

AB INITIO FORCE FIELDS OF ALANINE DIPEPTIDE IN FOUR NON-HYDROGEN BONDED CONFORMATIONS

T.C. CHEAM and S. KRIMM

Biophysics Research Division and Department of Physics, University of Michigan, Ann Arbor, MI 48109 (U.S.A.)

(Received 30 June 1989)

ABSTRACT

We have previously calculated the force fields and dipole-moment derivatives of the L-alanyl dipeptide, $\text{CH}_3\text{CONHCH}_2\text{CH}_2\text{CONHCH}_3$, in the C_5 , C_7^{eq} , and C_7^{ax} conformations with intramolecular $\text{NH}\cdots\text{OC}$ hydrogen bonding. We have now extended these studies with similar ones on four open, non-hydrogen-bonded conformers optimized by Scarsdale et al. — the β_2 , α_R , α_L and α' structures. The force constants were derived using the 4-21 Gaussian basis set and were scaled as before. The present results help to isolate the effects of conformation on the force fields and dipole derivatives, and also provide further insight into the effects of hydrogen bonding by comparison with the previous results. Additional effects can also be seen, such as those of the non-planarity of the peptide group, and the influence on the CO bond when the adjacent NH forms a hydrogen bond, and vice versa.

INTRODUCTION

In previous papers we have given the results of ab initio calculations of the force fields and dipole-moment derivatives of the glycine [1] and alanine [2] dipeptides, $\text{CH}_3\text{CONHCHRCONHCH}_3$ ($\text{R}=\text{H}, \text{CH}_3$), in the C_5 and C_7 conformations with intramolecular hydrogen bonding. These optimized conformations were obtained by Schäfer and co-workers [3, 4] using the 4-21 Gaussian basis set. These workers also derived several conformers of Gly and Ala dipeptides in which $\text{NH}\cdots\text{OC}$ hydrogen bonds are not present [3-6]. To see how the force fields vary with conformation alone, without additional complications from changes in hydrogen bonding, we performed calculations on four of these "open" conformers of Ala dipeptide denoted by Scarsdale et al. [4] as the β_2 , α_R , α_L , and α' structures. Besides helping to isolate the effects of conformation on the force constants and normal modes, one can also gain further insight into the effects of hydrogen bonding by comparison with earlier results on the C_5 , C_7^{eq} , and C_7^{ax} Ala dipeptide conformers. It is hoped that these force-field calculations on nine conformations of Gly and Ala dipeptides, together with the geometry optimization studies of Schäfer and co-workers, will provide

a large set of data for help in developing more reliable molecular mechanics energy functions for peptides and polypeptides [7].

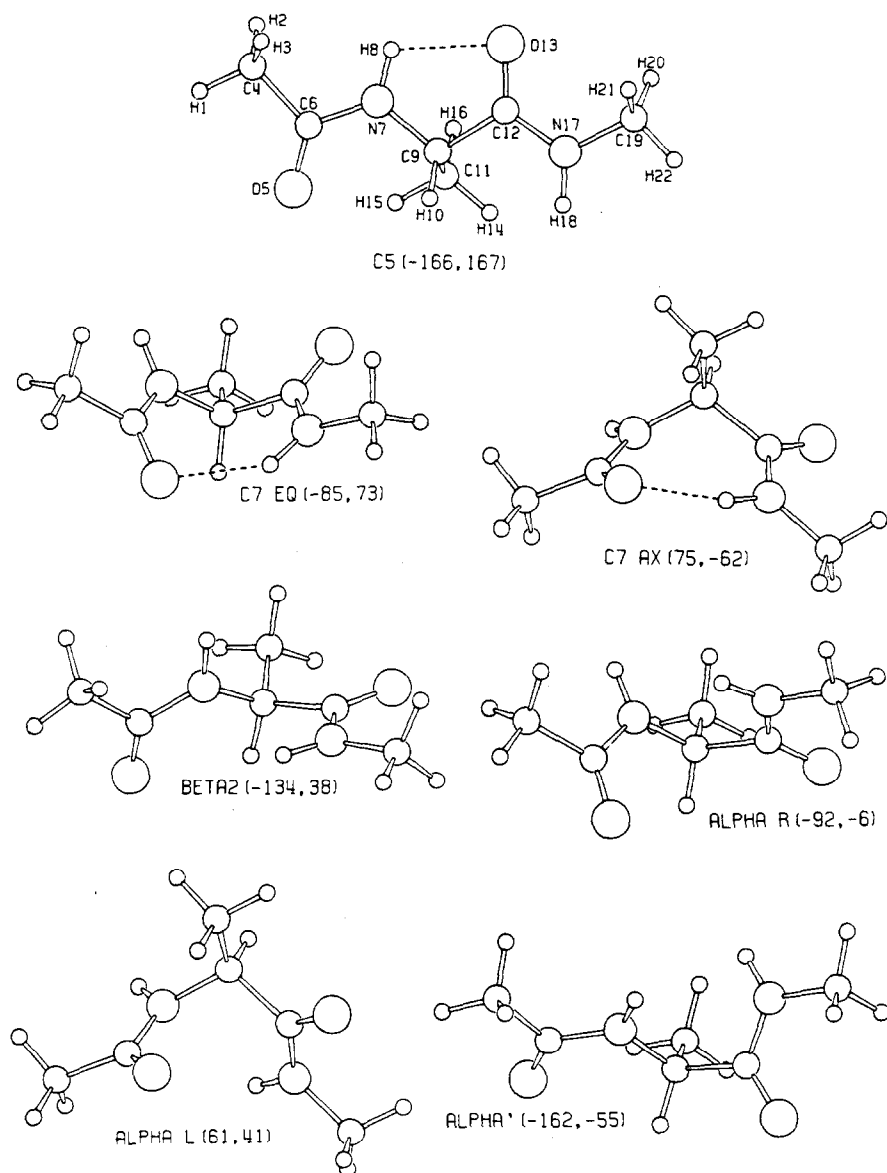


Fig. 1. Seven optimized conformations of Ala dipeptide, with the ϕ and ψ angles (in degrees) indicated.

TABLE 1

Internal coordinates and molecular dimensions

R	Atoms	β_2	α_R	α_L	α'
<i>Bond stretches (Å)</i>					
1	4-6	1.518	1.518	1.518	1.518
2	6-7	1.369	1.371	1.369	1.362
3	7-9	1.467	1.463	1.470	1.471
4	6-5	1.220	1.218	1.219	1.222
5	7-8	0.996	0.995	0.994	0.994
6	9-12	1.534	1.534	1.538	1.526
7	12-17	1.349	1.344	1.351	1.360
8	17-19	1.463	1.463	1.463	1.466
9	12-13	1.223	1.226	1.220	1.220
10	17-18	0.992	0.991	0.991	0.993
11	4-1	1.077	1.077	1.077	1.077
12	4-2	1.083	1.083	1.083	1.083
13	4-3	1.083	1.083	1.083	1.083
14	9-11	1.532	1.539	1.533	1.541
15	9-10	1.081	1.079	1.083	1.077
16	11-14	1.079	1.079	1.079	1.082
17	11-15	1.081	1.082	1.082	1.079
18	11-16	1.083	1.084	1.078	1.082
19	19-20	1.080	1.082	1.080	1.080
20	19-21	1.082	1.079	1.081	1.081
21	19-22	1.080	1.080	1.080	1.080
<i>Angle bends (°)</i>					
22	4-6-7	114.4	114.6	114.7	114.8
23	4-6-5	123.2	123.4	123.3	123.3
24	7-6-5	122.4	122.1	122.1	121.9
25	6-7-9	121.4	121.2	121.4	120.4
26	6-7-8	119.3	119.3	119.1	120.3
27	9-7-8	117.8	118.1	118.1	118.8
28	9-12-17	115.5	117.2	115.2	115.2
29	9-12-13	121.7	119.4	121.6	122.7
30	17-12-13	122.7	123.4	123.0	122.2
31	12-17-19	120.3	120.3	120.1	119.8
32	12-17-18	119.4	119.1	119.5	120.3
33	19-17-18	120.3	120.2	119.9	119.2
34	6-4-1	108.6	108.6	108.5	108.6
35	6-4-2	110.0	110.2	110.4	110.2
36	6-4-3	110.6	110.6	110.4	110.4
37	1-4-2	109.4	109.4	109.6	109.5
38	1-4-3	109.7	109.6	109.5	109.6
39	2-4-3	108.5	108.4	108.5	108.6
40	7-9-12	110.6	114.0	111.1	108.5
41	7-9-10	105.4	108.0	105.8	108.8
42	12-9-10	107.8	106.0	106.0	106.7
43	11-9-10	109.9	109.8	109.7	109.4

TABLE 1 (continued)

R	Atoms	β_2	α_R	α_L	α'
44	7-9-11	112.2	110.6	113.2	111.7
45	12-9-11	110.7	108.4	110.6	111.6
46	9-11-14	109.9	108.8	109.6	110.2
47	9-11-15	109.6	110.3	109.8	108.5
48	9-11-16	110.5	110.6	109.5	111.1
49	14-11-15	109.6	109.5	109.5	109.1
50	14-11-16	108.0	108.5	108.6	109.0
51	15-11-16	109.1	109.1	109.7	109.0
52	17-19-20	110.2	111.2	110.0	110.1
53	17-19-21	110.9	109.4	110.9	110.8
54	17-19-22	108.8	108.9	108.8	108.8
55	20-19-21	108.3	108.4	108.4	108.3
56	20-19-22	109.4	109.3	109.4	109.4
57	21-19-22	109.3	109.6	109.4	109.5
<i>Out-of-plane bends^a (°)</i>					
58	6-5	-0.4	-0.1	1.0	0.3
59	7-8	-12.6	-12.2	11.9	7.5
60	12-13	-1.9	1.9	-4.6	0.1
61	17-18	-0.4	6.4	-7.5	-8.8
<i>Torsions</i>					
62	4-6				
63	6-7				
64	7-9				
65	9-12				
66	12-17				
67	17-19				
68	9-11				

^aPositive: atoms C6, N17 move out of the C₅ plane in Fig. 1; N7, C12 move below the plane.

METHOD OF CALCULATION

The four open conformers of Ala dipeptide used in the calculations are shown in Fig. 1, where their ϕ (C6-N7-C9-C12) and ψ (N7-C9-C12-N17) dihedral angles are indicated. Also shown, for ease of comparison, are the C₅, C₇^{ga}, and C₇^{ax} conformers studied previously. The 4-21 SCF energies of the β_2 , α_R , α_L , and α' structures are, respectively, 3.9, 4.9, 6.7, and 7.9 kcal mol⁻¹ above that of the C₇^{ga}; the corresponding figures for C₅ and C₇^{ax} are 1.4 and 2.6 kcal mol⁻¹ [4]. It may be noted that the ϕ or ψ angles are similar in several pairs of conformers: ϕ in C₅ and α' , ϕ in C₇^{ga} and α_R , ϕ in C₇^{ax} and α_L , ψ in C₇^{ax} and α' , and ψ in β_2 and α_L . These relations can be useful in looking for regularities in the variations with ϕ , ψ or hydrogen bonding in the geometries, force constants and normal modes.

The primitive internal coordinates and equilibrium molecular dimensions are listed in Table 1. The quadratic force constants and dipole-moment derivatives were computed with the 4-21 basis set [8] as in Ref. 1, using two-sided displacements along group, or local symmetry, coordinates. These group coordinates for Ala dipeptide, constructed from the primitive internal coordinates, are as given in Ref. 2. Because of the sizeable deviations from planarity in several of the out-of-plane bends (Table 1), we have used the expressions for the **B** matrix elements appropriate for non-planar groups [9]. The force constants were scaled as in our previous papers, using the set of six scale factors derived for some amides by Fogarasi and Balázs [10], two of which we modified [1].

RESULTS AND DISCUSSION

The scaled diagonal and off-diagonal force constants in the group-coordinate basis are given in Tables 2 and 3 for all seven Ala dipeptide conformations; only off-diagonal terms of magnitude ≥ 0.05 in at least one of the conformations are shown. The harmonic frequencies, infrared intensities, and potential-energy distributions for the β_2 , α_R , α_L and α' structures computed with all $|F_{ij}| \geq 0.01$ are listed in Table 4.

The NH stretch2 (str2) force constant is very nearly the same in C_5 and all the open conformations, where N17H18 is free. This shows that the significant decreases in this term in C_7^{eq} and C_7^{ax} are due entirely to hydrogen bonding. The free NH str1 term in the C_7 and open conformations varies slightly; among the latter its value is lowest in α_R , where N7H8 is most nearly *cis* to $C^\alpha C^\beta$ (Fig. 1), indicating the effect of the side group [11–13]. The difference in $f(\text{NH str1})$ between C_7^{ax} and α_L , even though the NH and side chain are oriented similarly in both structures, may be a result of the hydrogen bonding; the somewhat higher $f(\text{NH str1})$ in C_7^{eq} compared with α_R is consistent with this relation, particularly when we recall that the hydrogen bond is strongest in C_7^{ax} [2]. Another likely reason for these differences between C_7 and α may be the higher degree of non-planarity at N7 in α_R and α_L (Table 1). That the free $f(\text{NH str1})$ is systematically lower than the free $f(\text{NH str2})$ may be due to the different substituents. This difference in the free NH stretch terms means that even open conformations of Ala dipeptide can exhibit two NH str frequencies, whose separation can be as much as 64 cm^{-1} (Table 4), thereby possibly complicating the identification of hydrogen-bonded structures in solution [11–13 and references therein]. However, our results indicate that although the C_5 conformer may indeed be difficult to distinguish from open conformers using the NH stretch bands, the C_7 conformers have bonded NH stretch frequencies well below 3400 cm^{-1} [2], whereas the free NH stretch frequencies in all conformations are above 3400 cm^{-1} . Moreover, the infrared intensities (Table 4) of both NH stretch modes in the open conformers are expected to be much

TABLE 2

Scaled diagonal force constants of Ala dipeptides^a

	C_5	C_7^{eq}	C_7^{x}	β_2	α_R	α_L	α'
NH str1	6.363	6.453	6.577	6.521	6.415	6.448	6.471
CO str1	11.040	10.652	10.550	11.400	11.542	11.486	11.300
CN str1	6.661	6.635	6.631	6.186	6.121	6.108	6.382
MC str	4.170	4.187	4.167	4.169	4.169	4.165	4.159
NC ^α str	5.168	4.856	4.922	4.799	4.857	4.832	4.847
NH str2	6.666	6.239	6.134	6.607	6.656	6.632	6.676
CO str2	10.922	11.026	10.965	11.221	11.044	11.385	11.479
CN str2	6.794	6.901	7.032	6.692	6.792	6.573	6.405
C ^α C str	4.259	4.126	4.039	4.166	4.078	4.135	4.139
NM str	5.206	5.289	5.282	5.235	5.260	5.272	5.218
MH1 str	4.971	4.982	4.991	4.981	4.984	4.980	4.982
MH2 str	4.796	4.804	4.785	4.781	4.778	4.787	4.781
MH3 str	4.797	4.789	4.805	4.794	4.791	4.779	4.790
C ^α C ^β str	4.088	4.373	4.131	4.283	4.246	4.289	4.105
C ^α H ^α str	4.801	4.918	4.941	4.904	4.926	4.755	4.965
CH16 str	4.822	4.872	5.042	4.780	4.731	4.992	4.779
CH14 str	4.778	4.865	4.812	4.940	4.945	4.932	4.799
CH15 str	4.946	4.804	4.782	4.814	4.801	4.772	4.938
MH22 str	4.875	4.857	4.860	4.848	4.830	4.831	4.856
MH20 str	4.820	4.799	4.756	4.821	4.744	4.822	4.833
MH21 str	4.820	4.751	4.796	4.768	4.875	4.782	4.797
MCN def	0.946	0.968	1.034	0.993	0.987	0.974	0.979
CO ib1	1.153	1.208	1.242	1.183	1.146	1.143	1.163
CNC ^α def	0.924	1.149	1.432	0.952	0.910	1.001	0.952
NH ib1	0.553	0.585	0.614	0.597	0.595	0.601	0.586
C ^α CN def	1.018	1.164	1.256	1.117	1.111	1.088	1.047
CO ib2	1.276	1.163	1.107	1.187	1.115	1.169	1.110
CNM def	0.794	0.814	0.826	0.799	0.814	0.805	0.814
NH ib2	0.585	0.656	0.659	0.573	0.564	0.575	0.583
M1 sb	0.549	0.551	0.551	0.550	0.549	0.549	0.549
M1 ab1	0.521	0.519	0.519	0.521	0.521	0.520	0.521
M1 ab2	0.522	0.521	0.522	0.523	0.522	0.523	0.523
M1 rock1	0.649	0.652	0.656	0.651	0.649	0.651	0.649
M1 rock2	0.605	0.607	0.606	0.607	0.606	0.602	0.604
NC ^α C def	1.020	1.043	1.882	0.991	1.029	1.152	1.124
H ^α b1	0.637	0.666	0.708	0.649	0.641	0.651	0.657
H ^α b2	0.697	0.736	0.744	0.691	0.703	0.723	0.708
C ^β b1	1.393	1.410	1.116	1.325	1.369	1.342	1.036
C ^β b2	1.109	1.134	0.956	1.127	1.065	1.129	1.012
C ^β sb	0.556	0.556	0.560	0.558	0.555	0.561	0.556
C ^β ab1	0.539	0.533	0.533	0.534	0.539	0.526	0.544
C ^β ab2	0.536	0.533	0.545	0.531	0.542	0.538	0.534
C ^β rock1	0.669	0.673	0.690	0.671	0.674	0.688	0.669
C ^β rock2	0.649	0.664	0.674	0.671	0.655	0.672	0.648

TABLE 2 (continued)

	C_5	C_7^{α}	$C_7^{\alpha x}$	β_2	α_R	α_L	α'
M2 sb	0.607	0.602	0.601	0.604	0.602	0.603	0.606
M2 ab1	0.544	0.548	0.548	0.547	0.546	0.547	0.545
M2 ab2	0.535	0.540	0.541	0.538	0.538	0.538	0.537
M2 rock1	0.783	0.781	0.780	0.782	0.781	0.781	0.782
M2 rock2	0.796	0.792	0.791	0.796	0.780	0.795	0.799
CO ob1	0.777	0.803	0.825	0.763	0.761	0.775	0.778
NH ob1	0.220	0.243	0.293	0.197	0.208	0.237	0.206
CO ob2	0.802	0.790	0.787	0.786	0.779	0.806	0.816
NH ob2	0.234	0.255	0.303	0.233	0.205	0.194	0.206
MC tor	0.060	0.058	0.062	0.064	0.065	0.065	0.063
CN tor1	0.446	0.546	0.561	0.404	0.419	0.462	0.435
NC $^{\alpha}$ tor	0.385	0.544	0.724	0.272	0.312	0.451	0.359
C $^{\alpha}$ C tor	0.320	0.397	0.552	0.294	0.344	0.422	0.357
CN tor2	0.374	0.498	0.522	0.417	0.416	0.388	0.404
NM tor	0.050	0.054	0.055	0.051	0.051	0.053	0.054
C $^{\alpha}$ C $^{\beta}$ tor	0.163	0.121	0.142	0.127	0.157	0.135	0.153

^aUnits: stretches, $\text{mdyn } \text{\AA}^{-1}$; bends and torsions, $\text{mdyn } \text{\AA} \text{ rad}^{-2}$. Group coordinates are defined in Ref. 2.

weaker than those of the bonded NH stretch modes in the C_5 and C_7 structures [2]. To conclude our discussion of the NH stretch force constants, we note that our results do not show clear evidence of an $\text{NH}\cdots\text{N}$ interaction that Scarsdale et al. [4] proposed to explain certain structural relations; the $\text{H18}\cdots\text{N7}$ distances are no shorter than 2.30 \AA (α_R), which would suggest a very weak interaction at best.

The CO str1 force constants in the open structures are relatively constant. The much reduced $f(\text{CO str1})$ values in C_7^{α} and $C_7^{\alpha x}$ are evidently due to the hydrogen bonding. That this term in C_5 is also significantly lowered (compare especially with α' where ϕ is nearly identical) suggests that the CO stretch force constant is affected when the adjacent NH forms a hydrogen bond, undoubtedly because of the electronic resonance in the peptide group. Also, the C6O5 bond is longer in C_5 (and the C6N7 bond shorter) than in the open structures, and an analysis of the Mulliken populations shows an increase in the partial charge on O5 in the C_5 conformer as compared with the open conformers. Furthermore, $f(\text{CO str2})$ is considerably lower in $C_7^{\alpha x}$ than in α' , where ψ is similar. These results point to the significance of cooperative electronic effects [14] in structures, in particular crystals, where both the CO and NH groups of a peptide unit participate in hydrogen bonds.

CO str2, being adjacent to C^{α} , exhibits more variability in the open structures; there is a distinct tendency for $f(\text{CO str2})$ to increase as ψ increases in magnitude (Fig. 2(a)). The ψ angles are larger in C_5 and C_7 , but the force constant may be lowered by the hydrogen bonding, either directly on CO str2

TABLE 3

Scaled off-diagonal group coordinate force constants of Ala dipeptides, $|F_{ij}| \geq 0.05^a$

Term	C_5	C_7^{sq}	C_7^{ax}	β_2	α_R	α_L	α'
1-3	-0.04	-0.05	-0.01	-0.05	-0.06	-0.06	-0.05
1-5	0.13	0.04	0.0	0.02	0.02	-0.01	0.01
1-7	-0.10	-0.01	0.0	0.0	0.03	0.05	0.02
1-8	0.05	0.0	0.0	0.0	-0.01	-0.02	-0.04
1-9	-0.06	0.0	-0.02	0.0	0.0	-0.02	0.0
1-22	0.0	-0.01	-0.05	-0.04	-0.03	-0.03	-0.03
1-24	-0.11	-0.09	-0.08	-0.10	-0.10	-0.09	-0.09
1-25	-0.11	0.02	0.04	0.01	0.02	0.03	0.02
2-3	1.37	1.36	1.30	1.34	1.31	1.28	1.33
2-4	0.36	0.36	0.38	0.37	0.37	0.38	0.37
2-5	-0.09	-0.09	-0.09	-0.11	-0.10	-0.10	-0.10
2-6	0.0	-0.14	-0.17	0.0	0.01	0.02	0.0
2-7	0.05	0.05	0.04	0.07	0.05	0.03	0.05
2-8	0.0	0.05	0.06	-0.03	-0.03	-0.03	-0.02
2-22	-0.55	-0.55	-0.49	-0.52	-0.52	-0.51	-0.53
2-23	-0.16	-0.14	-0.05	-0.10	-0.11	-0.09	-0.13
2-26	-0.02	0.08	0.07	0.0	-0.03	-0.03	0.0
2-27	0.05	0.05	0.06	0.0	0.02	0.02	0.0
2-35	0.03	-0.02	0.08	0.02	0.0	0.03	0.0
2-38	0.04	0.07	0.03	0.0	-0.02	-0.05	0.0
2-39	0.05	0.0	0.03	0.03	0.02	0.0	0.04
2-57	-0.02	0.04	-0.02	-0.05	-0.05	0.03	0.0
3-4	0.31	0.30	0.31	0.30	0.31	0.31	0.31
3-5	0.20	0.24	0.30	0.21	0.18	0.21	0.20
3-7	-0.01	-0.02	-0.02	-0.04	-0.06	-0.05	-0.04
3-8	-0.03	-0.09	-0.11	0.04	0.05	0.04	0.02
3-9	-0.03	0.04	0.07	-0.01	0.0	0.0	0.0
3-15	-0.04	-0.05	-0.02	-0.07	-0.06	-0.01	-0.03
3-22	0.19	0.16	0.17	0.15	0.18	0.19	0.17
3-23	-0.45	-0.50	-0.49	-0.51	-0.47	-0.46	-0.47
3-24	0.21	0.22	0.23	0.24	0.20	0.19	0.22
3-25	0.17	0.19	0.22	0.19	0.19	0.20	0.19
3-26	0.0	0.03	0.06	0.03	0.06	0.04	0.02
3-29	0.0	-0.05	-0.05	0.04	0.05	0.04	0.01
3-35	-0.02	-0.02	0.19	-0.04	0.01	0.0	0.0
3-37	-0.05	-0.05	0.03	-0.01	-0.03	0.02	-0.05
3-51	0.0	-0.07	0.06	0.14	0.12	-0.14	-0.07
3-55	0.01	-0.07	0.09	-0.01	0.03	-0.02	0.0
3-56	0.02	-0.06	0.06	-0.02	0.02	0.0	0.02
3-57	0.0	-0.03	0.02	0.02	0.0	0.05	0.0
4-22	0.21	0.21	0.21	0.20	0.21	0.20	0.21
4-23	0.25	0.25	0.26	0.26	0.25	0.25	0.25
4-30	-0.29	-0.30	-0.30	-0.30	-0.29	-0.29	-0.29
5-7	0.05	0.10	0.10	0.05	0.08	0.02	0.02
5-8	-0.03	0.07	0.05	0.09	0.12	0.12	0.09

TABLE 3 (continued)

Term	C_5	C_7^{eq}	C_7^{ax}	β_2	α_R	α_L	α'
5-9	0.17	0.32	0.38	0.18	0.21	0.21	0.15
5-14	0.25	0.16	0.25	0.21	0.16	0.24	0.24
5-15	0.11	0.08	0.03	0.05	0.07	0.05	0.09
5-22	0.02	-0.03	-0.08	0.02	0.03	0.0	0.02
5-23	0.06	0.0	-0.13	0.07	0.08	0.03	0.06
5-24	0.26	0.42	0.60	0.26	0.22	0.32	0.27
5-25	-0.18	-0.18	-0.20	-0.18	-0.18	-0.18	-0.20
5-26	0.11	0.11	0.20	-0.04	-0.05	-0.04	-0.05
5-27	-0.10	0.04	0.07	0.09	0.11	0.09	0.08
5-35	0.17	0.06	0.67	0.14	0.16	0.29	0.16
5-36	-0.16	-0.24	-0.09	-0.17	-0.15	-0.17	-0.16
5-37	0.31	0.31	0.29	0.30	0.31	0.29	0.31
5-38	0.21	0.46	0.32	0.23	0.24	0.23	0.19
5-39	0.38	0.30	0.35	0.32	0.31	0.35	0.36
5-43	-0.05	-0.04	0.0	-0.05	-0.04	-0.01	-0.06
5-44	0.07	0.07	0.06	0.08	0.06	0.07	0.06
5-51	0.0	-0.07	0.08	0.05	0.09	-0.08	-0.03
5-52	0.02	0.05	-0.01	0.05	0.0	0.0	-0.05
5-53	0.0	0.05	-0.06	0.02	0.0	0.0	-0.03
5-56	0.07	-0.19	0.16	0.0	-0.02	-0.06	0.07
5-57	0.04	0.17	-0.19	0.03	0.02	0.0	-0.02
5-58	0.0	0.09	-0.10	0.04	0.0	0.03	-0.05
6- 7	0.0	0.02	0.01	0.04	0.04	0.06	0.0
6-8	-0.01	0.05	0.07	0.0	0.01	0.0	-0.02
6-9	0.0	0.0	0.0	-0.05	-0.07	-0.04	-0.02
6-10	-0.07	-0.05	-0.03	-0.05	-0.05	-0.05	-0.08
6-26	-0.05	0.05	0.05	-0.07	-0.09	-0.06	-0.07
6-28	-0.09	-0.07	-0.06	-0.09	-0.09	-0.10	-0.08
6-29	0.04	0.11	0.12	0.07	0.07	0.06	0.03
6-38	0.0	0.0	0.0	-0.07	-0.09	-0.06	0.01
6-53	0.01	0.06	-0.04	0.0	-0.02	0.02	0.03
6-57	0.01	0.05	-0.04	-0.02	0.02	-0.04	-0.02
7- 8	1.31	1.30	1.28	1.32	1.34	1.32	1.30
7- 9	0.41	0.37	0.40	0.36	0.41	0.38	0.34
7-10	-0.08	-0.07	-0.07	-0.07	-0.07	-0.07	-0.06
7-25	-0.06	-0.01	0.0	0.0	0.0	-0.01	0.01
7-26	-0.54	-0.47	-0.47	-0.50	-0.49	-0.51	-0.50
7-27	-0.05	-0.09	-0.09	-0.11	-0.09	-0.11	-0.12
7-35	0.03	-0.02	0.12	0.02	0.06	-0.01	0.05
7-37	-0.04	-0.07	0.0	-0.05	-0.03	-0.04	0.0
7-38	0.03	0.10	0.08	0.10	0.11	0.08	0.03
7-39	-0.04	0.0	-0.08	0.0	-0.04	-0.01	-0.07
7-55	0.0	-0.05	0.05	-0.01	-0.01	0.01	0.0
7-56	0.0	-0.06	0.06	-0.04	0.0	-0.02	0.02

TABLE 3 (continued)

Term	C_5	C_7^{eq}	C_7^{ax}	β_2	α_R	α_L	α'
8-9	0.24	0.23	0.19	0.26	0.19	0.27	0.31
8-10	0.10	0.11	0.11	0.09	0.10	0.09	0.10
8-21	-0.05	-0.05	-0.05	-0.04	-0.05	-0.04	-0.05
8-22	0.0	0.04	0.06	0.0	0.0	0.0	0.0
8-23	0.0	0.05	0.08	0.0	0.0	-0.01	-0.02
8-24	0.03	-0.05	-0.09	0.03	0.02	0.04	0.0
8-26	0.18	0.14	0.08	0.14	0.09	0.15	0.20
8-27	-0.45	-0.42	-0.42	-0.44	-0.44	-0.44	-0.45
8-28	0.18	0.15	0.17	0.17	0.19	0.18	0.18
8-29	0.19	0.25	0.26	0.18	0.17	0.18	0.19
8-35	-0.02	0.05	-0.10	0.02	-0.01	0.04	0.05
8-36	0.0	0.0	-0.06	-0.02	-0.03	-0.01	-0.02
8-37	-0.04	0.0	-0.07	0.0	-0.02	-0.02	-0.05
8-38	-0.02	-0.04	-0.04	-0.02	-0.03	0.0	0.06
8-39	-0.05	-0.08	0.0	-0.06	-0.03	-0.05	-0.01
8-48	0.07	0.07	0.08	0.07	0.06	0.07	0.06
8-50	0.0	-0.06	0.07	-0.01	-0.01	0.02	0.0
8-52	0.03	0.0	-0.04	0.0	-0.04	0.07	0.04
8-53	0.01	0.08	-0.06	0.0	-0.09	0.08	0.09
8-55	0.0	0.10	-0.11	0.01	0.01	-0.02	-0.02
8-56	-0.01	0.13	-0.17	0.03	0.0	0.0	-0.06
8-57	-0.02	0.02	0.0	0.0	0.02	-0.05	-0.06
9-14	0.19	0.18	0.17	0.19	0.19	0.19	0.18
9-16	0.0	-0.06	0.0	-0.02	0.0	-0.02	-0.01
9-17	0.0	-0.02	0.0	-0.06	-0.05	-0.05	0.0
9-23	-0.02	-0.08	-0.13	0.0	0.0	0.01	0.0
9-24	0.0	0.18	0.29	0.0	-0.01	0.0	0.01
9-26	0.11	0.36	0.46	0.31	0.38	0.31	0.29
9-27	0.43	0.29	0.22	0.31	0.24	0.31	0.24
9-29	0.02	0.04	0.06	0.02	0.02	0.02	0.02
9-35	0.28	0.10	0.40	0.23	0.20	0.26	0.17
9-36	-0.10	-0.19	-0.05	-0.11	-0.12	-0.10	-0.13
9-37	-0.18	-0.19	-0.17	-0.17	-0.19	-0.16	-0.18
9-38	0.47	0.19	0.23	0.15	0.24	0.17	0.17
9-39	-0.20	-0.31	-0.18	-0.36	-0.26	-0.35	-0.17
9-50	0.0	0.06	-0.06	0.0	0.0	0.0	0.0
9-51	0.0	-0.10	0.13	-0.03	-0.05	0.04	0.0
9-52	0.0	-0.05	0.05	-0.07	0.0	-0.07	0.03
9-55	0.0	-0.11	0.12	0.0	0.0	0.0	0.0
9-56	-0.03	-0.24	0.27	-0.04	-0.02	-0.03	-0.02
9-57	-0.06	0.06	-0.05	0.0	-0.06	0.0	0.02
10-20	0.10	0.11	0.13	0.09	0.13	0.10	0.10
10-21	0.10	0.13	0.11	0.12	0.08	0.12	0.11
10-26	0.07	0.07	0.07	0.08	0.08	0.08	0.09
10-27	0.10	0.10	0.10	0.10	0.10	0.10	0.09
10-28	0.21	0.23	0.24	0.22	0.23	0.22	0.22
10-29	-0.18	-0.18	-0.19	-0.18	-0.18	-0.18	-0.18

TABLE 3 (continued)

Term	C_5	C_7^{ca}	C_7^{ca}	β_2	α_R	α_L	α'
10-45	-0.51	-0.50	-0.50	-0.50	-0.50	-0.50	-0.51
10-48	-0.05	-0.05	-0.04	-0.05	-0.05	-0.05	-0.05
11-22	0.06	0.06	0.06	0.06	0.06	0.06	0.06
11-23	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
11-31	-0.10	-0.10	-0.09	-0.10	-0.09	-0.09	-0.09
11-33	0.10	0.10	0.10	0.10	0.10	0.10	0.10
12-30	0.05	0.06	0.05	0.05	0.05	0.06	0.05
12-31	0.06	0.05	0.06	0.06	0.06	0.05	0.06
12-32	0.10	0.09	0.10	0.10	0.10	0.10	0.10
12-33	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
12-34	0.09	0.09	0.09	0.09	0.09	0.09	0.09
13-30	0.06	0.05	0.06	0.06	0.06	0.05	0.05
13-31	0.06	0.06	0.05	0.05	0.06	0.05	0.05
13-32	-0.09	-0.10	-0.10	-0.09	-0.10	-0.10	-0.10
13-33	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
13-34	-0.09	-0.09	-0.09	-0.09	-0.09	-0.09	-0.09
14-24	0.02	0.04	0.06	0.01	0.04	0.04	0.01
14-26	0.02	0.08	0.02	0.07	0.04	0.06	0.02
14-35	0.10	0.15	0.16	0.13	0.15	0.16	0.14
14-36	0.23	0.20	0.22	0.21	0.22	0.21	0.22
14-38	-0.25	-0.26	-0.24	-0.26	-0.29	-0.28	-0.23
14-39	-0.07	-0.07	-0.02	-0.11	-0.07	-0.11	-0.05
14-40	-0.33	-0.33	-0.35	-0.33	-0.33	-0.34	-0.33
15-23	0.01	0.03	0.01	0.05	0.04	0.0	0.02
15-24	-0.05	-0.07	0.0	-0.09	-0.07	0.02	-0.04
15-26	-0.04	-0.05	0.07	-0.02	0.02	-0.02	-0.05
15-27	0.02	0.02	-0.06	0.0	-0.03	0.02	-0.05
15-35	-0.12	-0.12	-0.11	-0.14	-0.12	-0.15	-0.11
16-24	0.0	0.0	-0.09	0.0	0.0	-0.05	0.0
16-35	-0.04	-0.06	-0.12	-0.04	-0.03	-0.09	-0.08
16-38	0.01	0.02	0.05	0.0	0.0	0.03	0.02
16-40	0.06	0.06	0.06	0.07	0.06	0.05	0.08
16-41	-0.11	-0.11	-0.09	-0.12	-0.12	-0.10	-0.12
16-43	0.08	0.09	0.06	0.09	0.10	0.08	0.07
16-56	0.0	0.0	0.08	0.0	0.0	0.05	0.0
17-39	0.08	0.05	0.04	0.10	0.08	0.10	0.05
17-40	0.07	0.06	0.05	0.05	0.05	0.06	0.06
17-41	0.06	0.05	0.05	0.05	0.05	0.05	0.05
17-42	0.10	0.10	0.10	0.09	0.08	0.09	0.10
17-43	-0.04	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
17-44	0.07	0.08	0.09	0.08	0.08	0.07	0.09
18-39	-0.07	-0.05	-0.04	-0.05	-0.05	-0.05	-0.07
18-40	0.05	0.06	0.07	0.06	0.06	0.06	0.05
18-41	0.05	0.05	0.05	0.05	0.05	0.06	0.05
18-42	-0.08	-0.09	-0.10	-0.09	-0.10	-0.10	-0.08
18-44	-0.07	-0.08	-0.07	-0.08	-0.08	-0.08	-0.07

TABLE 3 (continued)

Term	C_5	C_7^{eq}	C_7^{ax}	β_2	α_R	α_L	α'
19-45	0.06	0.06	0.06	0.06	0.06	0.06	0.06
19-46	-0.12	-0.12	-0.12	-0.12	-0.12	-0.12	-0.12
19-48	0.08	0.08	0.08	0.08	0.08	0.08	0.08
20-45	0.06	0.06	0.06	0.06	0.06	0.06	0.06
20-46	0.06	0.06	0.07	0.06	0.06	0.07	0.06
20-47	0.10	0.10	0.10	0.09	0.10	0.10	0.10
20-49	0.05	0.05	0.05	0.05	0.05	0.05	0.05
21-28	-0.04	-0.03	-0.04	-0.03	-0.05	-0.03	-0.03
21-45	0.06	0.06	0.06	0.06	0.05	0.06	0.06
21-46	0.06	0.07	0.06	0.06	0.06	0.06	0.06
21-47	-0.10	-0.10	-0.10	-0.10	-0.09	-0.10	-0.10
21-49	-0.05	-0.05	-0.05	-0.05	-0.06	-0.05	-0.05
22-23	0.16	0.19	0.20	0.17	0.15	0.15	0.17
22-24	0.04	-0.02	-0.09	0.0	0.03	0.03	0.02
22-26	0.02	-0.03	-0.06	0.0	0.0	0.0	0.0
22-33	0.12	0.12	0.11	0.12	0.12	0.12	0.12
22-35	0.01	0.05	-0.19	0.03	0.03	-0.06	0.03
22-38	0.02	-0.06	-0.02	0.02	0.0	0.0	0.04
23-24	-0.04	-0.16	-0.29	-0.08	-0.04	-0.06	-0.07
23-25	-0.05	-0.05	-0.05	-0.05	-0.06	-0.06	-0.05
23-26	0.01	-0.09	-0.14	0.0	0.0	0.0	-0.01
23-33	-0.09	-0.08	-0.08	-0.08	-0.08	-0.08	-0.08
23-35	0.01	0.08	-0.36	0.04	0.03	-0.10	0.03
23-36	0.0	0.04	-0.05	0.0	0.0	0.0	0.0
23-38	0.02	-0.15	-0.08	0.02	0.0	0.0	0.04
23-51	-0.02	0.06	-0.07	0.0	0.0	0.01	-0.01
23-55	-0.02	0.06	-0.05	0.0	-0.02	0.03	-0.02
23-56	-0.04	0.13	-0.13	0.03	-0.01	0.02	-0.05
23-57	0.0	-0.05	0.06	-0.01	-0.01	0.01	0.0
24-26	0.04	0.20	0.35	-0.02	0.0	0.0	-0.02
24-28	-0.01	-0.03	-0.05	0.0	0.0	0.0	0.02
24-35	-0.02	-0.12	0.78	-0.03	-0.02	0.20	-0.04
24-36	0.02	-0.10	0.10	-0.02	0.0	-0.03	0.02
24-38	-0.05	0.33	0.21	0.0	0.0	0.0	-0.05
24-39	0.09	0.04	0.08	0.02	0.03	0.06	0.09
24-43	0.0	0.0	0.06	0.0	0.0	0.04	0.0
24-51	0.03	-0.11	0.12	0.04	0.05	-0.08	0.0
24-52	0.02	-0.06	0.08	0.04	0.03	-0.07	-0.05
24-53	0.0	0.07	-0.10	0.0	0.0	0.0	0.02
24-55	0.03	-0.06	0.04	-0.02	0.0	-0.03	0.04
24-56	0.07	-0.22	0.21	-0.05	0.04	-0.07	0.07
24-57	0.03	0.24	-0.31	0.07	0.09	-0.10	0.02
24-58	0.02	0.08	-0.11	0.04	0.02	-0.02	0.0
26-27	0.02	0.04	0.06	0.06	0.09	0.07	0.13
26-29	-0.01	0.05	0.07	-0.02	-0.03	-0.03	-0.02
26-35	0.0	-0.04	0.40	0.04	0.09	0.02	0.07
26-36	0.04	-0.08	0.04	-0.03	-0.03	-0.03	-0.05
26-37	0.0	0.0	-0.06	0.02	-0.06	0.03	-0.08

TABLE 3 (continued)

Term	C_5	C_7^{eq}	C_7^{ax}	β_2	α_R	α_L	α'
26-38	0.0	0.23	0.21	0.15	0.20	0.12	0.0
26-39	-0.06	-0.02	-0.03	-0.03	0.0	-0.04	0.0
26-50	0.0	0.07	-0.09	0.0	0.0	0.0	-0.01
26-51	0.0	-0.11	0.15	-0.04	-0.07	0.04	0.02
26-55	-0.01	-0.10	0.12	0.01	0.03	-0.03	0.01
26-56	-0.02	-0.26	0.34	-0.05	-0.02	-0.02	0.02
26-57	-0.01	0.05	-0.09	0.07	-0.05	0.10	-0.02
27-28	0.04	0.05	0.05	0.04	0.04	0.04	0.03
27-29	-0.06	-0.06	-0.06	-0.06	-0.07	-0.06	-0.06
27-35	0.09	0.06	0.0	0.05	0.03	0.06	0.04
27-38	0.16	-0.05	0.02	-0.01	0.03	0.0	0.05
27-39	-0.02	-0.07	-0.04	-0.09	-0.05	-0.08	-0.04
27-56	0.0	0.06	-0.06	0.02	0.01	-0.01	-0.04
28-29	-0.02	-0.07	-0.08	-0.02	-0.02	-0.02	-0.02
28-35	0.03	0.04	-0.12	0.0	-0.04	0.0	-0.05
28-38	0.05	-0.07	-0.05	-0.06	-0.08	-0.07	-0.01
28-56	0.01	0.06	-0.07	0.02	0.0	0.02	-0.03
29-35	0.0	0.0	0.07	0.0	0.0	0.0	0.02
34-50	0.08	0.08	0.08	0.08	0.08	0.08	0.08
35-36	0.03	0.07	0.18	0.04	0.06	0.02	0.03
35-37	-0.06	-0.05	-0.04	-0.08	-0.08	-0.09	-0.05
35-38	0.27	-0.19	0.31	0.03	0.15	0.02	0.10
35-39	0.06	-0.06	0.04	-0.04	0.02	0.0	-0.01
35-43	-0.08	-0.06	-0.02	-0.08	-0.07	-0.05	-0.06
35-50	0.0	-0.03	-0.08	-0.01	-0.01	0.0	0.0
35-51	0.03	0.01	0.19	0.0	-0.05	-0.03	0.05
35-52	-0.03	0.05	0.08	0.01	0.03	-0.03	0.0
35-53	-0.02	-0.02	-0.05	0.02	0.0	0.0	-0.02
35-55	0.0	0.07	0.11	0.01	0.04	-0.02	0.0
35-56	0.0	0.15	0.38	0.03	0.06	-0.04	-0.04
35-57	-0.08	-0.04	-0.21	-0.02	-0.07	-0.02	-0.04
35-58	0.0	-0.05	-0.05	-0.04	-0.01	-0.01	0.0
36-38	-0.03	-0.14	0.11	-0.04	0.0	-0.02	0.0
36-43	0.07	0.07	0.06	0.07	0.07	0.07	0.06
36-51	0.04	0.04	0.06	0.02	0.0	0.0	0.05
36-55	0.0	0.05	0.08	-0.02	0.02	0.04	0.0
36-56	0.05	0.14	0.18	0.02	0.06	0.07	0.04
36-57	-0.05	-0.06	-0.09	-0.05	-0.04	-0.05	-0.05
37-55	0.03	0.05	0.07	0.02	0.0	0.04	0.03
37-56	0.11	0.06	0.12	0.05	0.02	0.10	0.11
37-57	0.05	0.09	0.09	0.06	0.09	0.10	0.07
37-58	0.0	0.05	0.05	0.02	0.02	0.02	0.02
38-39	-0.06	0.03	-0.14	0.05	0.0	0.03	-0.09
38-43	0.06	0.04	0.02	0.05	0.05	0.03	0.05
38-44	-0.02	-0.04	-0.03	-0.05	-0.03	-0.05	-0.02
38-50	-0.01	0.06	-0.08	-0.02	-0.02	0.0	0.0
38-51	-0.05	-0.20	0.22	-0.08	-0.12	0.13	-0.05

TABLE 3 (continued)

Term	C_5	C_7^{sq}	C_7^{ax}	β_2	α_R	α_L	α'
38-52	-0.01	-0.03	0.02	-0.05	0.03	-0.08	0.0
38-55	0.0	-0.08	0.10	0.04	0.06	-0.03	0.0
38-56	-0.05	-0.36	0.34	-0.06	-0.02	0.03	-0.05
38-57	0.02	0.17	-0.17	0.12	0.02	0.10	-0.08
39-44	0.10	0.11	0.12	0.10	0.12	0.09	0.13
39-50	0.0	0.04	0.05	0.03	0.02	0.02	0.0
39-51	0.07	0.0	-0.08	0.02	0.01	-0.07	0.05
39-55	0.0	-0.05	-0.10	-0.03	-0.02	-0.04	0.01
39-56	0.01	-0.07	-0.16	-0.04	-0.04	-0.10	0.02
39-57	0.02	-0.08	-0.12	-0.02	-0.04	-0.06	-0.11
39-58	0.01	-0.04	-0.06	0.0	-0.02	-0.02	-0.02
49-59	0.05	0.05	0.05	0.05	0.05	0.05	0.06
50-51	-0.05	-0.08	-0.13	-0.05	-0.05	-0.07	-0.06
50-55	-0.08	-0.14	-0.15	-0.06	-0.07	-0.10	-0.09
50-56	-0.10	-0.18	-0.24	-0.08	-0.08	-0.12	-0.12
50-57	0.0	-0.05	-0.07	-0.01	-0.02	-0.04	0.0
51-55	-0.08	-0.02	0.05	-0.07	-0.07	-0.04	-0.07
51-56	0.0	0.16	0.25	0.02	0.05	0.14	0.08
51-57	-0.10	-0.02	-0.02	-0.05	0.03	0.09	-0.08
52-53	-0.07	-0.07	-0.09	-0.07	-0.05	-0.05	-0.07
52-55	0.02	-0.06	-0.05	-0.05	-0.05	-0.04	0.0
52-56	0.10	0.02	0.02	-0.08	-0.11	-0.13	-0.07
52-57	-0.01	-0.08	-0.10	0.0	0.08	-0.04	-0.09
53-55	0.02	0.08	0.09	0.04	0.01	0.0	0.02
53-56	-0.02	0.07	0.09	0.07	0.06	0.04	0.04
53-57	0.06	0.15	0.19	0.07	0.06	0.06	0.07
53-58	-0.09	0.0	0.0	-0.07	-0.06	-0.05	-0.08
55-56	0.13	0.29	0.39	0.10	0.13	0.20	0.14
55-57	0.09	0.08	0.09	0.07	0.04	0.03	0.09
56-57	0.10	0.05	0.06	0.07	0.15	0.17	0.09
56-58	0.04	0.06	0.06	-0.03	-0.01	0.01	0.0
57-58	0.03	0.17	0.24	0.07	0.11	0.08	0.09

^aUnits: energy in mdyn Å, stretching coordinates in Å, bending coordinates in radians. Group coordinates are defined in ref. 2.

(C_5) or indirectly through the adjacent NH (C_7). There also seems to be an inverse relationship between the CO stretch and CN stretch force constants of each peptide unit; this is demonstrated in Fig. 2(b) and can be attributed to the electronic resonance in the peptide group. The points for $f(\text{CO str1})$ versus $f(\text{CN str1})$ in C_7^{sq} and C_7^{ax} are exceptional probably because of the strong hydrogen bonds; that is, the CO bond is expected to be more affected than the CN bond by hydrogen bonding.

The changes in $f(\text{CO str1})$ and $f(\text{CO str2})$ also seem to be related to the planarity of the peptide groups. Figure 2(c) shows a tendency for these terms

TABLE 4

Normal modes of Ala dipeptides using scaled force constants

ν (cm^{-1})	I^a (km mol^{-1})	Potential-energy distribution > 10%
β_2		
3455	39	NH str2(98)
3431	40	NH str1(98)
3023	2	MH1 str(86)
3010	3	CH14 str(83), CH15 str(14)
2996	3	C $^{\alpha}$ H $^{\alpha}$ str(61), CH16 str(19), CH15 str(17)
2993	8	MH22 str(65), MH20 str(31)
2971	11	MH21 str(49), MH20 str(38)
2968	3	MH3 str(51), MH2 str(50)
2966	25	C $^{\alpha}$ H $^{\alpha}$ str(36), CH15 str(29), CH16 str(26)
2904	1	MH2 str(43), MH3 str(39), MH1 str(14)
2902	15	CH16 str(45), CH15 str(35), CH14 str(15)
2900	33	MH21 str(43), MH20 str(28), MH22 str(27)
1719	211	CO str1(78)
1694	252	CO str2(81)
1550	382	NH ib2(53), CN str2(27)
1532	306	NH ib1(61), CN str1(18)
1478	2	M2 ab1(92)
1466	6	C $^{\beta}$ ab2(85)
1456	14	C $^{\beta}$ ab1(89)
1455	6	M2 ab2(95)
1447	12	M1 ab2(93)
1435	26	M1 ab1(91)
1412	2	M2 sb(103)
1379	9	C $^{\beta}$ sb(104)
1371	32	M1 sb(101)
1321	32	H $^{\alpha}$ b1(30), C $^{\alpha}$ C str(23), H $^{\alpha}$ b2(17), CN str2(11)
1301	27	H $^{\alpha}$ b1(41), H $^{\alpha}$ b2(38)
1265	169	CN str1(28), CN str2(12), CO ib1(12)
1252	108	H $^{\alpha}$ b2(27), CN str2(16), CN str1(14)
1170	1	M2 rock1(58)
1146	75	NC $^{\alpha}$ str(41), C $^{\beta}$ rock2(20)
1135	1	M2 rock2(88)
1126	7	C $^{\alpha}$ C $^{\beta}$ str(37), C $^{\beta}$ rock1(13)
1089	9	C $^{\beta}$ rock1(24), NM str(11)
1064	15	M1 rock2(70), CO ob1(15)
1043	8	NM str(25), C $^{\beta}$ rock2(22), M1 rock1(19)
1001	12	M1 rock1(34), C $^{\alpha}$ C $^{\beta}$ str(17), NM str(16)
943	7	MC str(32)
897	1	C $^{\beta}$ rock1(18), NC $^{\alpha}$ str(14), CN str1(12), CNC $^{\alpha}$ def(11)
849	7	C $^{\alpha}$ C str(16), CN str2(11), M2 rock1(11)
764	32	CO ob2(42), CO ib2(13)
672	164	NH ob2(42), NH ob1(35), CN tor2(20), CN tor1(17), NC $^{\alpha}$ tor(13)
657	1	CO ob2(21), CNC $^{\alpha}$ def(14), MC str(14), CO ib2(12), CO ib1(11)

TABLE 4 (continued)

ν (cm ⁻¹)	I^a (km mol ⁻¹)	Potential-energy distribution > 10%
628	16	CO ob1(74), M1 rock2(19)
571	81	CO ib1(30), CN tor2(14), NH ob2(11)
558	113	NH ob2(48), NH ob1(38), CN tor1(23), CN tor2(21), NC ^{α} tor(14), CO ib1(13)
480	25	C ^{β} b1(26), C ^{α} CN def(22), CN tor1(11)
427	7	NC ^{α} C def(38), MCN def(33), C ^{β} b2(16)
355	15	CO ib2(21), MCN def(17), CNM def(15)
340	6	C ^{β} b2(38)
292	5	CNM def(30), C ^{β} b1(13)
261	0	C ^{α} C ^{β} tor(88)
215	6	CNC ^{α} def(29), CN tor2(23), NH ob2(12), MCN def(11)
196	2	C ^{α} CN def(33), CNM def(17), C ^{β} b2(12)
180	0	MC tor(100)
167	4	NM tor(32), CNC ^{α} def(20), NC ^{α} C def(18), CN tor2(12)
150	1	NM tor(96), NH ob2(16)
108	9	CN tor1(41), NC ^{α} tor(14), C ^{β} b1(11)
94	6	C ^{α} C tor(123), CN tor2(16)
81	6	NC ^{α} tor(85), NH ob1(15), C ^{α} C tor(10)
α_R		
3467	33	NH str2(99)
3403	15	NH str1(99)
3024	2	MH1 str(86)
3014	1	CH14 str(75), C ^{α} H ^{α} str(12)
2998	1	MH21 str(35), C ^{α} H ^{α} str(32), MH22 str(21)
2998	7	C ^{α} H ^{α} str(38), MH21 str(28), MH22 str(18)
2970	14	MH20 str(49), MH22 str(34), MH21 str(19)
2968	1	MH3 str(50), MH2 str(48)
2960	18	CH15 str(46), CH16 str(31), C ^{α} H ^{α} str(18)
2903	0	MH2 str(45), MH3 str(40), MH1 str(14)
2899	35	MH20 str(51), MH22 str(29), MH21 str(19)
2893	12	CH16 str(56), CH15 str(30), CH14 str(13)
1726	236	CO str1(84)
1679	236	CO str2(84)
1552	368	NH ib2(57), CN str2(33)
1526	320	NH ib1(74), CN str1(20)
1477	3	M2 ab1(91)
1465	1	C ^{β} ab2(90)
1461	18	C ^{β} ab1(93)
1455	10	M2 ab2(94)
1445	11	M1 ab2(93)
1435	24	M1 ab1(91)
1406	3	M2 sb(105)
1371	27	M1 sb(89), C ^{β} sb(12)
1371	15	C ^{β} sb(92), M1 sb(12)
1322	6	H ^{α} b2(89)

TABLE 4 (continued)

ν (cm ⁻¹)	I^a (km mol ⁻¹)	Potential-energy distribution > 10%
1292	88	CN str2(29), C ^{α} C str(22), NH ib2(22), CO ib2(12)
1277	119	H ^{α} b1(44), CN str1(19), CO ib1(10)
1253	99	H ^{α} b1(33), CN str1(24), NH ib1(11)
1166	7	M2 rock1(62)
1162	49	NC ^{α} str(35), C ^{β} rock2(19)
1125	6	M2 rock2(86)
1108	7	C ^{β} rock1(31), C ^{α} C ^{β} str(30)
1097	12	NM str(36), C ^{α} C str(11)
1063	13	M1 rock2(71), CO ob1(15)
1041	10	C ^{β} rock2(28), M1 rock1(23), NM str(17)
996	10	M1 rock(30), C ^{α} C ^{β} str(12), NM str(11)
931	4	MC str(30), C ^{α} C ^{β} str(24)
899	2	CN str1(17), C ^{β} rock1(15), C ^{β} rock2(15), CNC ^{α} def(13), NC ^{α} str(10)
844	8	C ^{α} C str(16), CN str2(12), CO ib2(12), CNM def(12), M2 rock1(12)
758	22	CO ob2(56)
657	152	NH ob2(28), NH ob1(24), CN tor2(11)
651	21	CO ob1(42), M1 rock2(12), CN tor2(12)
637	58	CO ib1(19), MC str(17), NH ob1(16)
592	6	CO ob1(34), CN tor2(11)
547	82	NH ob1(61), CN tor1(47), NH ob2(36), NC ^{α} tor(28), CN tor2(18)
516	37	CO ib1(22), MCN def(20), CO ib2(12), C ^{α} CN def(10)
393	13	NC ^{α} C def(27), C ^{β} b1(25)
353	14	MCN def(33), CO ib2(23)
333	8	CNM def(19), C ^{β} b1(12), C ^{β} b2(12), C ^{α} C ^{β} tor(12)
298	7	C ^{α} C ^{β} tor(50), CNM def(16)
276	4	C ^{β} b2(36), C ^{α} C ^{β} tor(33)
219	6	C ^{α} CN def(27), CNM def(16)
203	1	C ^{α} CN def(14), C ^{α} C tor(13), CN tor2(12), NH ob2(11)
183	0	MC tor(100)
165	2	CNC ^{α} def(30), NC ^{α} C def(21), NM tor(14)
151	0	NM tor(101)
110	6	CN tor1(46)
88	4	C ^{α} C tor(63), CN tor2(24), CO ob2(10)
78	6	NC ^{α} tor(137), C ^{α} C tor(115), CO ob2(14)
α_L		
3461	16	NH str2(98)
3413	12	NH str1(98)
3030	1	CH16 str(75), CH14 str(19)
3023	2	MH1 str(85)
3001	3	CH14 str(63), CH15 str(30)
2990	8	MH22 str(62), MH20 str(34)
2973	15	MH21 str(57), MH20 str(38)
2967	4	MH2 str(52), MH3 str(49)

TABLE 4 (continued)

ν (cm ⁻¹)	I^a (km mol ⁻¹)	Potential-energy distribution > 10%
2936	6	C ^{α} H ^{α} str(95)
2911	22	CH15 str(67), CH14 str(18), CH16 str(13)
2902	1	MH3 str(44), MH2 str(41), MH1 str(14)
2900	34	MH21 str(39), MH22 str(32), MH20 str(28)
1724	252	CO str1(79)
1703	181	CO str2(83)
1545	318	NH ib2(61), CN str2(28)
1536	250	NH ib1(68), CN str1(19)
1478	2	M2 ab1(92)
1476	12	C ^{β} ab2(89)
1455	5	M2 ab2(94)
1451	14	C ^{β} ab1(90)
1446	11	M1 ab2(93)
1434	24	M1 ab1(91)
1409	2	M2 sb(104)
1374	16	C ^{β} sb(104)
1371	31	M1 sb(101)
1314	52	H ^{α} b2(62), C ^{α} C str(12), NC ^{α} str(11)
1311	29	H ^{α} b1(57), C ^{α} C str(12)
1265	183	CN str1(39), CO ib1(17), MC str(14), NH ib1(13)
1247	81	CN str2(26), H ^{α} b2(22), H ^{α} b1(13), NM str(11)
1171	2	M2 rock1(55)
1145	29	NC ^{α} str(27), C ^{β} rock2(27)
1138	4	C ^{α} C ^{β} str(30), C ^{β} rock1(19)
1135	3	M2 rock2(84)
1077	5	NM str(20), C ^{β} rock1(20), H ^{α} b1(12), C ^{α} C str(10)
1063	19	M1 rock2(68), CO ob1(15)
1047	5	C ^{β} rock2(30), M1 rock1(18), NM str(17)
997	18	M1 rock1(31), NM str(18), C ^{α} C ^{β} str(17), MC str(11)
924	4	MC str(20), C ^{α} C ^{β} str(17), C ^{β} rock1(12), C ^{β} rock2(11)
891	1	CN str1(19), CNC ^{α} def(17)
827	13	CO ib2(14), CNM def(12), M2 rock1(12), C ^{α} C str(11)
772	34	CO ob2(53), NC ^{α} C def(15)
659	8	MC str(23), CO ib1(19), CO ib2(10), C ^{β} b2(10)
642	27	CO ob1(66), M1 rock2(19)
585	106	CN tor2(44), NH ob2(40)
573	45	NH ob2(40), CN tor2(13), C ^{α} C str(12), NH ob1(12), CO ob2(10)
546	170	NH ob1(113), CN tor1(67), NC ^{α} tor(65)
487	15	C ^{β} b1(30), C ^{α} CN def(21)
457	27	CO ib1(40), NC ^{α} C def(26)
349	12	CNM def(17), C ^{β} b1(15), C ^{β} b2(15), MCN def(14)
338	11	C ^{β} b2(29), NC ^{α} C def(13), CO ib2(12), MCN def(12)
301	9	MCN def(32), CNM def(25), C ^{β} b2(14), C ^{β} b1(12)
268	1	C ^{α} C ^{β} tor(93)
205	0	CNC ^{α} def(23), CN tor2(17), C ^{α} C tor(16), NH ob2(14), C ^{α} CN def(11)

TABLE 4 (continued)

ν (cm ⁻¹)	I^a (km mol ⁻¹)	Potential-energy distribution > 10%
199	2	C ^{α} CN def(34), CNM def(21)
186	1	MC tor(89)
177	3	NC ^{α} tor(22), CNC ^{α} def(20), NM tor(17), MC tor(16)
154	1	NM tor(105), NH ob2(13)
113	11	CN tor1(36), NC ^{α} tor(18)
107	4	C ^{α} C tor(116), NC ^{α} tor(36), CN tor2(12)
88	2	NC ^{α} tor(42), CN tor1(14)
α'		
3474	49	NH str2(99)
3418	24	NH str1(100)
3024	2	MH1 str(85)
3019	1	C ^{α} H ^{α} str(51), CH15 str(34), CH16 str(12)
3004	3	CH15 str(49), C ^{α} H ^{α} str(32), CH14 str(18)
2996	6	MH22 str(65), MH20 str(26)
2977	14	MH21 str(53), MH20 str(45)
2969	3	MH3 str(31), MH2 str(30), CH14 str(19), CH16 str(18)
2967	7	CH14 str(25), CH16 str(24), MH3 str(22), MH2 str(19), C ^{α} H ^{α} str(11)
2905	30	MH21 str(40), MH22 str(30), MH20 str(29)
2902	1	MH2 str(44), MH3 str(40), MH1 str(14)
2900	13	CH16 str(46), CH14 str(37), CH15 str(15)
1720	247	CO str2(83)
1710	207	CO str1(82)
1540	277	NH ib2(65), CN str2(25)
1529	421	NH ib1(68), CN str1(22)
1477	2	M2 ab1(91)
1470	18	C ^{β} ab1(90)
1454	8	C ^{β} ab2(87)
1454	7	M2 ab2(92)
1446	11	M1 ab2(94)
1435	29	M1 ab1(91)
1412	0	M2 sb(104)
1374	9	C ^{β} sb(100)
1371	29	M1 sb(99)
1326	9	H ^{α} b1(55), H ^{α} b2(28)
1295	158	C ^{α} C str(28), CN str2(27), NH ib2(12), CO ib2(11)
1291	51	CN str1(21), H ^{α} b2(18), H ^{α} b1(16)
1260	96	H ^{α} b2(37), CN str1(19), NH ib1(12)
1169	4	M2 rock1(58), NM str(11)
1137	21	NC ^{α} str(32), M2 rock2(28)
1136	8	M2 rock2(61), NC ^{α} str(15)
1110	16	NM str(42)
1099	8	C ^{α} C ^{β} str(35), C ^{β} rock1(31)
1063	17	M1 rock2(71), CO ob1(15)
1018	2	M1 rock1(39), C ^{β} rock2(20)
979	27	C ^{β} rock2(23), M1 rock1(16), NM str(14)

TABLE 4 (continued)

ν (cm ⁻¹)	I^a (km mol ⁻¹)	Potential-energy distribution > 10%
947	8	MC str(33), CNC ^{α} def(10)
899	4	C ^{α} C ^{β} str(21), C ^{β} rock1(16), NC ^{α} str(15)
840	6	CN str2(17), M2 rock1(13), CNM def(12), C ^{α} C str(12), CO ib2(11)
765	39	CO ob2(71)
681	8	CO ib2(19), MC str(17)
640	30	CO ob1(63), M1 rock2(17)
605	98	NH ob2(47), NH ob1(45), CN tor2(29), CN tor1(21), NC ^{α} tor(16), CO ob1(11)
594	10	CO ib1(30), NC ^{α} C def(17), C ^{α} CN def(11)
524	31	CO ib1(20), NC ^{α} C def(17), CO ib2(16), MCN def(11)
504	163	NH ob1(71), NH ob2(55), CN tor1(53), NC ^{α} tor(43), CN tor2(38)
375	21	MCN def(48), C ^{β} b1(13), CO ib1(11)
366	11	C ^{β} b2(24), CO ib2(22), C ^{β} b1(13), NC ^{α} C def(11)
305	8	CNM def(41), C ^{β} b2(27)
287	0	C ^{α} C ^{β} tor(99)
264	5	C ^{β} b1(17), C ^{β} b2(17), NH ob2(15), CN tor2(11)
218	7	CNC ^{α} def(35), C ^{α} CN def(26), MCN def(13), CNM def(13)
191	2	CN tor2(17), MC tor(10), C ^{β} b2(10)
179	0	MC tor(96)
161	1	NM tor(117), NH ob2(12), M2 rock2(10)
148	7	C ^{α} C tor(54), NH ob1(28), CN tor1(12), C ^{α} CN def(10)
120	5	CN tor1(31), C ^{β} b1(24), C ^{α} C tor(14)
110	8	NC ^{α} tor(57), CN tor2(15)
85	4	C ^{α} C tor(83), NC ^{α} tor(43), CN tor2(18)

^aInfrared intensity.

in the open structures to increase as the OCNH dihedral angle deviates from planarity (180°), whereas those in the C₅ and C₇ structures decrease. Figure 2(d) shows that, although the CO stretch force constants in the β_2 and α structures do not correlate well with ω (the CC(O)NC dihedral angle), those in the hydrogen-bonded conformers decrease almost linearly as ω departs from 180°. Because the non-planarity of the CONH group reduces the electronic resonance in the CO and CN bonds, the increase in $f(\text{CO str})$ with non-planarity, as measured by the OCNH angle, in the open structures is not surprising. The lack of correlation with ω probably reflects the fact that this angle is not as direct a measure of the planarity of CONH when the out-of-plane angles at C and N are sizeable. That $f(\text{CO str})$ in the C₅ and C₇ conformers decrease with non-planarity suggests that higher degrees of non-planarity are associated with stronger hydrogen bonds. Such significant variations in force constants with the peptide group planarity are important because the deviations from planarity seen in these Ala dipeptide conformers (ω ranging from 174.5° to 187.6° [4]) are not unusual in actual peptide structures. A recent crystal-structure

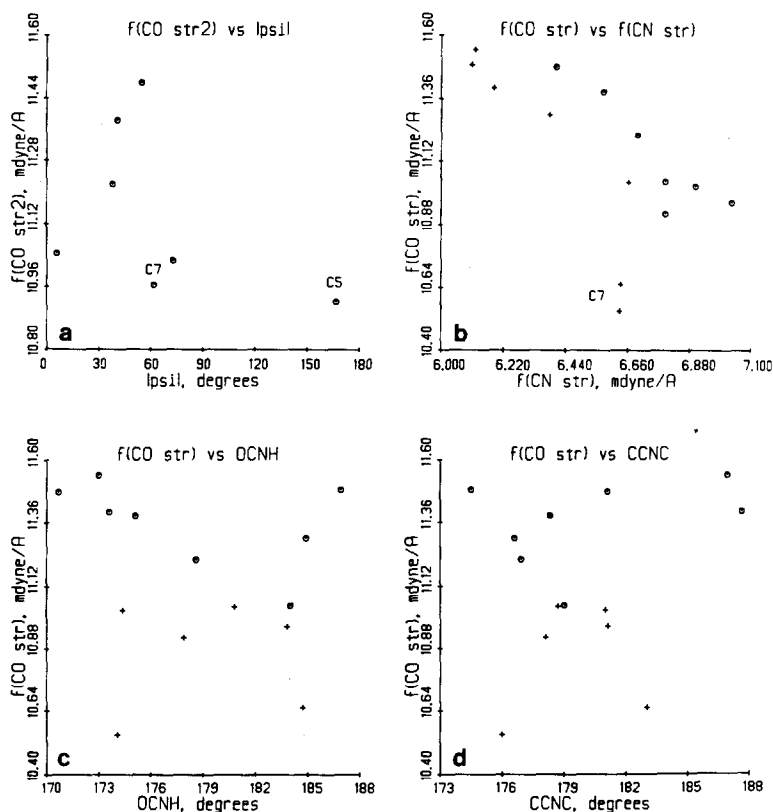


Fig. 2. Plots of the scaled CO stretch force constant: (a) versus $|\psi|$; (b) versus scaled CN stretch force constant; (c) versus OCNH dihedral angle; and (d) versus CC(O)NC dihedral angle. (b) \times , $f(\text{CO str1})$ and $f(\text{CN str1})$; \circ , $f(\text{CO str2})$ and $f(\text{CN str2})$. (c) and (d): \times , C_5 and C_7 conformers; \circ , open conformers.

survey [15] found values of ω in the range $157\text{--}201^\circ$, and in crystalline Ala dipeptide itself ω values of $171.9\text{--}191.6^\circ$ were derived in an X-ray study [16].

The CO and NH in-plane and out-of-plane bend (ib and ob) force constants do not vary significantly in the open conformations. Among the other diagonal and off-diagonal terms, as we concluded previously [1, 2], it is primarily those involving the C^α atom that vary appreciably with conformation. Also notable are the changes in the $C^\beta\text{H}$ stretches.

To summarize some of our results on the force fields of these Gly and Ala dipeptide structures, we again plot in Fig. 3 the scaled NH, CO, CN and CH stretch force constants against their respective equilibrium bond lengths. As before [2], we have fitted each set of points with a straight line, and the following least-squares slopes result (in units of mdyn \AA^{-2}): -62 , -75 , -31 , and -35 , respectively. Except for the CH stretch slope, these are smaller than

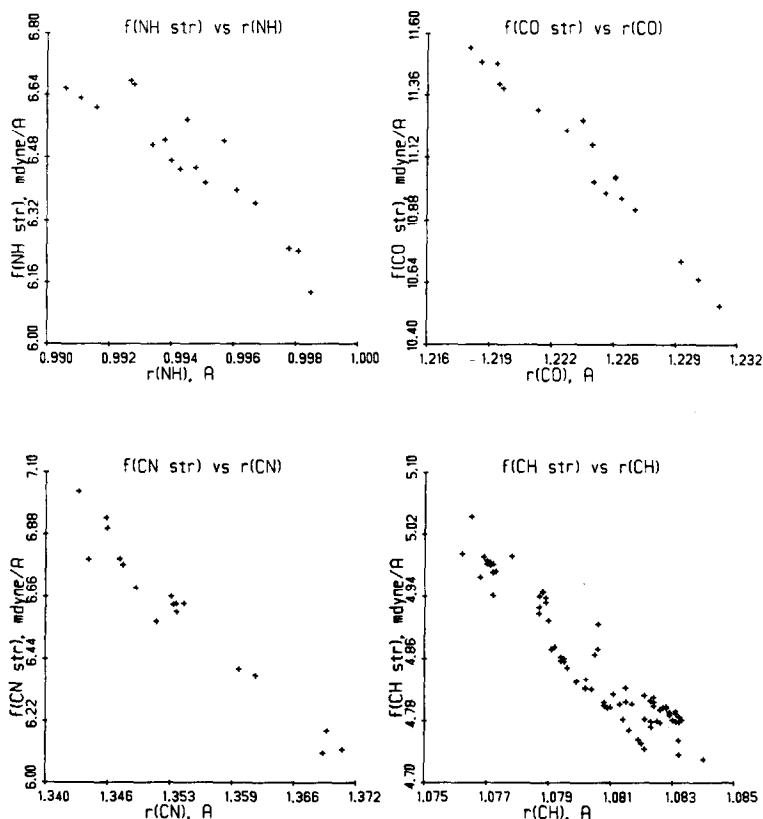


Fig. 3. Scaled NH, CO, CN and CH stretch diagonal force constants plotted against their respective equilibrium bond lengths.

obtained previously with much smaller sets of points. Even so, we continue to see close agreements of these slopes with the average diagonal cubic force constants, the values of which are -63 , -85 , -48 , and -35 $\text{mdyn } \text{Å}^{-2}$, respectively.

Turning to the normal modes, some of the amide modes in the seven Ala dipeptide conformations are summarized in Table 5. In the $1200\text{--}1300$ cm^{-1} region, the amide III mixes strongly, and to varying degrees, with the H^α bends (H^α b). This mixing can be removed by looking at the "pure" amide III in CD^α -Ala dipeptide and the "pure" H^α b in the *N*-deuterated isotopomer; the resulting frequencies are given in Table 5.

Because of their localized nature, the NH stretch frequencies reflect closely the differences in the force constants that were discussed above. Notable are the substantially lowered frequencies on hydrogen bonding, the systematically higher free NH str2 modes compared with the free NH str1, and the fact that both NH stretches show some sensitivity to conformation.

TABLE 5

Some calculated frequencies (in cm^{-1}) in normal and selectively deuterated Ala dipeptides

Mode	C_5	C_7^{eq}	C_7^{ax}	β_2	α_R	α_L	α'
NH str2	3471	3360	3334	3455	3467	3462	3474
NH str1	3390	3414	3446	3431	3403	3413	3418
Amide I (CO str2)	1698	1704	1699	1694	1679	1703	1720
Amide I (CO str1)	1668	1676	1682	1719	1726	1725	1710
Amide II (NH ib2)	1557	1587	1594	1550	1552	1546	1540
Amide II (NH ib1)	1525	1534	1551	1532	1526	1536	1529
Amide III (CN str2)/ CD^α	1321	1322	1327	1295	1294	1292	1295
Amide III (CN str1)/ CD^α	1276	1286	1294	1262	1263	1262	1278
H^α bend/(ND) ₂	1315	1314	1317	1300	1320	1305	1324
	1288	1305	1274	1296	1272	1283	1284
$C^\beta H_3$ asym str/ CD^α	3014	2997	3038	3010	3011	3028	3010
	2979	2990	2977	2977	2968	3001	2974
CH^α str/(CD_3) ₃	2955	2991	3000	2985	2993	2940	3007

In the open conformers, the amide I modes consisting primarily of CO str1 are quite constant in frequency, whereas the CO str2 vibrations vary significantly, as would be expected because CO str2 is adjacent to C^α . The much lower CO str1 frequencies in C_7^{eq} and C_7^{ax} arise from the C_7 hydrogen bonds; the amide I modes in C_5 are the most delocalized [2] and, consequently, do not reflect clearly the C_5 hydrogen bond. The amide II modes are seen to be hardly sensitive to conformation in the non-hydrogen bonded structures. Thus, in polypeptides the different amide II frequencies observed in different conformations [17] arise mainly from differences in hydrogen-bond strength and from transition dipole-dipole interaction [17, 18].

The amide III modes, when C^α is deuterated, hardly vary at all in the open conformers (with the exception of α'), and are systematically higher in frequency in the hydrogen-bonded structures. On the other hand, on *N*-deuteration, the H^α b modes vary markedly across all conformers. Thus, in normal *trans* peptides the amide III is sensitive to hydrogen bonding through its CN str and NH ib components, and to conformation mainly through its H^α b contributions.

Also listed in Table 5 are the $C^\beta H_3$ antisymmetric stretches (with C^α deuterated to remove accidental mixings) and the CH^α str (with C^β deuterated) to demonstrate that these modes are also affected by conformation, as we had

TABLE 6

Dipole-moment derivatives $\partial \vec{\mu} / \partial S$ (in D \AA^{-1} or D rad^{-1}) of Ala dipeptides referred to group axes^a

	$\partial \mu_x / \partial S$	$\partial \mu_y / \partial S$	$\partial \mu_z / \partial S$	$ \partial \vec{\mu} / \partial S $	θ^b
<i>C6 N7 O5</i>					
NH str1	0.90	0.43	0.04	1.00	26
	0.32	0.40	0.03	0.51	51
	0.67	0.75	-0.09	1.01	48
	0.51	0.64	-0.16	0.83	51
	0.29	0.21	-0.21	0.41	35
	0.25	0.20	0.18	0.36	39
	0.41	0.22	0.29	0.54	28
CO str1	4.23	4.47	-0.01	6.15	47
	4.25	5.10	-0.14	6.64	50
	3.99	5.22	0.16	6.57	53
	4.65	4.53	-0.00	6.49	44
	4.52	4.24	0.24	6.20	43
	3.97	4.07	-0.12	5.68	46
	4.34	4.48	-0.05	6.24	46
CN str1	-4.70	-0.20	0.11	4.71	-178
	-4.07	-0.22	-0.05	4.08	-177
	-3.74	-0.12	-0.09	3.74	-178
	-4.72	-0.06	-0.12	4.72	-179
	-4.30	-0.02	-0.40	4.32	-180
	-3.41	-0.22	-0.02	3.41	-176
	-4.47	-0.24	0.03	4.48	-177
NC ^{α} str	1.69	-1.32	-0.41	2.19	-38
	1.96	-2.09	0.10	2.87	-47
	2.11	-2.52	0.21	3.29	-50
	1.56	-1.48	-0.55	2.21	-44
	1.46	-1.36	-0.23	2.01	-43
	1.56	-1.59	0.53	2.29	-45
	1.11	-1.40	-0.47	1.85	-52
MCN def	-1.99	0.89	0.05	2.18	156
	-1.54	1.35	-0.20	2.06	139
	-1.69	1.31	0.20	2.15	142
	-1.32	0.92	-0.19	1.63	145
	-0.93	0.68	-0.14	1.16	144
	-0.83	0.50	0.16	0.98	149
	-1.52	0.59	-0.04	1.63	159
CO ib1	-3.16	2.14	0.08	3.81	146
	-2.92	2.43	-0.34	3.81	140
	-2.86	2.68	0.24	3.93	137
	-2.87	2.00	-0.05	3.50	145
	-2.69	1.94	-0.15	3.31	144
	-2.75	2.07	0.15	3.45	143
	-2.99	1.92	0.05	3.56	147

TABLE 6 (continued)

	$\partial\mu_x/\partial S$	$\partial\mu_y/\partial S$	$\partial\mu_z/\partial S$	$ \partial\vec{\mu}/\partial S $	θ^b
CNC $^\alpha$ def	4.20	-1.38	-0.06	4.42	-18
	2.84	-3.08	0.23	4.20	-47
	2.79	-3.44	-0.16	4.43	-51
	1.83	-1.98	0.12	2.70	-47
	1.03	-1.30	-0.17	1.67	-52
	0.96	-1.00	0.05	1.39	-46
	2.40	-1.05	0.19	2.63	-24
NH ib1	0.91	-0.37	0.14	0.99	-22
	0.53	-0.26	-0.01	0.59	-26
	0.50	-0.11	-0.05	0.52	-13
	0.42	-0.24	-0.30	0.57	-30
	0.46	-0.24	-0.34	0.62	-27
	0.43	-0.11	0.33	0.55	-14
CO ob1	0.68	-0.25	0.24	0.76	-20
	-0.09	0.01	0.80	0.81	174
	0.20	-0.02	1.52	1.54	-7
	-0.05	0.05	1.63	1.63	133
	0.03	-0.09	1.16	1.16	-72
	0.11	-0.05	1.11	1.12	-23
NH ob1	-0.11	0.15	1.16	1.17	126
	-0.43	0.28	1.21	1.31	147
	0.01	0.04	2.27	2.27	74
	-0.26	-0.13	1.03	1.07	-153
	0.18	0.03	0.77	0.79	9
	0.30	0.28	1.14	1.22	43
CN tor1	0.19	0.02	1.21	1.22	6
	-0.04	-0.24	1.23	1.26	-99
	0.40	-0.60	1.07	1.29	-56
	0.22	-0.13	-3.47	3.48	-31
	-0.50	0.43	-3.39	3.45	139
	0.37	-0.46	-3.37	3.42	-51
NC $^\alpha$ tor	-0.19	-0.27	-2.36	2.38	-125
	-0.11	0.04	-2.22	2.23	160
	-0.03	-0.04	-2.43	2.43	-128
	0.07	0.68	-2.02	2.13	84
	0.17	-0.07	-3.36	3.36	-24
	-0.19	0.81	-4.90	4.97	103
	0.13	-1.03	-5.19	5.29	-83
	-0.96	0.20	-3.86	3.98	168
	-0.55	0.16	-3.31	3.36	164
	0.80	-0.08	-3.40	3.50	-6
	1.40	-0.20	-3.07	3.38	-8

TABLE 6 (continued)

	$\partial\mu_x/\partial S$	$\partial\mu_y/\partial S$	$\partial\mu_z/\partial S$	$ \partial\vec{\mu}/\partial S $	θ^b
<i>C12 N17 O13</i>					
NH str2	0.62	0.72	-0.02	0.95	50
	0.19	1.40	-0.37	1.46	82
	0.14	1.85	0.47	1.91	86
	0.24	0.63	0.10	0.68	70
	0.13	0.62	0.32	0.71	78
	0.16	0.33	-0.27	0.46	64
	0.51	0.61	-0.18	0.81	50
CO str2	4.19	4.79	0.23	6.37	49
	4.47	4.68	-0.37	6.48	46
	4.45	4.96	0.12	6.67	48
	4.24	4.82	-0.10	6.42	49
	4.33	4.95	0.05	6.58	49
	4.24	4.84	-0.37	6.44	49
	3.87	4.95	0.12	6.29	52
CN str2	-4.42	-0.40	0.09	4.44	-175
	-3.87	-0.30	0.21	3.89	-176
	-3.52	-0.43	-0.28	3.56	-173
	-4.18	-0.74	-0.01	4.24	-170
	-3.91	-0.96	-0.25	4.04	-166
	-3.88	-0.80	0.16	3.96	-168
	-3.83	-1.10	-0.02	3.99	-164
C $^{\alpha}$ C str	0.30	0.16	-0.19	0.39	28
	0.62	-0.53	0.43	0.92	-41
	0.97	-0.87	-0.22	1.32	-42
	0.41	-0.32	-0.00	0.52	-38
	0.60	-0.42	0.19	0.75	-35
	0.24	-0.14	-0.48	0.55	-30
	0.52	-0.37	-0.02	0.64	-35
C $^{\alpha}$ CN def	1.08	-1.42	-0.02	1.78	-53
	0.40	-2.96	0.34	3.01	-82
	0.20	-3.07	-0.31	3.09	-86
	0.54	-1.68	0.06	1.76	-72
	-0.47	-1.35	-0.17	1.44	-109
	-1.06	-0.80	-0.11	1.33	-143
	0.55	-0.11	-0.52	0.77	-11
CO ib2	-3.23	2.41	0.05	4.03	143
	-2.58	2.40	-0.05	3.53	137
	-2.21	2.30	-0.11	3.19	134
	-2.68	2.28	-0.11	3.52	140
	-2.37	2.17	-0.14	3.22	137
	-2.41	2.16	-0.11	3.24	138
	-2.57	1.82	0.20	3.16	145

TABLE 6 (continued)

	$\partial\mu_x/\partial S$	$\partial\mu_y/\partial S$	$\partial\mu_z/\partial S$	$ \partial\vec{\mu}/\partial S $	θ^b
CNM def	0.73	0.32	0.01	0.79	24
	0.99	0.84	-0.06	1.30	40
	1.15	0.87	0.02	1.44	37
	0.88	0.42	-0.04	0.97	26
	1.36	0.27	-0.01	1.39	11
	1.47	0.12	0.07	1.47	5
NH ib2	0.91	-0.05	0.29	0.96	-3
	0.59	-0.12	-0.03	0.61	-12
	0.73	-0.45	0.27	0.90	-32
	0.66	-0.54	-0.18	0.87	-39
	0.59	-0.41	0.04	0.72	-35
	0.55	-0.46	-0.07	0.72	-40
	0.57	-0.27	0.13	0.65	-25
CO ob2	0.59	-0.24	-0.05	0.64	-22
	-0.05	-0.02	0.85	0.85	-160
	0.06	-0.21	-0.33	0.39	-75
	-0.08	0.17	-0.38	0.43	115
	0.72	-0.56	0.79	1.21	-38
	0.94	-0.98	0.28	1.39	-46
	-0.85	0.46	-0.07	0.97	151
NH ob2	-0.40	0.25	1.10	1.20	148
	-0.00	0.09	2.24	2.24	91
	0.20	0.08	2.66	2.67	22
	-0.05	-0.05	2.70	2.70	-139
	-0.32	0.09	2.07	2.10	164
	-0.68	0.22	2.22	2.33	162
	0.73	-0.25	2.39	2.51	-19
C $^\alpha$ C tor	0.45	0.28	1.90	1.98	31
	0.11	-0.15	3.38	3.39	-52
	-0.01	-0.29	4.37	4.38	-91
	0.11	0.51	4.32	4.35	78
	-0.74	-0.30	2.74	2.85	-158
	-1.19	0.30	3.24	3.47	166
	1.23	-0.83	2.90	3.26	-34
CN tor2	0.42	0.50	1.76	1.88	50
	-0.11	0.08	-0.06	0.15	143
	0.34	-0.38	-0.33	0.61	-48
	-0.19	0.36	-0.41	0.58	118
	0.51	-0.47	-0.01	0.69	-42
	0.54	-0.52	-0.43	0.86	-44
	-0.29	0.36	-0.41	0.62	128
-0.08	0.27	0.30	0.41	108	

TABLE 6 (continued)

	$\partial\mu_x/\partial S$	$\partial\mu_y/\partial S$	$\partial\mu_z/\partial S$	$ \partial\vec{\mu}/\partial S $	θ^b
<i>C11 C9 H16</i>					
$C^\alpha C^\beta$ str	0.17	0.47	0.46	0.68	71
	0.23	0.19	0.68	0.75	40
	0.24	0.33	0.56	0.69	55
	0.29	0.39	0.56	0.74	54
	0.40	0.67	0.65	1.02	59
	0.26	-0.08	0.77	0.82	-18
	0.41	0.59	0.45	0.85	55
$C^\alpha H^\alpha$ str	-0.05	0.36	0.04	0.36	98
	-0.13	0.08	-0.35	0.39	150
	-0.00	-0.08	-0.15	0.17	-93
	-0.19	0.39	-0.46	0.63	115
	-0.02	0.07	-0.37	0.38	101
	-0.31	0.08	0.07	0.32	166
	0.03	0.13	-0.15	0.20	79
$NC^\alpha C$ def	-2.03	1.95	-0.27	2.82	136
	-2.29	1.93	-0.14	3.00	140
	3.84	-2.08	-0.29	4.37	-29
	-1.92	1.06	0.65	2.28	151
	-0.40	0.21	0.21	0.50	152
	0.54	-0.08	-0.10	0.55	-9
	-0.24	-0.23	0.79	0.86	-136
H^α b1	-0.02	-0.03	0.04	0.05	-126
	-1.23	0.65	0.12	1.39	152
	1.03	-1.11	0.10	1.51	-47
	-0.66	0.40	0.87	1.16	149
	-0.27	0.41	0.55	0.74	124
	-0.27	-0.67	0.26	0.77	-112
	0.69	-0.10	0.91	1.15	-8
H^α b2	0.15	-0.05	1.09	1.10	-19
	0.61	0.85	-0.23	1.07	55
	-0.51	-0.97	-0.60	1.25	-118
	0.68	0.39	0.12	0.79	30
	0.09	0.51	-0.50	0.72	80
	0.21	-0.52	-0.84	1.01	-68
	-0.03	-0.15	0.36	0.39	-101
C^β b1	-3.26	2.20	-0.14	3.94	146
	1.56	-1.90	-0.46	2.50	-51
	-0.02	-0.98	0.18	0.99	-92
	-0.22	-1.80	-0.17	1.82	-97
	0.82	-1.47	-0.34	1.72	-61
	0.49	-1.23	0.11	1.33	-68
	-2.35	0.08	-0.29	2.37	178

TABLE 6 (continued)

	$\partial\mu_x/\partial S$	$\partial\mu_y/\partial S$	$\partial\mu_z/\partial S$	$ \partial\vec{\mu}/\partial S $	θ^b
C^β b2	0.20	-0.32	-0.58	0.69	-57
	-0.48	-1.46	0.31	1.56	-108
	0.61	0.65	0.32	0.95	47
	0.00	-1.12	-0.23	1.15	-90
	-0.11	-1.14	0.16	1.16	-96
	-0.11	-0.45	0.63	0.78	-104
	0.55	-0.31	-0.32	0.70	-29

^aLocal axes of group A B C defined thus: $\hat{x} = AB$, $\hat{z} = AC \times AB$. Entries are for C_5 (first line), C_7^{eq} , C_7^{ax} , β_2 , α_R , α_L , and α' (subsequent lines).

^bAngle from \hat{x} in x - y plane, in degrees.

found in our experimental study of cyclo (D-Ala-L-Ala) in two crystalline forms [19]. The precise nature of these frequency-conformation correlations is still not clear, given the small number of data points available at present. However, the CH^α stretch frequency does seem to decrease with ψ , which is consistent with our experimental observation [19] of a 21 cm^{-1} decrease when ψ changes from -2.8° to 4.2° in a *cis* peptide.

The sets of frequencies for all seven conformers of Ala dipeptide yield the following vibrational free energies at 298.15 K (using the usual harmonic oscillator expression [20], in kcal mol^{-1}): 109.68 (C_5), 109.85 (C_7^{eq}), 110.30 (C_7^{ax}), 109.55 (β_2), 109.45 (α_R), 109.66 (α_L), and 109.51 (α'). The free energies, given by the sum of the SCF energy and the vibrational free energy, in units of kcal mol^{-1} relative to that of C_7^{eq} , are: 1.2 (C_5), 3.1 (C_7^{ax}), 3.6 (β_2), 4.5 (α_R), 6.5 (α_L), and 7.6 (α'). Thus, the order of stability of the conformers is unchanged from that given by the SCF energies alone, and each conformer is slightly closer in energy to the C_7^{eq} except for the C_7^{ax} structure.

Table 6 lists the dipole-moment derivatives $\partial\mu/\partial S_i$ with respect to the group coordinates (excluding those of the methyl groups) referred to local axes fixed within each group [1]; see the footnote to the table for the definitions of the local axes. To help in comparison, all seven Ala dipeptide conformers are tabulated.

The NH str1 derivatives show marked variations in the open conformers and, unlike in the C_5 and C_7 structures, have sizeable components perpendicular to the plane of the peptide group; this is probably related to the deviations from planarity at N7 (Table 1). The NH str2 derivatives clearly show a strong increase due to the C_7 hydrogen bonds. Except for CO str1 in α_L , the CO stretch derivatives are all very similar in magnitude and direction even in the hydrogen-bonded structures, pointing to a high degree of transferability. (Because CO str2 is more representative of the CO groups in polypeptides, the α_L exception seems of little consequence.)

The NH ib derivatives are not very conformationally sensitive, at least in their magnitudes, and as expected they increase when the NH group is bonded. All CO ib1 and CO ib2 derivatives have nearly the same magnitude and direction. The NH ob1 derivatives are systematically smaller in magnitude than the NH ob2 and in the open conformers the former are all virtually identical. (Note that NH ob1 is the more representative of NH groups in polypeptides.) There is the expected increase on hydrogen bonding and interestingly, a decrease in NH ob1 in the C_7 structures where the NH belongs to the acceptor peptide unit. Similar decreases in the CO ob derivatives are seen when the CO is in the donor peptide group. The situation in proteins and peptide crystals, where each CONH is usually both a hydrogen-bond donor and acceptor, is likely to be more complicated.

CONCLUSIONS

We have extended our previous studies of the force fields of Ala dipeptide in C_5 and C_7 conformations with intramolecular hydrogen bonding by doing similar calculations on four open, non-hydrogen-bonded conformations. These results have provided further insights into how force constants vary with conformation and hydrogen bonding, and should be helpful in developing and testing force fields for normal mode and molecular mechanics calculations of peptides and polypeptides.

ACKNOWLEDGEMENT

This research was supported by NSF grants DMB-8816756 and DMR-8806975. We thank The University of Michigan Computing Center for a generous special allocation of computing funds.

REFERENCES

- 1 T.C. Cheam and S. Krimm, *J. Mol. Struct.*, 193 (1989) 1. (In Table 3 of this reference, the 2-33 element for GLY7 should read -0.03 , and in Table 8 the last group heading should read C16N14H19.)
- 2 T.C. Cheam and S. Krimm, *J. Mol. Struct. (Theochem)*, 188 (1989) 15. (In Table 3 of this reference, the 4-30 and 4-23 terms should be interchanged, and the 17-41 and 17-42 elements for ALA 7A should read 0.05 and 0.10, respectively.)
- 3 L. Schäfer, C. Van Alsenoy and J.N. Scarsdale, *J. Chem. Phys.*, 76 (1982) 1439.
- 4 J.N. Scarsdale, C. Van Alsenoy, V.J. Klimkowski, L. Schäfer and F.A. Momany, *J. Am. Chem. Soc.*, 105 (1983) 3438.
- 5 L. Schäfer, V.J. Klimkowski, F.A. Momany, H. Chuman and C. Van Alsenoy, *Biopolymers*, 23 (1984) 2335.
- 6 V.J. Klimkowski, L. Schäfer, F.A. Momany and C. Van Alsenoy, *J. Mol. Struct. (Theochem)*, 124 (1985) 143.

- 7 K. Rasmussen, *Potential Energy Functions in Conformational Analysis*, Springer-Verlag, Berlin, 1985.
- 8 P. Pulay, G. Fogarasi, F. Pang and J.E. Boggs, *J. Am. Chem. Soc.*, 101 (1979) 2550.
- 9 E.B. Wilson, Jr., J.C. Decius and P.C. Cross, *Molecular Vibrations*, Dover, New York, 1980, p. 60.
- 10 G. Fogarasi and A. Balázs, *J. Mol. Struct. (Theochem)*, 133 (1985) 105.
- 11 M. Marraud, J. Néel, M. Avignon and P.V. Huong, *J. Chim. Phys.*, 67 (1970) 959.
- 12 J. Néel, *Pure Appl. Chem.*, 31 (1972) 201.
- 13 I.M. Ginzburg, *J. Gen. Chem.*, 52 (1982) 1445.
- 14 R.P. Sheridan, R.H. Lee, N. Peters and L.C. Allen, *Biopolymers*, 18 (1979) 2451.
- 15 T. Ashida, Y. Tsunogae, I. Tanaka and T. Yamane, *Acta Crystallogr., Sect. B*, 43 (1987) 212.
- 16 Y. Harada and Y. Iitaka, *Acta Crystallogr., Sect. B.*, 30 (1974) 1452.
- 17 S. Krimm and J. Bandekar, *Adv. Protein Chem.*, 38 (1986) 181.
- 18 T.C. Cheam and S. Krimm, *Chem. Phys. Lett.*, 107 (1984) 613.
- 19 T.C. Cheam and S. Krimm, *Spectrochim. Acta, Part A*, 44 (1988) 185.
- 20 J.C. Slater, *Introduction to Chemical Physics*, McGraw-Hill, New York, 1939, p. 217.