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Conformational Analysis of 1,2-Ethanediamine and 1,3-Propanediamine by CFF, PCILO and *ab initio* Methods

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Ten equilibrium conformations of 1,2-ethanediamine (en) and twenty-five of 1,3-propanediamine (tn) were calculated using convergent energy minimisation, both with a potential energy function (PEF) which has proven its value for coordinated amines, and with the semirigorous quantum mechanical method PCILO. All conformers of en and four selected conformers of tn, in the geometries produced by PEF computations, were also analysed with *ab initio* molecular orbital theory (extended 6 −31 G basis set). Conformational predictions of molecular geometries made with PEF are in better agreement with available experimental data than those made by PCILO. There are noticeable differences in the Boltzmann populations, not only as regards the single conformers, but also the "gross" conformations defined by the central torsions only: At this level, the agreement between PEF and *ab initio* is closer than between either and PCILO. This leads to the prediction that tn exists in an AG "gross" conformation or as a mixture of AG and GG'.

As a preliminary to the development of a potential energy function (PEF) for amines by the Consistent Force Field (CFF),[1] we have calculated the equilibrium conformations (conformers) of 1,2-ethanediamine (en) and 1,3-propanediamine (tn), using convergent energy minimisation in a well-tried PEF, and with PCILO. In addition, all en conformers and selected conformers of tn are studied by *ab initio* calculations using GAUSSIAN-70.

Our ultimate goal is a CFF for linear and cyclic saturated polyamines. Such work requires a good initial parameter set for the PEF, and experience has shown that proper modelling of non-bonded interactions is crucial, and that *ab initio* calculations may be of help in this particular problem. We have previously made such studies for several molecules; in a rather conventional way using the total SCF energy for each of a number of conformations[2] and, in a more economical way[3,4] using Bond Energy Analysis (BEA).[5,6] The present work provides a comparison between CFF and PCILO for calculation of conformer geometry and relative energy, with *ab initio* as a check on the latter. At the same time this study gives data for a subsequent development of a better PEF.

The two primary diamines en and tn (using the spectrochemical abbreviations accepted in coordination chemistry) were chosen as model substances in this initial study for a number of reasons. (1) They represent systems with large though manageable numbers of conformers; (2) they show intramolecular hydrogen bonding; (3) they are of prime importance in coordination chemistry; (4) we already have a reasonable PEF which has proven its worth in many calculations on tris-(diamine) coordination complexes.[7]

The presence of hydrogen bonding means that we should include Coulomb interactions in the modelling of non-bonded interactions.[8] We intend to do so in the monopole approximation which has worked well in many cases.[9]

The scope of the present work is thus to test the existing PEF towards PCILO results, with geometry optimisation, and to use *ab initio* results to check the PEF and PCILO results for selected conformers; to estimate fractional atomic charges for later use as PEF parameters; and to obtain data for analytic functions for non-bonded interactions.

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PREVIOUS WORK

Theoretical conformational analysis on en has been performed before. Jhon *et al.* made an extended Hückel study;[10] using fixed bond lengths and valence angles they calculated the energies of all ten conformers and all saddle points with respect to torsion around the C–C bond. The C–C torsional angle was varied in steps of 60°, and no geometry optimisation was attempted.

Concurrent with this work, Hadjiliadis *et al.* also made an extended Hückel study on one *anti* and one *gauche* conformer,[11] using a fixed valence geometry, and varying the C–C torsion in steps of 20° and, near the minima, in steps of 2°. To some extent, the C–N torsions were also varied. Thus a certain amount of geometry optimisation was done.

Shortly after, Graffeuil *et al.* published a CNDO/2 study,[12] in which they mapped the entire torsional space of three torsions in steps of 60°, still with fixed valence geometry. They calculated further the equilibrium distribution over the six conformers of lowest energy, neglecting statistical weights and all degrees of freedom except the three torsions. Based on this, they got an average dipole moment in good agreement with the experimental.

Recently, Zahradnik *et al.* reported another CNDO/2 study,[13] in which they used geometry optimisation on bond lengths and angles for a number of conformers. They list energies and some bond angles of twelve conformations, some of them eclipsed.

Radom *et al.* undertook the first *ab initio* study,[14] using GAUSSIAN-70 with the 4-31G extended basis set. They calculated the energies of all ten conformers using standard geometry and found two G conformers to be well below the others on the energy scale.

The next attempt at an extensive conformational analysis was made by Cetina *et al.* who used PCILO to study eight of the ten conformers of en plus a large number of other conformations.[15] In this way they were able to plot sections of the Born-Oppenheimer (BO) surface in conformational space. They give the total energies and the conformational energy differences, and the C–C torsional angles of some conformers, but no further data. Unfortunately, there are inconsistencies between energy values in figures and in the table.

Finally, a preliminary *ab initio* study was made with MOLECULE by Johansen and Hald.[16] They studied only one *gauche* conformer, with fixed geometry, except for using three values of the C–C torsion near the experimental value. Unfortunately, they chose, for reasons of economy, a structure with C_2 symmetry, which has a rather high energy

Table 1. Experimentally determined conformers of 1,2-ethanediamine.[a]

Ref.	19		20		21
Method	ED, r_g, r_α		MV, r_o		X
Temp. (°C)	−118		−30		−60
Conformer	−G−	GGG′		AGG′	AAA
CC	1.545(8)		1.546[b]		1.51(2)
CN	1.469(4)		1.469[b]		1.47(1)
CH	1.109(10)		1.093[b]		1.015[c] (135)
NH	1.0302[b]		1.017[b]		0.865[c] (135)
CCN	110.2(7)	109.0(10)		111.5(10)	114.5(10)
CNH	112.1[b]		109.48[b]		106.5(40)
NCH	–		–		110[c] (4)
CCH	111.9(46)		109.48[b]		107[c] (4)
HNH	105.9[b]		109.48[b]		102 (6)
HCH	112.7(85)		109.48[b]		108 (6)
NCCN	64.0(45)	63(2)		63(2)	180 (0)
lpNCC[b]	81, −160 or −52(9)	60,[b] −60[b]		180,[b] −60[b]	
μ		1.770(33)		2.203(6)	
Population		0.64(5)		0.36(5)	

[a] Bond lengths in Ångström, angles in degree, dipole moments in Debye. [b] Assumed and fixed. [c] Average. [d] A torsional angle involving a lone pair, such as C–C–N–lp, is defined as the supplement to the angle halving the two C–C–N–H torsional angles around the same N–C bond.

relative to the conformers found by previous workers using simpler programs. They used GTO, (7*s* 3*p*) contracted to ⟨4*s* 2*p*⟩ for N and C, taken from Roos and Siegbahn,[17] and (4*s*) contracted to ⟨2*s*⟩ for H, taken from Huzinaga.[18]

No theoretical study seems to have appeared on the conformations of tn.

EXPERIMENTAL BACKGROUND

The conformation of en is well-known in both gaseous and crystalline phases.

Yokozeki and Kuchitsu derived the r_g structure from gas phase electron diffraction.[19] They found a *gauche* conformer with a C−C torsional angle of 64°, any other conformer being present to less than 5%. Their results are reproduced in Table 1.

Marstokk and Møllendal made a penetrating study of the microwave spectrum.[20] In spite of having only one isotopomer they managed to derive such crucial conformational details as the CCN angle and the CC torsion for two very similar *gauche* conformers. Their dipole moments were also determined. From intensity measurements, relative populations and thence K and ΔG were derived. Those data important to the present study are reproduced in Table 1.

In the crystal, en takes the *anti* conformation, as found by Jamet-Delcroix.[21] Her results are also cited in Table 1.

CFF CALCULATIONS

The ten conformers of en were constructed with the CFF program and minimised in a PEF

Table 2. Energies and populations of 1,2-ethanediamine conformers. Energy in kJ mol^{-1}.

No.	Conformer	Stat. wt.	CFF ΔE	CFF ΔE + st.wt.	CFF ΔG	PCILO ΔE	PCILO ΔE + st.wt.	PCILO[15] ΔE	4-31G[14] ΔE	4-31G[14] ΔE + st.wt.
1	AAA	1	0.064	3.470	5.428	15.431	18.868	18.368	9.205	12.642
2	AAG	4	0.031	0.000	0.000	11.125	11.125	10.753	6.862	6.862
3	GAG	2	0.000	1.688	3.174	2.770	4.489	3.013	5.439	7.157
4	GAG′	2	0.052	1.740	1.530	3.013	4.732	2.552	4.770	6.488
5	AGA	2	1.839	3.527	5.876	13.740	15.459	0.753	16.443	18.161
6	AGG	4	2.241	2.210	2.492	9.188	9.188	–	13.012	13.012
7	AGG′	4	0.042	0.011	0.340	8.611	8.611	6.736	0.000	0.000
8	GGG	2	2.429	4.117	5.886	1.130	2.849	0.000	8.452	10.170
9	GGG′	4	0.127	0.096	0.196	0.000	0.000	15.565	1.088	1.088
10	G′GG′	2	0.017	1.705	3.313	0.916	2.521	–	24.560	26.278
	ΣXAX									
	ΣXGX									

No.	6-31G ΔE	6-31G ΔE + st.wt.	CFF $n(\Delta E$ + st.wt.)	CFF $n(\Delta G)$	PCILO $n(\Delta E)$	PCILO $n(\Delta E$ + st.wt)	4-31G[14] $n(\Delta E$ + st.wt.)	6-31G $n(\Delta E$ + st.wt.)	Exp.[20] n
1	6.602	10.039	0.04	0.03	0.00	0.00	0.00	0.01	
2	5.611	5.611	0.18	0.22	0.00	0.01	0.03	0.06	
3	5.763	7.482	0.09	0.06	0.11	0.08	0.03	0.02	
4	5.167	6.886	0.09	0.12	0.10	0.07	0.04	0.03	
5	5.891	7.610	0.04	0.02	0.00	0.00	0.00	0.02	
6	5.550	5.550	0.07	0.08	0.01	0.01	0.00	0.06	
7	0.000	0.000	0.18	0.19	0.01	0.01	0.54	0.53	0.36
8	4.945	6.664	0.03	0.02	0.21	0.15	0.01	0.04	
9	2.106	2.106	0.17	0.20	0.33	0.49	0.35	0.23	0.64
10	25.006	26.725	0.09	0.06	0.23	0.18	0.00	0.00	
			0.40	0.43	0.21	0.16	0.10	0.12	0.00
			0.58	0.57	0.79	0.84	0.90	0.88	1.00

Table 3. Conformers of 1,2-ethanediamine from CFF calculations.

No.	Conformer	N–H	C–H	C–C	N–C	N–C–C	C–N–H	N–C–H	C–C–H	H–N–H	H–C–H	lp–N–C–C	N–C–C–N	C–C–N–lp	σ
1	AAA	1.012	1.094	1.548	1.475	110.6	110.6	109.2	109.6	109.7	108.6	−178.5	180.0	178.5	2
2	AAG	1.012	1.094	1.547	1.475	110.3	110.5	109.3	109.5	109.6	108.7	−178.4	−179.1	62.7	1
3	GAG	1.012	1.095	1.546	1.474	110.0	110.4	109.5	109.5	109.3	108.9	62.1	−178.3	63.7	2
4	GAG′	1.012	1.095	1.546	1.474	110.0	110.3	109.5	109.5	109.2	108.9	62.1	180.0	−62.1	1
5	AGA	1.011	1.094	1.550	1.475	111.7	111.1	109.1	109.3	110.2	108.2	173.3	62.9	167.8	2
6	AGG	1.011	1.094	1.549	1.475	111.5	110.8	109.2	109.2	109.6	108.4	173.1	64.9	167.8	1
7	AGG′	1.012	1.094	1.548	1.475	110.6	110.5	109.0	109.4	109.4	108.5	180.0	60.8	−61.9	1
8	GGG	1.011	1.094	1.548	1.475	111.2	110.5	109.4	109.1	108.8	108.6	71.8	66.1	72.5	2
9	GGG′	1.012	1.094	1.547	1.475	110.4	110.3	109.5	109.4	109.1	108.7	63.1	61.9	−61.9	1
10	G′GG′	1.012	1.094	1.546	1.475	110.1	110.4	109.5	109.4	109.4	108.7	−63.3	58.8	−61.6	2

Table 4. Conformers of 1,2-ethanediamine from PCILO calculations.

No.	Conformer	N–H	C–H	C–C	N–C	N–C–C	C–N–H	N–C–H	C–C–H	lp–N–C–C	N–C–C–N	C–C–N–lp	μ	μ(6–31G)
1	AAA	1.083	1.139	1.485	1.424	115.9	110.3	108.1	110.8	179.5	180.0	180.0	0.079	0.000
2	AAG	1.083	1.139	1.486	1.423	113.7	110.2	108.5	110.2	−179.1	179.9	60.3	3.048	2.833
3	GAG	1.082	1.140	1.484	1.421	111.8	110.4	110.3	110.8	58.9	−178.7	59.6	3.021	2.742
4	GAG′	1.083	1.140	1.484	1.422	111.7	110.4	110.3	110.8	58.9	−179.4	−58.4	0.098	0.000
5	AGA	1.083	1.139	1.486	1.425	115.8	110.4	107.9	110.5	176.1	57.2	−177.5	0.752	0.214
6	AGG	1.083	1.139	1.484	1.423	113.7	110.3	108.4	110.4	175.5	59.0	60.9	2.976	2.837
7	AGG′	1.082	1.139	1.485	1.424	113.1	110.2	108.5	110.7	179.6	54.6	−60.7	2.775	2.868
8	GGG	1.083	1.139	1.484	1.423	111.7	110.4	110.1	110.9	54.8	58.4	58.2	0.300	0.088
9	GGG′	1.083	1.139	1.483	1.422	110.9	110.4	110.3	111.1	59.1	54.7	−58.6	2.888	2.731
10	G′GG′	1.083	1.139	1.483	1.422	111.0	110.4	110.3	111.0	−58.4	54.0	−59.2	2.542	2.761

Table 5. Energies and populations of 1,3-propanediamine conformers. Energy in kJ mol^{-1}.

No.	Conformer	Stat. wt.	CFF ΔE	CFF ΔE + st.wt.	CFF ΔG	PCILO ΔE	PCILO ΔE + st.wt.	6−31G ΔE	6−31G ΔE + st.wt.	CFF $n(\Delta E$ + st.wt.)	CFF $n(\Delta G)$	PCILO $n(\Delta E$ + st.wt.)	6−31G $n(\Delta E$ + st.wt.)
1	AAAA	1	0.108	3.483	3.697	21.690	25.127			0.03	0.03	0.00	
2	AAAG	4	0.092	0.058	0.000	17.640	17.640	1.790	1.790	0.10	0.12	0.00	0.25
3	GAAG	1	0.072	3.495	4.892	9.661	13.098			0.03	0.02	0.00	
4	GAAG′	2	0.078	1.763	1.464	9.623	11.342			0.05	0.07	0.01	
5	AG′AA	4	2.095	2.061	2.723	20.184	20.184			0.04	0.04	0.00	
6	G′G′AA	4	2.570	2.536	2.844	14.949	14.949			0.04	0.04	0.00	
7	GG′AA	4	0.071	0.037	0.308	15.042	15.042			0.10	0.11	0.00	
8	AG′AG′	4	2.129	2.095	2.410	16.096	16.096			0.04	0.04	0.00	
9	G′G′AG′	4	2.601	2.567	2.627	7.874	7.874			0.04	0.04	0.03	
10	GG′AG′	4	0.076	0.042	0.073	7.699	7.699			0.10	0.12	0.03	
11	AG′AG	4	1.995	1.961	2.388	16.138	16.138			0.05	0.05	0.00	
12	G′G′AG	4	2.465	2.431	2.508	7.828	7.828			0.04	0.04	0.03	
13	GG′AG	4	0.034	0.000	0.027	7.958	7.958	0.000	0.000	0.10	0.12	0.03	0.50
14	AG′G′A	2	3.941	5.626	9.452	18.163	19.882			0.01	0.00	0.00	
15	AG′G′G′	4	4.184	4.150	5.850	14.117	14.117			0.02	0.01	0.00	
16	AG′G′G	4	1.797	1.763	2.631	13.715	13.715			0.05	0.04	0.00	
17	G′G′G′G′	2	4.750	6.435	9.511	6.180	7.899			0.01	0.00	0.03	
18	G′G′G′G	4	2.277	1.803	2.749	5.690	5.690			0.05	0.04	0.07	
19	GG′G′G	2	0.000	1.685	3.785	5.782	7.501	1.931	3.650	0.05	0.03	0.03	0.12
20	AG′GA	2	12.873	14.558	16.711	24.870	26.589			0.00	0.00	0.00	
21	AG′GG′	4	4.183	4.149	5.427	8.000	8.000			0.02	0.01	0.03	
22	AG′GG	4	12.991	12.957	14.371	20.179	20.179			0.00	0.00	0.00	
23	G′G′GG′	4	4.791	8.194	5.252	0.000	0.000	3.442	3.442	0.00	0.01	0.68	0.13
24	G′G′GG	2	12.874	14.499	15.644	11.715	13.434			0.00	0.00	0.00	
25	GG′GG′	2	0.883	2.568	3.287	6.226	7.945			0.04	0.03	0.03	
	Σ XAAX									0.20	0.23	0.01	0.25
	Σ XAGX									0.55	0.59	0.12	0.50
	Σ XGGX									0.19	0.12	0.13	0.12
	Σ XGG′X									0.06	0.06	0.74	0.13

Table 6. Conformers of 1,3-propanediamine from CFF calculations.

No.	Conformer	N–H	C–H	C–C	N–C	N–C–C	C–C–C	C–N–H	N–C–H
1	AAAA	1.012	1.094	1.548	1.475	110.6	110.3	110.7	109.1
2	AAAG	1.012	1.094	1.547	1.475	110.2	110.3	110.6	109.3
3	GAAG	1.012	1.094	1.546	1.474	109.9	110.4	110.4	109.4
4	GAAG′	1.012	1.094	1.546	1.474	109.9	110.4	110.4	109.4
5	AG′AA	1.012	1.094	1.549	1.475	111.1	111.6	111.0	109.0
6	G′G′AA	1.012	1.094	1.549	1.475	110.8	111.7	110.7	109.1
7	GG′AA	1.012	1.094	1.548	1.475	110.5	110.6	110.5	109.3
8	AG′AG′	1.012	1.094	1.549	1.475	110.8	111.6	110.9	109.1
9	G′G′AG′	1.012	1.094	1.548	1.475	110.6	111.7	110.8	109.3
10	GG′AG′	1.012	1.094	1.547	1.475	110.2	110.7	110.4	109.4
11	AG′AG	1.012	1.094	1.549	1.475	110.8	111.6	110.9	109.1
12	G′G′AG	1.012	1.094	1.548	1.475	110.5	111.7	110.6	109.1
13	GG′AG	1.012	1.094	1.547	1.475	110.2	110.7	110.4	109.4
14	AG′G′A	1.011	1.094	1.551	1.475	111.9	113.1	111.2	109.1
15	AG′G′G	1.011	1.094	1.551	1.475	111.6	113.1	111.1	109.2
16	AG′G′G	1.012	1.094	1.549	1.475	111.1	112.0	110.9	109.3
17	G′G′G′G′	1.011	1.094	1.550	1.475	111.4	113.3	110.5	109.4
18	G′G′G′G	1.012	1.094	1.549	1.475	110.9	112.1	110.6	109.4
19	GG′G′G	1.012	1.094	1.548	1.475	110.4	111.0	110.4	109.5
20	AG′GA	1.011	1.094	1.552	1.476	112.4	112.9	111.2	109.4
21	AG′GG′	1.012	1.094	1.550	1.475	111.9	112.5	110.6	109.1
22	AG′GG	1.011	1.094	1.551	1.476	111.9	112.9	111.0	109.1
23	G′G′GG′	1.012	1.094	1.550	1.475	111.5	112.6	110.5	109.3
24	G′G′GG	1.011	1.094	1.551	1.475	111.6	112.9	110.8	109.2
25	GG′GG′	1.012	1.094	1.549	1.475	110.9	111.4	110.3	109.4

developed for use with coordination complexes of diamines.[7]

The 25 conformers of tn were constructed by removal of a hydrogen atom from each methyl group of the four conformers of n-pentane, which were available from a previous study.[9] They were then minimised in the same PEF.

The nomenclature of the conformers may be exemplified by tn conformer No. 4 GAAG′: lone-pair1 *gauche* to C2, N1 *anti* to C3, C1 *anti* to N2, C2 minus- *gauche* to lone-pair2. For tn conformers No. 5–25 the names in Table 6 of Niketić and Rasmussen[7] represent the mirror images of the actual conformers.

Detailed results on energy terms for these two series are given by Niketić and Rasmussen,[7] and relative energies, free enthalpies and conformer populations are reproduced in Tables 2 and 5. Geometric details are given in Tables 3 and 6.

QUANTUM MECHANICAL CALCULATIONS

(a) Preliminary comments. Before exposing our quantum mechanical computations, a brief discussion on their interplay with CFF appears in order. As remarked by Gund *et al.*[22] *ab initio* is a deductive method which describes the average disposition of electrons about an assemblage of fixed nuclei, according to the Schrödinger equation: it therefore aims at the *electronic* level of the BO approximation. CFF is an inductive method, which finds the positions of atomic nuclei, through a common analytical representation of their motion in a field of fast-moving electrons: it therefore aims at the *nuclear* level of the BO approximation. PCILO, like all other semirigorous quantum methods containing empirical parameters, is partly inductive. This distinction should be borne in mind when comparing results on a class of molecules obtained with all of these approaches.

A second point which deserves careful attention is that such a comparison is hampered by the fact that

C–C–H	H–N–H	H–C–H	lp–N–C–C	N–C–C–C	C–C–C–N	C–C–N–lp	σ
109.5	109.7	108.7	−178.5	−180.0	180.0	178.5	2
109.5	109.6	108.8	−178.4	−179.9	−179.2	58.1	1
109.5	109.5	108.9	58.2	−179.2	−179.2	58.2	2
109.5	109.5	108.9	58.1	−179.2	179.2	−58.1	1
109.4	110.2	108.5	−173.5	−63.4	−175.9	179.7	1
109.4	109.5	108.5	−53.4	−65.5	−175.7	179.7	1
109.5	109.6	108.6	58.3	−61.0	−179.5	179.3	1
109.4	110.1	108.6	−173.4	−63.4	−176.6	−58.0	1
109.3	109.4	108.6	−53.4	−65.5	−176.4	−57.9	1
109.4	109.5	108.6	58.3	−61.1	179.8	−58.1	1
109.4	110.1	108.6	−173.5	−63.2	−174.0	58.2	1
109.3	109.4	108.7	−53.5	−65.3	−174.8	58.2	1
109.4	109.5	108.7	58.3	−61.0	−178.6	58.2	1
109.2	109.5	108.7	−173.1	−58.8	−59.7	−175.6	2
109.2	110.1	107.9	−172.9	−58.7	−66.7	−53.2	1
108.2	110.2	108.1	−173.4	−61.7	−56.6	58.3	1
109.1	109.4	108.0	−52.9	−60.1	−60.1	−52.9	2
109.3	109.4	108.2	−53.3	−63.6	−56.4	58.3	1
109.4	109.5	108.5	58.2	−60.2	−60.2	58.2	2
109.2	110.0	107.9	178.0	−93.6	60.9	173.2	1
109.1	109.5	108.1	−172.9	−63.3	71.9	−58.1	1
109.1	109.6	108.0	176.8	−92.4	59.3	48.1	1
109.1	109.3	108.3	−50.1	−64.7	71.8	−59.0	1
109.1	109.4	108.1	−59.3	−93.0	59.2	48.3	1
109.3	109.2	108.4	59.0	−64.1	64.1	−59.0	1

each method has its own equilibrium values for any kind of intramolecular force, which in general do not coincide with those of the others. For example, in the CFF case, equilibrium values are calculated through a parameter set chosen and fitted in such a way as to reproduce values derived from experimental measurements of conformational quantities with the best possible accuracy. For this reason, CFF predictions of molecular geometries are highly reliable. This is not the case with the PCILO method in CNDO Hamiltonian approximation, which tends to grossly overestimate bond lengths between heavy ($Z>1$) and hydrogen atoms, and to underestimate bond lengths between heavy atoms. Moreover, for a given displacement of a bond length from its equilibrium value, the PCILO restoring force is consistently stronger than with usual PEF's used in the CFF context.[23] In consequence, the narrow scatter of final bond lengths and angles observed in conformers minimised in a PEF, which gives very small contributions to stretching and bending energies, would give rise to fairly large contributions, should we analyse these geometries with PCILO, thus obscuring the order of stability due to torsion. Hence the need for a particular strategy in the PCILO computations, which will be discussed later. This phenomenon should be present in *ab initio* computations to a negligible extent only, since, in general, equilibrium values resulting from all-electron computations are in nice agreement with experiments. A direct computation on geometries produced by CFF minimisation is therefore meaningful.

The results are clearly subject to the errors inherent in this approximation. Complete *ab initio* energy minimisation with respect to all internal degrees of freedom should give the most accurate results, but this is at present too expensive. In addition, the use of the flexible rotor approach, instead of the rigid rotor, has in general a marked effect on the relative energies of maxima and minima of internal rotation curves, but affects little the energy differences between the various minima.

(b) PCILO calculations. There are three main

Table 7. Conformers of 1,3-propanediamine from PCILO calculations.

No.	Conformer	N–H	C–H	C–C	N–C	N–C–C	C–C–C	C–N–H
1	AAA	1.083	1.139	1.486	1.426	116.5	113.4	110.4
2	AAAG	1.083	1.140	1.485	1.424	114.5	114.0	110.3
3	GAAG	1.082	1.140	1.486	1.422	112.2	113.7	110.5
4	GAAG′	1.082	1.140	1.485	1.423	112.0	113.9	110.4
5	AG′AA	1.083	1.140	1.486	1.424	116.6	113.9	110.4
6	G′G′AA	1.083	1.140	1.486	1.424	114.4	114.0	110.5
7	GG′AA	1.084	1.139	1.486	1.424	114.4	113.9	110.5
8	AG′AG′	1.083	1.140	1.486	1.424	114.4	113.9	110.4
9	G′G′AG′	1.083	1.140	1.486	1.423	112.0	113.8	110.5
10	GG′AG′	1.083	1.140	1.486	1.423	111.9	113.5	110.6
11	AG′AG	1.084	1.140	1.485	1.424	114.4	114.1	110.4
12	G′G′AG	1.083	1.140	1.486	1.423	112.0	113.8	110.6
13	GG′AG	1.083	1.140	1.486	1.422	112.0	113.5	110.7
14	AG′G′A	1.084	1.139	1.487	1.424	116.9	114.2	110.6
15	AG′G′G′	1.085	1.139	1.486	1.424	114.7	114.4	110.4
16	AG′G′G	1.083	1.139	1.486	1.425	114.4	113.6	110.2
17	G′G′G′G′	1.083	1.140	1.487	1.423	112.5	114.1	110.6
18	G′G′G′G	1.083	1.139	1.486	1.423	112.1	113.5	110.4
19	GG′G′G	1.083	1.139	1.485	1.423	111.8	113.2	110.5
20	AG′GA	1.084	1.139	1.487	1.425	116.8	113.7	110.5
21	AG′GG′	1.085	1.139	1.486	1.426	114.3	113.3	110.0
22	AG′GG	1.083	1.139	1.486	1.426	114.5	113.8	110.4
23	G′G′GG′	1.085	1.139	1.488	1.424	112.0	113.3	110.2
24	G′G′GG	1.083	1.139	1.487	1.422	112.1	114.0	110.5
25	GG′GG′	1.083	1.139	1.486	1.424	112.0	113.0	110.5

reasons for the preference we give to PCILO over other quantum–mechanical techniques.

(1) This method, although semirigorous, was claimed to be extremely reliable for angular conformational analysis,[24] especially due to the fact that, thanks to a limited configuration interaction, it takes account, to some extent, of correlation effects.

(2) We have available a version[25] which is a special implementation of the standard QCPE version,[26] in that a minimisation routine, based on the Powell algorithm,[27] was inserted into the program, thus enabling it to compute directly not only the energy of a molecule in a certain geometry, but also the whole set of energies along the descent pathway towards the nearest minimum on the conformational energy hypersurface.

(3) Because it avoids the time-consuming SCF step, PCILO is much faster than any other quantum–mechanical program with comparable performances.

By now, our version of PCILO is dimensioned to treat a maximum of 9 different internal degrees of freedom simultaneously, whether bond lengths or valence angles or internal rotation angles. Since the number of variables both in en and in tn exceeds 9, a complete minimisation cannot be performed in a single run. We therefore devised a minimisation strategy based on a three–step procedure. Taking as starting geometries the coordinates produced by CFF minimisation, we first optimised all bond lengths (C–C, C–N, C–H, N–H) and four bond angles (N–C–C, N–C–H, C–N–H, C–C–H for en, and C–C–C, C–C–N, C–N–H, C–C–H for tn), with torsions kept fixed; then we optimised, on the conformations yielded by the first step, internal rotation angles at fixed valence geometry; finally a re-optimisation of bond lengths and angles was made. Results are given in Tables 4 and 7. The gain in energy is large in the first step (on average, 150 kJ mol^{-1} for en and 180 kJ mol^{-1} for tn) and small both in the second (2 kJ mol^{-1}) and in the third (0.1 kJ mol^{-1}). This is explained by the fact already mentioned, and illustrated quantitatively by Tables 3 and 4, and 6 and 7, that PCILO equilibrium values of bond lengths and, to a much smaller extent, of bond angles are different from those resulting

C–C–H	lp–N–C–C	N–C–C–C	C–C–C–N	C–C–N–lp	μ	μ(6–31G)
110.5	−179.5	−180.0	180.0	180.0	2.844	
110.4	180.0	−179.9	−179.2	60.0	2.149	2.028
110.6	60.0	−177.0	−178.7	60.0	1.611	
110.7	60.1	−177.0	−179.1	−60.1	3.485	
110.5	176.9	−63.1	−179.1	−179.5	2.444	
110.6	−61.7	−67.4	−179.3	−179.7	1.721	
110.5	61.5	−58.7	179.4	180.0	3.754	
110.6	178.8	−63.4	179.6	−60.5	2.058	
110.8	−60.1	−67.7	−176.8	−59.0	3.440	
110.7	60.5	−58.8	178.3	−59.6	1.798	
110.7	179.5	−63.0	−179.1	62.0	2.533	
110.8	−60.0	−67.4	−178.9	60.3	2.139	
110.8	59.5	−58.6	−178.5	60.3	2.236	2.014
110.5	−179.8	−57.7	−56.8	179.9	1.697	
110.6	−179.5	−57.9	−56.1	−59.3	2.435	
110.6	−179.7	−61.4	−53.2	60.6	3.627	
110.6	−58.9	−61.5	−59.4	−59.4	2.252	
110.7	−59.3	−65.6	−56.3	60.2	2.136	
110.8	58.9	−57.7	−56.5	60.0	2.032	1.703
110.7	179.8	−92.6	57.9	180.0	2.141	
110.7	163.4	−62.2	58.9	−55.2	4.013	
110.8	179.1	−91.5	55.6	57.5	1.945	
110.7	−68.3	−66.7	60.3	−55.5	2.570	2.006
110.9	−61.5	−94.6	55.8	55.5	3.259	
110.5	−61.0	−61.7	55.3	−59.9	2.190	

from CFF computations (N–H and C–H lengths are higher by *ca.* 7 and 4%, and C–C and C–N lengths are lower by *ca.* 4%).

(c) Ab initio *calculations. Ab initio* calculations were carried out using GAUSSIAN-70 with the extended 6–31 G basis set.[28] In addition to the ten conformers of en, four selected conformers of tn (Nos. 2, 13, 19 and 23), chosen in such a way as to be representative of all possible pairs of central rotations (AA, AG, GG, GG'), were analysed. The results are shown in Tables 2 and 5. The absolute energy of the most stable conformer of en (AGG') is −189.184101 hartree (0.2 hartree closer to the Hartree-Fock limit than the energy reached with the 4–31 G basis set[14]), and of tn (GG'AG) is −228.200043 hartree.

DISCUSSION

Energy and population. In Tables 2 and 5 we list also the relative energies ΔE corrected for statistical weight, and conformer populations based on these. In this way, statistical summation over internal degrees of freedom is left out, which introduces some error. This is not too serious, because the differences between conformers are modest, as judged from CFF calculations of populations based on ΔE and ΔG, and certainly much lower than the rather large energy differences emerging from the quantum mechanical calculations. Inclusion of statistical weights is imperative in the CFF context, less so in the PCILO and the *ab initio* because of the much higher energy differences.

One important difference between the CFF and the quantum mechanical calculations is the complete neglect of hydrogen bonding in the PEF of Niketić and Rasmussen,[7] leading to too high populations of C–C *anti* conformers. This is of no consequence in calculations on coordinated amines but unacceptable for free amines. The populations calculated from the PCILO results should be more reliable, though showing unrealistic predominance of some *G* conformations, a phenomenon already observed in n-butane.[29]

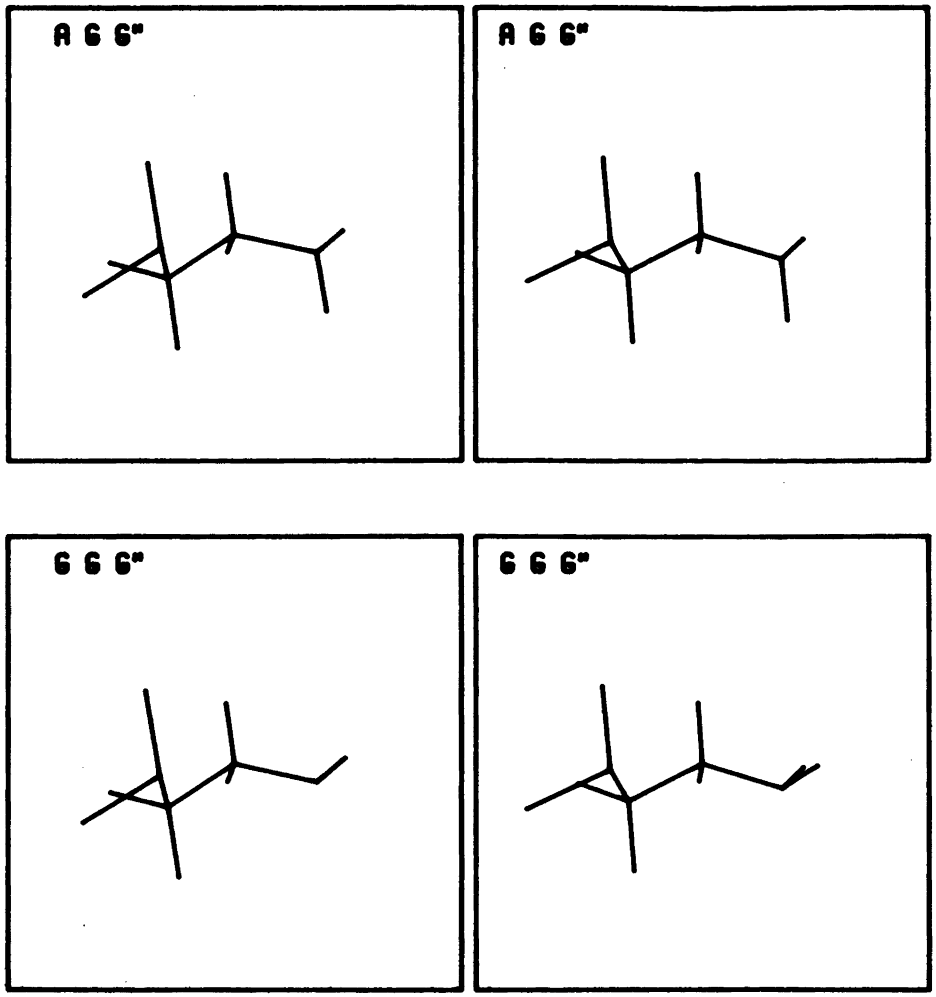

Fig. 1. The two most populated conformers of 1,2-ethanediamine.

For en we find that one conformer, No. 9 GGG′, contributes with almost half of the total to the equilibrium distribution. The overall C–C *gauche* : *anti* ratio is 0.84:0.16, in fair agreement with experimental data.

The distribution on *gauche* conformers is not quite correct in the PCILO results; only the predominance of No. 9 GGG′ is supported by experiment. In the CFF results there is a better balance between the two conformers actually found.

For tn, the pronounced population of one particular conformer is even more striking: No. 23 G′G′GG′ (or GGG′G) contributes two-thirds of the total.

For en, our CFF results on the low-energy conformers are at variance with the *ab initio* results, which are in fair agreement, except for the two conformers AGA and AGG, with those of Radom *et al.*[14] The discrepancy cannot be attributed to the use of different geometries.

Dipole moment and atomic charges. The PCILO dipole moments for the two conformers of en known from microwave measurements are 2.775 and 2.888 D, and the *ab initio* values are similar, 2.868 and 2.731 D, against the measured values 2.203 and 1.770 D. The population weighted dipole moment of en is 2.24 D (PCILO) and 2.55 D (*ab initio*); the experimental value is 1.90 D at 298 K in solution

extrapolated to zero concentration [30] and 1.96 D in the gas phase at 355 K.[31]

The population weighted PCILO dipole moment of tn is 2.52 D.

The gross atomic charges derived from the PCILO results are numerically much lower than from *ab initio* results; the averages for en are N −0.1422, C +0.1103, H(N) +0.0485, H(C) −0.0323 (PCILO) against N −0.809, C −0.118, H(N) +0.308, H(C) +0.156 (*ab initio*). Johansen and Hald[16] found N −0.7609, C −0.1400, H(N) +0.2645, H(C) +0.1859.

In tn, the charge distribution is almost the same as in en, except for the central carbon atom, +0.011 (PCILO), −0.295 (*ab initio*), and its hydrogens, −0.013 (PCILO), +0.151 (*ab initio*).

Geometry. When comparing calculated with measured geometry we see first of all that PCILO underestimates C−C and N−C bond lengths grossly, and that C−H and maybe N−H are similarly overestimated. In this respect, CFF is of course far more reliable, as it is based on empiry. For the N−C−C angle, CFF makes all conformers almost equal, whereas PCILO differentiates between the known GGG′, AGG′ and AAA in the correct sence, though giving too large values. If bond lengths could just be made proper, angles might be expected to fit perfectly.

The central torsional angle N−C−C−N is much too small in the PCILO results, but fitted to within the standard deviation by the CFF. Torsional angles in general show the same pattern in the CFF and PCILO series. The *gauche* angles are, without exception, numerically somewhat smaller in the PCILO than in the CFF results.

Stereo drawings of the two *gauche* conformers, Nos. 7 and 9, are shown in Fig. 1.

Just the same picture of the relative merits of CFF and PCILO emerges from the tn calculations. Stereo drawings of conformers Nos. 2 and 13 are shown in Fig. 2.

An observation concerning molecular symmetry may be of interest. Where the conformer name implies the presence of a symmetry element, here a twofold axis, this is, for en, not observed in any case. Nos. 1, 3, 5, 8 and 10 display lower symmetry than the theoretical C_2, and this applies to CFF as well as to PCILO calculations. Had it been the case only for CFF, we might have ascribed it to inadequacies in the PEF; as matters now stand, the effect may be real.

For tn, the picture is different. In the CFF results, Nos. 1 and 14 do not attain the theoretical C_2 symmetry, whereas Nos. 3, 17 and 19 do. In the PCILO results, no conformer has C_2 symmetry.

The deviation from C_2 symmetry is so small that it has not been taken into account in the summations over rotational degrees of freedom when calculating ΔG in the CFF context.

A comment of a general nature may be added here. It has been postulated by Ermer[32] that Newton minimisation always keeps a symmetry element present at the beginning of the minimisation. This property is certainly undesirable in a minimisation algorithm intended for general use. Therefore it is gratifying that the fault is absent from our algorithm, as has also been noted before.[7,9] Ermer's remark is of course not an error; it must pertain to a simpler algorithm which does not modify the Hessian matrix when it is not positive definite.

CONCLUSION

It would seem that CFF calculations give much better geometries than PCILO. This depends of course on the availability of an adequate PEF. In the absence of this, PCILO can give reasonable though crude estimates. If we take *ab initio* results as reference, CFF gives better relative energies than PCILO, whether we look at single conformers or at the "gross" conformations defined by chain atoms such as A and G for en. It is likely that introduction into the PEF used here[7] of an explicit term accounting for hydrogen bonding would lead to a decrease in the population of *anti* conformers and would thereby improve the agreement with *ab initio*. On this basis we predict that tn exists as an AG 'gross' conformer or as a mixture of AG and GG′.

Similar conclusions on the relative merits of CFF and PCILO were reached in work on two disaccharides.[33,34]

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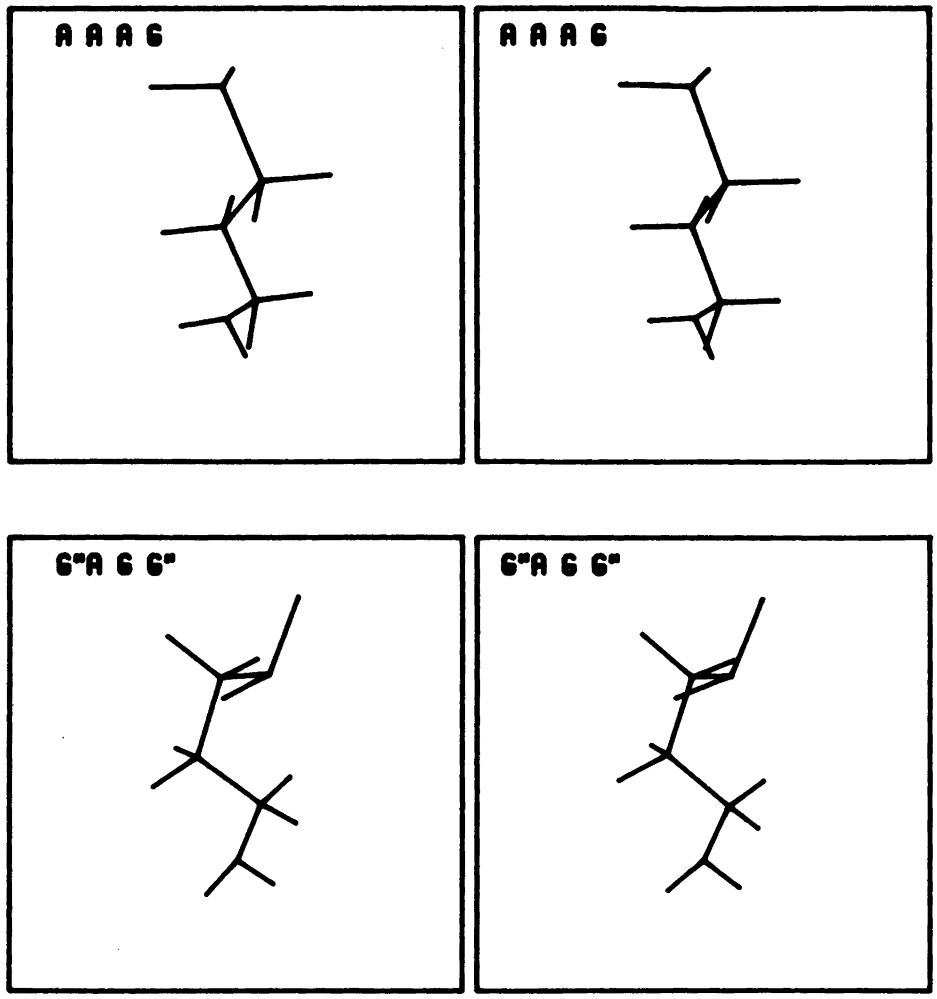

Fig. 2. Two of the most populated conformers of 1,3-propanediamine.

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