

Peptide models

XV. The effect of basis set size increase and electron correlation on selected minima of the ab initio 2D-Ramachandran map of For–Gly–NH₂ and For–L-Ala–NH₂

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Abstract

A total of eleven basis sets from 3-21G to 6-3111++G(d,p) have been used at the HF and MP2 levels of theory for geometry optimizations of the global, γ_L , ($\phi = -75^\circ$, $\Psi = +75^\circ$) and the second lowest, β_L , ($\phi = -150^\circ$, $\Psi = +150^\circ$) minimum energy conformations of the L enantiomer of HCO–NH–CH(CH₃)–CO–NH₂. The results showed that due to fortuitous cancellation of correlation and basis set effects, the HF/3-21G energy-difference of these conformers agrees well with the MP2/6-3111++G(d,p) energy difference, while the HF/6-3111++G(d,p) energy difference converges erroneously toward zero.

The other legitimate conformers were optimized at the HF/3-21G, HF/6311++G(d,p), and MP2/6-3111++G(d,p) levels of theory. The results showed that one of the minima disappeared at HF/6-3111++G(d,p) and one more of the minima did not occur at the MP2/6-3111++G(d,p) level of theory. The correlation and basis set effects stabilized the higher energy conformers.

Keywords: Ab initio Ramachandran map; Basis set size; For–Gly–NH₂; For–L-Ala–NH₂; Peptide model; Electronic structure

1. Introduction

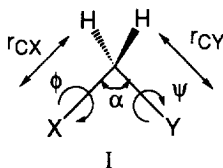
Compounds containing geminally substituted carbons (I), where the substituents (X and Y) contain

either lone pairs or pi-electronic systems with spatially extended electron density, may show unusual conformational behaviour with respect to hydrocarbons. For example in difluorine derivatives (X,Y = F) the F–C–F bond angle becomes too small.

The potential energy surface (PES) of hydrocarbons

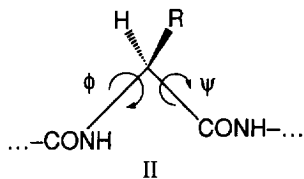
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(e.g. X,Y = CH₃) contains nine minima corresponding to nine legitimate conformations (cf. Scheme 1).



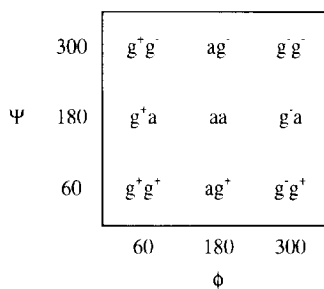
However, in substituted compounds some of these nine critical points may not occur. For example, in compounds where X and Y are OH, SH or other heteroatom-containing groups the $E(\phi, \Psi)$ PES of hydrocarbons may be altered dramatically by the interacting groups.

In peptides (II) two amide groups are attached differently to the central carbon atom (one at the C terminus, the other at the N terminus).

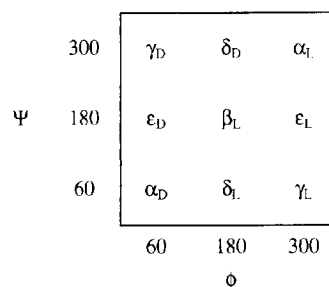


Nevertheless, if the system behaves in an ideal fashion one can expect the existence of nine legitimate minima [1] on the 2D-conformational PES (cf. Scheme 1). For peptides the traditional notation for the nine legitimate minima, utilized in Scheme 1, is replaced by another symbolism, involving subscripted Greek letters (cf. Scheme 2).

In examining Schemes 1 and 2, note that the traditional 2D-Ramachandran map [2], in the IUPAC-IUB convention [3], represents a different cut of the PES

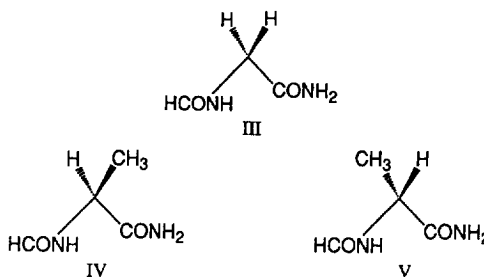


Scheme 1.

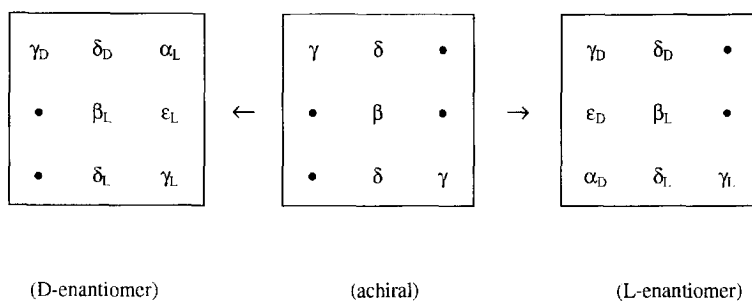


Scheme 2.

which is shown by a square of broken lines at the centre of Fig. 1. We should distinguish two types of N- and C-protected amino acid derivatives: *achiral*, for which glycine (III) is the sole example, and *chiral* for which we have numerous examples, L-alanine (IV) and D-alanine (V) being the simplest. Ab initio calculations have been carried out for *N*-formylglycinamide (III) and *N*-formylalanine amide (IV and V).



The calculations revealed that in the achiral case (III), the annihilation of the critical points is symmetrical, the degenerate pairs of the α_L and α_D conformations and the degenerate pairs of the ϵ_L and ϵ_D conformations were missing from the 2D-PES (left-hand side of Scheme 3). In chiral molecules (e.g. IV), as might be expected, fewer critical points were missing in a nonsymmetric way. In the case of HCO-L-Ala-NH₂ the α_L and ϵ_L minima disappeared (cf. middle of Scheme 3) and in the case of HCO-D-Ala-NH₂ the α_D and ϵ_D minima disappeared (cf. right-hand side of Scheme 3). Such distortion of the PES clearly indicates that the geminal substituents strongly interact. Scheme 3 is derived from the results of HF/3-21G calculations. If the HF method is implemented with larger basis sets these missing minima do not



Scheme 3.

reappear [4]. Furthermore, at the HF/6-31 G(d) level of theory another minimum (δ_L) has disappeared.

More recently, Schäfer and coworkers [5] have shown, for the γ_L and β_L conformations of For-L-Ala-NH₂, that the relative stabilities and geometrical

parameters of these conformations are also sensitive to the inclusion of correlation energy. For this reason, it seemed highly desirable to perform systematic 'benchmark' type calculations, with increasing basis set size and with the inclusion of electron correlation,

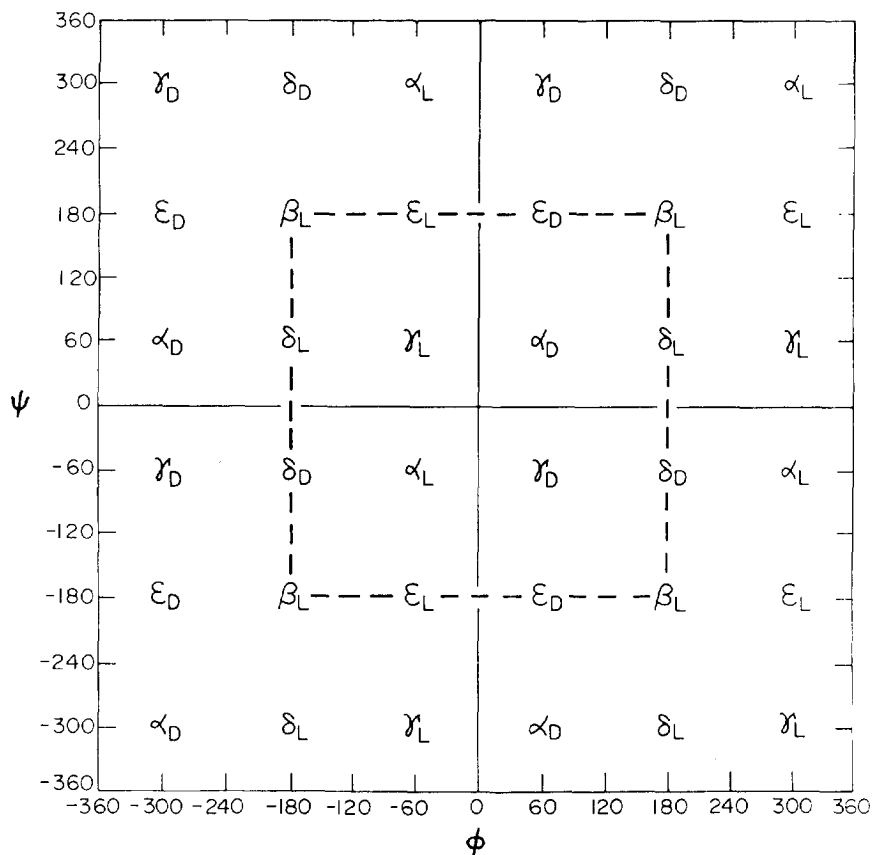


Fig. 1. Idealized PES topology for a single amino acid residue involving two complete cycles of rotation in both ϕ and Ψ . Location of the minima are specified by their names in terms of subscripted Greek letters. (Schemes 1 and 2 are equivalent to each of the four quadrants.)

on selected conformers of some simple peptides. In this study we discuss the results for For–Gly–NH₂ and *N*-formyl-L-alanine amide (IV).

2. Computational methods

Ab initio HF and MP2 geometry optimizations on typical backbone conformations (labelled α_L , α_D , β_L , γ_L , γ_D , δ_L , δ_D , ε_L , ε_D), were performed. The GAUSSIAN 90 program[6] was used and the geometries were optimized until the largest gradient was decreased below 1.5×10^{-5} a.u. (OTP = tight).

The HF and MP2 methods were implemented with 11 standard basis sets for β_L and γ_L conformations for a complete study, and only some selected basis sets were employed for the other conformations. The 11 standard basis sets employed are listed below:

1	3-21G
2	4-21G
3	4-31G
4	6-31G
5	6-31++G
6	6-31G(d,p)
7	6-31++G(d,p)
8	6-311G
9	6-311++G
10	6-311G(d,p)
11	6-311++G(d,p)

The MP2 calculations were performed even with low quality basis sets in order to present a more complete

study; it was, however, not expected that basis sets without polarization function perform well in combination with the MP2 method.

3. Results and discussion

We have carried out preliminary computations on the β_L and γ_L conformations of For–Gly–NH₂ and For–Ala–NH₂. From the results presented in Table 1 it is clear that their energy difference

$$\Delta E(\beta_L - \gamma_L) = E(\beta_L) - E(\gamma_L)$$

computed at the lowest (HF/3-21G) and highest (MP2/6-311++G(d,p)) levels of theory provided surprisingly similar results. Consequently the basis set extension effects and the electron correlation effects, introduced here at the MP2 level of theory, cancel each other for these molecules. This effect is well known and frequently used for molecular geometry studies [7]; it is, however, quite rare for energy differences. In order to explore the frontiers of the validity of the above mentioned cancellation we carried out a detailed investigation on the dependence of the value of $\Delta E(\beta_L - \gamma_L)$ on the level of quantum theory applied.

In the *first part* of this paper we present the HF and MP2 results for the β_L and γ_L conformations of For–L-Ala–NH₂. The numerical results are summarized in Table 2. This table includes torsional angles ϕ, Ψ for conformers β_L and γ_L and total energies for the two

Table 1

Total and relative energies for β_L and γ_L conformations for For–Gly–NH₂ and For–Ala–NH₂ computed at various levels of theories

Basis set	E^{HF} (Hartree)		ΔE^{HF} (kcal mol ⁻¹)	E^{MP2} (Hartree)		ΔE^{MP2} (kcal mol ⁻¹)
	β_L	γ_L		β_L	γ_L	
For–Gly–NH ₂						
3-21G	-373.647749	-373.648787	0.65	–	–	–
6-311G(d,p)	-375.853161	-375.852293	-0.54	-377.00726 ^a	-377.00949 ^a	1.40
6-311++G(d,p)	-375.863521	-375.862320	-0.75	-377.02815 ^b	-377.03043 ^b	1.43
For–Ala–NH ₂						
3-21G	-412.472783	-412.474780	1.25	-413.301276	-413.305097	2.40
6-311G(d,p)	-414.900210	-414.900685	0.30	-416.36077 ^c	-416.363014 ^c	1.41
6-311++G(d,p)	-414.909098	-414.909271	0.11	-416.38278 ^c	-416.384696 ^c	1.21

^a Geometry optimized at MP2 = FC/6-31G(d,p) level of theory.

^b MP2 = FC/6-311++G(d,p)//MP2 = FC/6-311G(d,p).

^c Geometry optimized at MP2 = FULL/6-311++G(d,p) level of theory.

Table 2
Torsional angles, total and relative energies for β_L and γ_L conformations of HCO–NHCHMeCO–NH₂ as computed at the HF and MP2 levels of theory using eleven different basis sets

G basis set	HF conformations										MP2 conformations										$\Delta E_{\beta_L, \gamma_L}^{MP2}$ (kcal mol ⁻¹)
	β_L					γ_L					β_L					γ_L					
	No.	Symbol	Type	ϕ	ψ	E_{total}	ϕ	ψ	E_{total}	$\Delta E_{\beta_L, \gamma_L}^{HF}$ (kcal mol ⁻¹)	No.	Symbol	Type	ϕ	ψ	E_{total}	ϕ	ψ	E_{total}	$\Delta E_{\beta_L, \gamma_L}^{MP2}$ (kcal mol ⁻¹)	
1	○	3-21	-168.33	170.55	-412.472783	-84.48	67.26	-412.474780	1.25	1	○	3-21	-170.24	174.09	-413.301276	-81.87	68.35	-413.305097	2.40		
2	○	4-21	-166.60	-169.90	-413.822868	-84.70	66.80	-413.830881	1.38	2	○	4-21	-169.46	174.55	-414.664930	-81.58	68.23	-414.668857	2.46		
3	○	4-31	-161.50	164.50	-414.172776	-85.50	69.40	-414.173491	0.45	3	○	4-31	-160.69	166.39	-415.014579	-83.25	68.52	-415.016624	1.28		
4	□	6-31	-160.63	164.04	-414.599426	-85.06	69.68	-414.599943	0.32	4	□	6-31	-159.49	165.41	-415.434232	-83.07	69.02	-415.435985	1.10		
5	□	6-31++	-158.42	163.97	-414.613125	-85.57	69.67	-414.613544	0.26	5	□	6-31++	-151.56	158.17	-415.471295	-83.38	69.78	-415.472966	1.05		
6	□	6-31(d,p)	-157.90	162.20	-414.805517	-85.30	76.00	-414.805988	0.30	6	□	6-31(d,p)	-159.76	166.58	-416.073963	-82.98	77.57	-416.076269	1.45		
7	□	6-31++(d,p)	-155.56	160.44	-414.818863	-86.23	76.43	-414.819091	0.14	7	□	6-31++(d,p)	-155.81	161.41	-416.107264	-83.21	78.53	-416.109247	1.24		
8	△	6-311	-159.16	163.25	-414.699393	-85.24	71.79	-414.699566	0.11	8	△	6-311	-155.06	160.91	-415.722450	-83.57	74.85	-415.723635	0.74		
9	△	6-311++	-158.15	163.87	-414.708746	-85.61	70.37	-414.708908	0.10	9	△	6-311++	-147.42	155.70	-415.748698	-84.37	72.72	-415.749819	0.70		
10	△	6-311(d,p)	-156.80	162.20	-414.900290	-85.50	78.30	-414.900685	0.25	10	△	6-311(d,p)	-158.82	168.32	-416.360765	-81.76	81.83	-416.363014	1.41		
11	△	6-311++(d,p)	-160.95	160.95	-414.909098	-86.24	78.75	-414.909271	0.11	11	△	6-311++(d,p)	-157.06	163.15	-416.382776	-82.79	80.60	-416.384696	1.21		

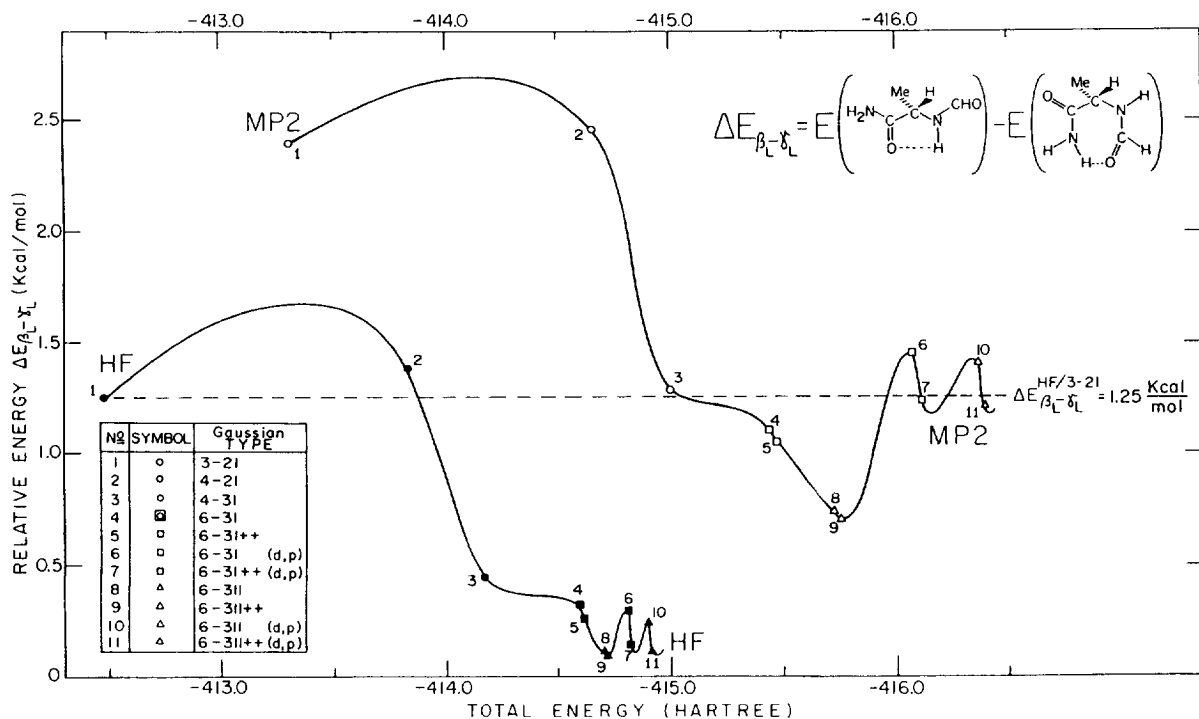


Fig. 2. Correlation of relative energy of the β_L conformation, with respect to the global minimum (γ_L), [$\Delta E = E(\beta_L) - E(\gamma_L)$], for For-Ala-NH₂ with computed total energy $E(\gamma_L)$ that measures the quality of the wave function according to the variational theorem in the HF formalism. The different solid and open points, shown on the HF and MP2 curves respectively, symbolize different basis sets.

conformations, $E(\beta_L)$ and $E(\gamma_L)$ in Hartrees, as well as the relative energies, ΔE , in kcal mol⁻¹ computed at the HF and MP2 levels of theory implemented with eleven basis sets. The relative energy values are presented in Fig. 2 as a function of $E(\gamma_L)$. This presentation is suitable because lower energy means a better quality wave function, according to the Variational Theorem for the HF method. It should be noted that the MP2 method is not variational, however; the energy decreases with the improvement of the basis set. The convergence of ϕ and Ψ angle values with increasing basis set size are plotted in Fig. 3. Fig. 4 shows the same information as Fig. 3 from a bird's eye point of view.

From Table 2 and Fig. 2 it is clear that the HF method converges to an unrealistically small energy difference as the basis set size increases. Only the HF/3-21G and 4-21G methods provide an energy difference; this result is very close to that obtained at the MP2/6-311++G(d,p) level of theory. Needless to say, small basis sets are the only hope for any effort that

aims to carry out ab initio computations on oligopeptides.

The results in Table 2 clearly show the limited utility of the non-polarized basis set at the MP2 level of theory. The results calculated with the four basis sets (nos. 6, 7 and 10, 11), including polarization functions, indicate very good agreement with each other; all non-polarized results, however, provide rather large variation (in the range 0.70 to 2.46 kcal mol⁻¹). However, the discrepancy is not all that large, in fact, it is within 2 kcal mol⁻¹ for all conformations. The average energy difference of the MP2 method implemented with the four basis sets using the polarization function is 1.33 kcal mol⁻¹.

In the *second part* of this paper the calculations were attempted at the HF/3-21G, HF/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory for all of the nine legitimate conformations (α_D , α_L , β_L , γ_D , γ_L , δ_D , δ_L , ϵ_D , ϵ_L) of For-Ala-NH₂). These results are summarized in Table 3 and shown graphically in Fig. 5. The results in Fig. 5 indicate that the relative order of

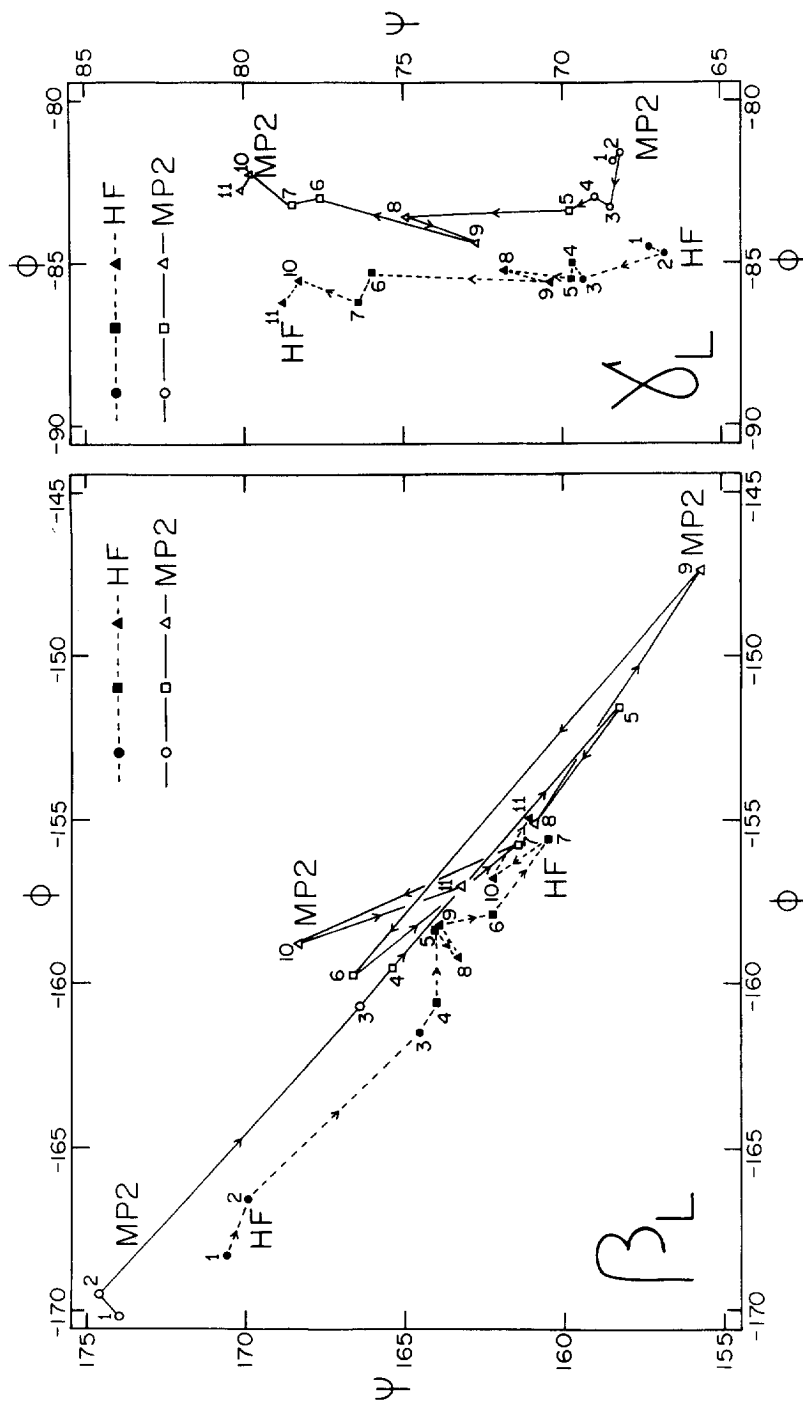


Fig. 3. Basis set size dependence of ϕ and ψ values of β_L and γ_L For-Ala-NH₂ at the HF and MP2 levels of theory.

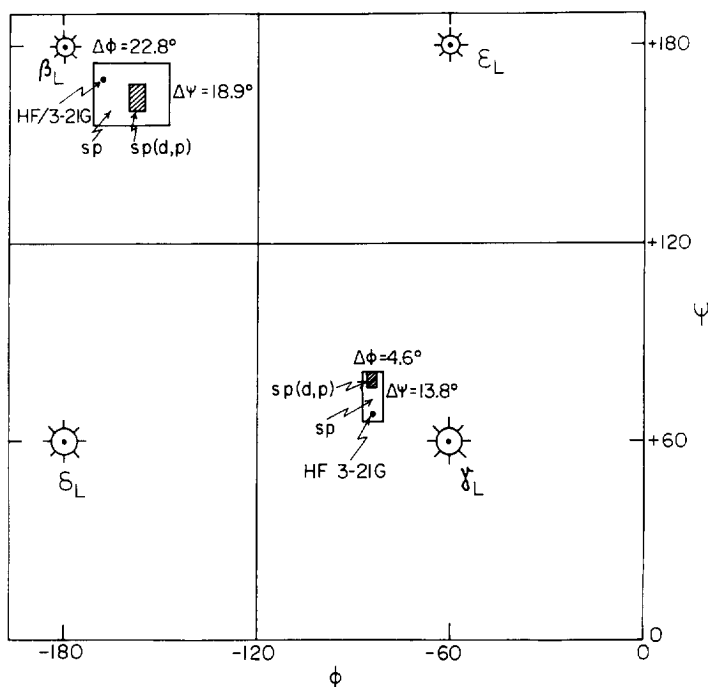


Fig. 4. Birds-eye point of view of Fig. 3.

the minima is conserved on going from the HF/13-21G to the MP2/6-311++G(d,p) level of theory; the differences do change, however. It is interesting to note that when electron correlation is included the higher is the relative energy for a given conformation and the lower is the ΔE . Consequently, the relative instability of the various conformers is decreased by the correlation effects. The energy reduction due to correlation energy contribution is illustrated in Fig. 6.

Considering the change in torsional angles, one can see in Fig. 3 a general trend in the shifting of the location of the minima with the increase of the basis set size. The position of β_L is shifted towards the γ_L conformational centre and the position of γ_L towards the ε_L conformational centre. These shifts represent a general basis set effect which is only slightly modified by the inclusion of electron correlation (Fig. 3). The minimum corresponding to the ε_D conformation disappears at the HF/6-311++G(d,p) level of theory. This was the highest energy conformer at the HF/3-21G level of theory. This minimum does not reappear at the MP2/6-311++G(d,p) level of theory; moreover

another minimum, the δ_L conformation disappears. This was a low lying minimum at the HF/3-21G level of theory, shifted toward the large basin around the γ_L minimum. This shift was more than 50° of ϕ at the HF/3-21G level of theory. This very shallow minimum disappears from the MP2/6-311++G(d,p) PES.

In view of such systematic trends in torsional angles it appeared to be worth examining other geometrical parameters. Table 4 shows some selected geometrical parameters as a function of basis set size increase and the inclusion of electron correlation. In general the MP2 molecular volume is larger than the HF value. It is well known from the literature [7] that the improper treatment of electron correlation in the HF method causes bond lengths to be underestimated with a good quality basis set (close to the HF limit). Since in the HF calculations the electron–electron repulsion terms are underestimated, the electrons tend to move too close to one another which results in compact bonds. Earlier studies showed [8] an inverse relationship between the quality of the basis set and the predicted bond lengths at the HF

Table 3
Torsional angles, total and relative energies for all existing conformations HCO-NH-CH-Me-CONH₂ as computed at the HF/3-21G, HF/6-311++G(d,p) and MP2/6-311++G(d,p)

Conformation	HF/3-21G			HF/6-311++G(d,p)			MP2/6-311++G(d,p)			ΔE^b	E^a	ΔE^b	ΔE^b	ΔE^b	ΔE^b	ΔE^b	ΔE^b
	ϕ	ψ	E^a	ΔE^b	ϕ	ψ	E^a	ΔE^b	ϕ								
α_D	63.8	32.7	-412.46529	5.95	69.0	26.9	-414.902009	4.56	2.436715	63.1	35.5	-416.37851	3.88	1.47650			
α_L	Not found																
β_L	-168.3	170.6	-412.47278	1.25	-155.1	161.0	-414.909098	0.11	2.436315	-157.1	163.2	-416.38278	1.21	1.47368			
δ_D	-178.6	-44.1	-412.47278	7.31	165.2	42.1	414.900675	5.39	2.427892	-166.0	-39.9	-416.37600	5.45	1.47533			
δ_L	-128.1	29.8	-412.46868	3.83	-112.8	13.2	-414.905726	2.22	2.437046	Not found							
ϵ_D	67.2	-171.9	-412.46177	8.16	Not found												
ϵ_L	Not found																
γ_D	74.0	-57.4	-412.47075	2.53	75.3	-55.4	-414.905223	2.54	2.434473	74.4	-49.1	-416.38120	2.19	1.47597			
γ_L	-84.5	67.3	-412.47478	0.00	-86.2	78.8	-414.909271	0.00	4.434490	-82.8	80.6	-416.38470	0.00	1.47543			

^a In hartree.

^b In kcal mol⁻¹.

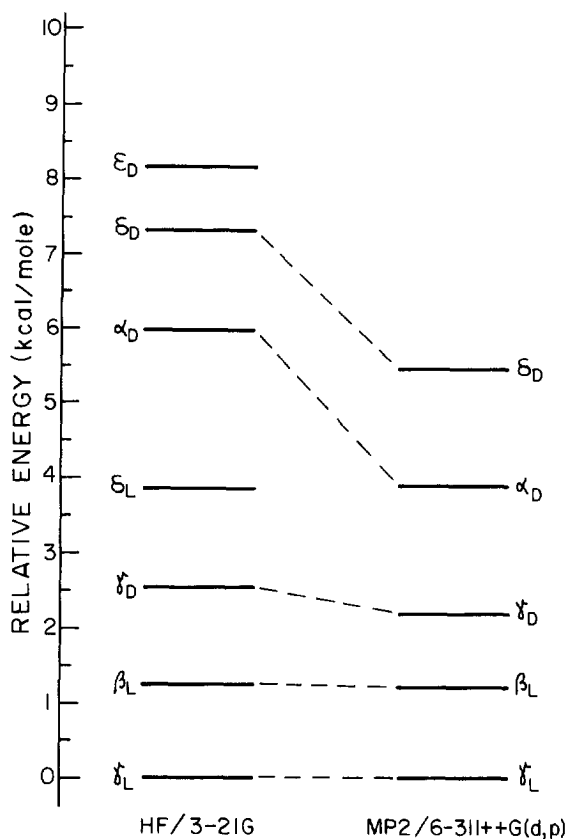


Fig. 5. The shift of relative energy values of all optimized conformations of For-Ala-NH₂ from the HF/3-21G to MP2/6-311++G(d,p) level of theory.

level of theory. Usually the simpler basis sets tend to compensate for the deficiency of the HF method and can give results quite close to the experimental values and to the results obtained at a much higher correlated level of theory. The results in Table 4 show that while the change in bond angles is not always in the same direction one can clearly see that at most of the basis set levels the HF calculations usually provide shorter bond lengths than the corresponding MP2 calculation. This effect is more visible at the chain ends, and less evident for internal bonds where the dihedral interactions may compensate the general bond shortening.

In Table 5 the effects of the geometry optimizations are summarized. Because of the high cost of the HF and MP2 geometry optimizations implemented with

large basis sets, it is always reasonable to try to optimize the molecular energy at lower level of theory and then perform a single point calculation with the extended basis sets. The idea behind this is that the energy decrease due to the basis set effects is nearly constant in a limited range around the minima because both energy hypersurfaces are flat here. Thus if the equilibrium geometries at the higher and lower level of theories are consistently in the same range, the energy differences calculated without further geometry optimizations will approximate well the true, i.e. large basis set, energy differences. The results in Table 5 show that the effect on the total energy resulting from further geometry optimization is only -0.003 or -0.004 Hartree at HF level of theory. Thus, on the basis of the above one would expect similar ΔE values between the HF/6-311++G(d,p)/HF/6-311++G(d,p) and the HF/6-311++G(d,p)/HF/3-21G calculations and this is indeed the case. In contrast to that, one would expect vastly different ΔE values between MP2/6-311++G(d,p)/MP2/6-311++G(d,p) and the MP2/6-311++G(d,p)/HF/3-21G calculations. Indeed it is remarkable that in this latter case the ΔE values are within less than $0.4 \text{ kcal mol}^{-1}$ even though the change in total energies is of the order of $100 \text{ kcal mol}^{-1}$ (-0.155 Hartree). Thus HF/3-21G optimized geometries can be used for the estimation of energy differences with correlated methods implemented with large basis sets, within the above error bars, for peptide and oligopeptide conformers. More interestingly the HF/3-21G energy differences of peptide conformers approximate well the energy differences calculated at very high levels of theory.

Acknowledgements

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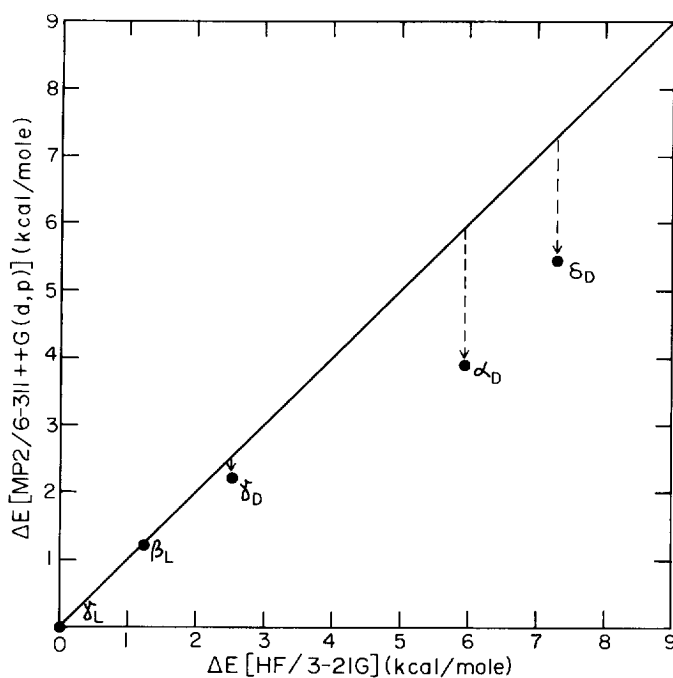


Fig. 6. The magnitude of correlation energy lowering of relative energy for the optimized conformations of For-Ala-NH₂.

Table 4
Selected geometrical parameters of HCO-NH-CH-Me-CONH₂ as a function of level of theory applied

No.	Basis set	Level	β_L			γ_L		
			N1-C1 (Å)	C1-C2 (Å)	C2-C1-N1 (°)	N1-C1 (Å)	C1-C2 (Å)	C2-C1-N1 (°)
1	3-21G	HF	1.4512	1.5222	106.39	1.4723	1.5350	109.81
		MP2	1.4681	1.5424	105.67	1.4914	1.5550	110.66
2	4-21G	HF	1.4522	1.5240	106.30			
		MP2	1.4697	1.5446	105.62	1.4928	1.5568	110.84
3	4-31G	HF	1.4460	1.5640	107.33			
		MP2	1.4643	1.5341	107.01	1.4854	1.5460	110.66
4	6-31G	HF	1.4482	1.5182	107.36	1.4662	1.5298	110.09
		MP2	1.4675	1.5370	107.09	1.4878	1.5485	110.80
5	6-31++G	HF	1.4495	1.5186	107.52	1.4661	1.5303	109.96
		MP2	1.4710	1.5337	107.31	1.4893	1.5471	110.20
6	6-31G(d,p)	HF	1.4423	1.5250	107.44			
		MP2	1.4422	1.5234	106.99	1.4599	1.5345	109.47
7	6-31++G(d,p)	HF	1.4439	1.5252	107.62	1.4585	1.5361	109.64
		MP2	1.4453	1.5223	107.31	1.4610	1.5349	109.02
8	6-311G	HF	1.4482	1.5155	107.51	1.4656	1.5270	109.94
		MP2	1.4625	1.5267	107.35	1.4817	1.5376	110.01
9	6-311++G	HF	1.4487	1.5163	107.59	1.4655	1.5282	110.05
		MP2	1.4649	1.5249	107.49	1.4830	1.5384	109.81
10	6-311G(d,p)	MP2	1.4423	1.5260	107.23	1.4594	1.5368	109.22
11	6-311++G(d,p)	HF	1.4441	1.5256	107.53	1.4584	1.5364	109.56
		MP2	1.4443	1.5245	107.53	1.4597	1.5371	109.13

Table 5

The basis set and geometry optimization effects on the energy differences between various conformations of HCO–NH–CH–Me–CONH₂

Conformation	HF/6-311++G(d,p)				MP2/6-311++G(d,p)			
	Optimized		HF/3-21G geometry		Optimized		HF/3-21G geometry	
	E^a	ΔE^b	E^a	ΔE^b	E^a	ΔE^b	E^a	ΔE^b
α_D	-414.902009	4.56	-414.898017	4.90	-416.378508	3.88	-416.223174	4.25
α_L	–	–	–	–	–	–	–	–
β_L	-414.909098	0.11	-414.905789	0.02	-416.382776	1.20	-416.227822	1.33
β_D	-414.900675	5.39	-414.896793	5.67	-416.376003	5.45	-416.220719	5.79
δ_L	-414.905726	2.22	-414.902639	2.00	–	–	-416.225329	2.89
ϵ_D	–	–	-414.895836	6.27	–	–	-416.219606	6.48
ϵ_L	–	–	–	–	–	–	–	–
γ_D	-414.905223	2.54	-414.901673	2.60	-416.381196	2.20	-416.226826	1.95
γ_L	-414.909271	0.00	-414.905824	0.00	-416.384696	0.00	-416.229940	0.00

^a In hartree.^b In kcal mol⁻¹.

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