H} is about the same as that found for formaldehyde

Table II. A Comparison of Calculated Orbital Energy Differences of Glycine and Glycylglycine with Differences Estimated Using the Charged Site Model

Orbital description[a]	Δε(SCF)	Δε(model)[b]
N 1s	+0.084	+0.07
C 1s	−0.07	−0.09
O 1s (O9–O5)	−0.10	−0.08
O 1s (O8–O4)	−0.06	−0.04
N–H	+0.083	+0.07
N–H	+0.090	+0.07
N–H	+0.088	+0.07
C–O	−0.04	−0.07
C–O	−0.07	−0.07
O_n	−0.06	−0.07
O_n	−0.06	−0.07
O_n	−0.07	−0.07
O_n	−0.07	−0.07
π_b	−0.05	−0.07
π_n	−0.064	−0.07

[a] The orbitals under consideration are assumed to be the same in glycine and in glycylglycine and localized on either the COO^- or NH_3^+ group; n, π_b, and π_n denote lone-pair, bonding π and nonbonding π orbitals, respectively. [b] The center of orbital charge is taken at the nucleus for a 1s orbital and either at the center of positive charge or at the center of negative charge for the other localized orbitals.

Table III. Polarization Parameters for Glycine and Glycylglycine

Glycine		Glycylglycine			
ϕ[a]	λ_{AB}	ϕ	λ_{AB}	ϕ	λ_{AB}
N1–H	0.44	N1–H	0.44	C6–H	0.62
N1–C2	0.58	N1–C2	0.58	C6–C7	0.80
C2–H	0.57	C2–H	0.56	O–C7 σ	0.80
C2–C3	0.72	C2–C3	0.98	O4–C3 π	0.95
O–C3 σ	1.08	O4–C3 σ	0.76	O4–N5 π	2.0
O–C3 π	1.40	N5–C3 σ	0.86	N5–C3 π	0.16
		N5–H	0.50	O–C7 π	1.55
		N5–C6	0.66		

[a] Bond orbitals, $\phi = \varphi_A + \lambda_{AB}\varphi_B$, where λ_{AB} multiplies the hybrid orbital on the less electronegative atom.

(14) The relative ordering of orbital energies in the same molecule, while not the important question here, may be very sensitive to the basis set and to substituent effects; see C. Brundle, D. Turner, M. Robin, and H. Basch, *Chem. Phys. Lett.*, 3, 292 (1969).

(15) This choice is further motivated by noting that the dipole moments for glycine and glycylglycine calculated from the molecular wave functions are 12.17 and 24.75 D, respectively; those estimated by assuming a point change of 0.7 situated on N1 and on one of the oxygens of the $-COO^-$ group are 12.16 and 20.66 D, respectively. Buckingham has measured the dipole moment of glycine in water solutions to be 13.3 D: A. D. Buckingham, *Aust. J. Chem.*, 6, 323 (1953).

(0.58) and $\lambda_{C_2C_3} \simeq 1.0$ for glycylglycine, as expected of a completely covalent bond between identical centers. On the carboxylate end of the molecules the values of the polarity parameters suggest a general shift of σ charge out of the region of net negative charge. In fact, because of its participation in the three-center π bond the carbon atom of the $-COO^-$ group suffers a net loss of charge. The relatively large coefficients for λ_{OC_3} in glycine and λ_{OC_7} in glycylglycine as compared to the value of 0.66 in formaldehyde show the effect of the extra electron. Finally, it is interesting to note that in spite of the potentiality for different extents of delocalization of charge in glycine and glycylglycine, there is very close agreement of the population analyses for the $-NH_3^+$ groups and the $-COO^-$ groups in the two molecules.

(D) The Peptide Bond. The atoms involved in the peptide linkage $-C(=O)N(H)-$ are thought to be coplanar as a consequence of a delocalization of the C, O, and N π electrons,[16] to form a three-center π system. In fact, the occurrence of such coplanarity is often assumed to be of general importance in determining the secondary structure of proteins.[17] This interpretation is reinforced by the marked shortening of the C–N bond. In order to investigate specifically the extent of π-bond delocalization in the peptide region, two orthonormal π bonds were formulated as $\pi_b = \lambda_{OC}p_z(C) + \lambda_{NC}p_z(N) + p_z(O)$ and $\pi_n = p_z(O) - \lambda_{ON}p_z(N)$. After orthogonalization to all other orbitals in the molecule, the polarization parameters were determined by energy minimization (see Table IV). In Table IV, the π-orbital population analysis is compared with corresponding results obtained for two extremes in the representation of π bonds: a completely delocalized π system $\pi_b = p_z(C) + p_z(N) + p_z(O)$, $\pi_n = p_z(N) - p_z(O)$ and the localized description $\pi_b = p_z(C) + p_z(O)$, $\pi_n = p_z(N)$. The comparison clearly shows that the latter description corresponds much more closely to the optimum π-bond description obtained above and that therefore the effective double-bond character of the C–N bond is quite small relative to that of the C–O bond.[18] The low-lying singlet and triplet states of glycine and glycylglycine were investigated by elementary CI treatments involving the orbitals indicated in Table I; however, at this simple level of treatment, calculated transition energies were found to be several electron volts higher than experimental[19–22] and semiempirical[23] values for the amide chromophore. The only good agreement with experiment obtained was for the direction of the transition moment for the intense 1850-Å absorption which was found to lie 12° away from the NO axis toward the CO axis compared with 9.1° determined experimentally.[21] This provides some support for the interpretation of this band as being due to a $^1(\pi \rightarrow \pi^*)$ promotion from a π orbital highly localized on the amide nitrogen.

Table IV. Population of the Atomic p_z Orbitals of C3, O4, and O5 of Glycylglycine Found for the Three Models for the Peptide Bond Given in the Text

Model	p_z(C3)	p_z(O4)	p_z(N5)
Optimized[a]	1.168	1.006	1.820
Delocalized[b]	0.758	1.649	1.601
Localized[c]	0.996	1.107	1.905

[a] $\pi_b = \lambda_{OC}p_z(C) + \lambda_{NC}p_z(N) + p_z(O)$, $\pi_n = p_z(O) - \lambda_{ON}p_z(N)$; similar populations were obtained for those orbitals identified as π orbitals in the canonical SCF treatment. Optimized values: $\lambda_{OC} = 0.95$, $\lambda_{NC} = 0.16$, $\lambda_{ON} = 2.0$. [b] $\lambda_{OC} = \lambda_{NC} = \lambda_{ON} = 1.0$. [c] $\lambda_{OC} = 1.0$, $\lambda_{NC} = 0$, $\pi_n = p_z(N)$.

III. Conclusions

It was found that the electron distribution in both glycine and glycylglycine was strongly influenced by the regions of positive and negative charge in the zwitterions. This influence was evident not only in the orbital energy variations but also in the values for the polarization parameter found for bond orbitals in the near neighborhood of the charged regions; however, the net delocalization of charge from these regions was small (0.3 electron). This correlates well with the observation that the effect of the charged sites on the orbital energies of localized orbitals could be reproduced using a simple point charge model. The peptide bond in glycylglycine is probably not strongly affected by these charged centers, since it is nearly halfway between the two charged centers. Corroborating evidence for this assertion may be derived from the close agreement between the C, N, and O total charge obtained by our population analysis with those found by Basch, *et al.*,[19] and Christensen, *et al.*,[24] for formamide. The close agreement between the population analysis results for glycine, and comparable regions in glycylglycine indicate that no major redistribution of electronic charge takes place upon formation of the peptide bond. It was found that the π description of the peptide bond corresponded to only very weak three-center π bonding and that the highest energy π orbital of the peptide region which is highly localized on the nitrogen is involved in the intense $\pi \rightarrow \pi^*$ absorption band.

Acknowledgments. The support of this research by National Science Foundation, Grant No. GP 18121, is gratefully acknowledged. Services and computer time made available by the State University of New York at Stony Brook have been invaluable in this study.

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