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Theoretical study of prebiotic precursors-2: about glycine, its *N*-carboxyanhydride and their protonated ions

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Abstract: This study was motivated by the fact that some amino acids are currently identified in carbonaceous chondrites but none are yet observed in the interstellar medium. The question of the relative stability of these prebiotic compounds with respect to the other possible species of the same chemical formula is addressed by means of quantum chemical simulations based on density functional theory (DFT). A preliminary investigation of molecules with the formula $C_2H_5O_2N$ shows that glycine (H_2NCH_2COOH) is not the most stable compound that can be formed: it is ~ 10 kcal mol^{-1} higher in energy than $CH_3NHCOOH$, which becomes the most likely candidate for a search in space. The same argument of relative stability used to explained why formamide $H_2N{-}HC{=}O$ was identified in the interstellar medium (rather than any of its isomers) provides here a rationalization of the permanent debate about the detection of glycine. A second investigation of protonated derivatives of the same series that may result from ion molecule chemistry shows that under its nitrogen protonated form ($H_3N^+CH_2COOH$) glycine does become the most stable compound. This suggests that, if glycine presently detected in chondrites has an interstellar origin, it must have been synthetized as its protonated form by ion–molecule processes. A similar study was carried out on the corresponding glycine *N*-carboxyanhydride. The calculated rotational constants (GHz) of glycine $A = 10.3603$; $B = 3.8590$; $C = 2.9037$ (Exp: 10.3418; 3.8762; 2.9123, respectively) served as the benchmark to derive the correcting factors necessary to estimate the rotational constants of the possible candidates within a few tenths of a percent. The dipole moments were determined and the values in the range 4–6 Debye obtained for the protonated species should be large enough to initiate laboratory experiments and/or observations. Theoretical infrared spectra are also provided to assist in the identification of these exotic species.

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Key words: amino acids, exobiology, infrared spectra, glycine, quantum chemistry, rotational constants.

Introduction

The production of amino acids from various mixtures of simple molecules believed to represent the major components of the early Earth atmosphere, such as CH_4, NH_3, H_2, H_2O, etc. (Miller 1953; Abelson 1956; Miller & Urey 1959) is generally considered to be the cornerstone of modern astrobiology and still stimulates experiments and theoretical developments. In most experiments, the energy necessary to initiate the reaction was provided in a 'violent form', as electric discharges to simulate lightning, particles beams to simulate cosmic rays or projectiles to simulate volcanic eruptions. All these conditions have in common that there is enough energy to reach the most stable species that can be formed.

On the other hand, according to the panspermia hypothesis, suggested by Richter in the nineteenth century and formalized by Arrhenius (1908), life (or at least the first 'living materials') could have an extra-terrestrial origin. The fact that most of the compounds found in the Urey–Miller type of experiments were identified in meteorites strongly supports this hypothesis. Over 70 amino acids, including eight out of the 20 present in living organisms (Cooper *et al.* 1992), were isolated in the Murchison meteorite (1969). This suggests that meteorites could play an important role in the origin of life, in particular carbonaceous chondrites of Murray (CM) and Ivunna (CI) types. These are the most primitive chondrites; in fact, CIs have exactly the composition of the Sun's photosphere, which means that they consist of matter inherited from the Solar nebula almost without any transformation. To explain the presence of amino acids in chondritic matter, it is interesting to note that amino acids (e.g. glycine) can be produced, without water, in experiments designed in order to simulate interstellar conditions

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Table 1. *Relative energies (kcal mol^{-1}) of glycine and isomers at the B3LYP/6-311G** level of theory including zero-point energy corrections*

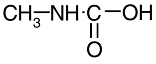
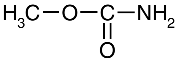
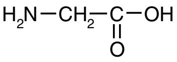
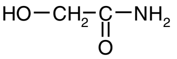
Chemical structure	E (kcal mol^{-1})
 $CH_3{-}NH{\cdot}\underset{\underset{O}{\|}}{C}{-}OH$	0.0
 $H_3C{-}O{-}\underset{\underset{O}{\|}}{C}{-}NH_2$	4.5
 $H_2N{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$	10.0
 $HO{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_2$	12.1

Table 2. *Relative energies (kcal mol^{-1}) of O-protonated glycine and isomers at the B3LYP/6-311G** level of theory including zero-point energy corrections*

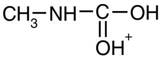
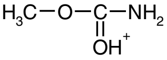
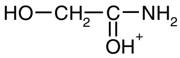
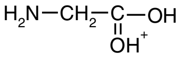
Chemical structure	E (kcal mol^{-1})
 $CH_3{-}NH{-}\underset{\underset{OH^+}{\|}}{C}{-}OH$	0.0
 $H_3C{-}O{-}\underset{\underset{OH^+}{\|}}{C}{-}NH_2$	2.3
 $HO{-}CH_2{-}\underset{\underset{OH^+}{\|}}{C}{-}NH_2$	3.6
 $H_2N{-}CH_2{-}\underset{\underset{OH^+}{\|}}{C}{-}OH$	23.1

Table 3. *Relative energies (kcal mol^{-1}) of N-protonated glycine and isomers at the B3LYP/6-311G** level of theory including zero-point energy corrections*

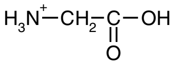
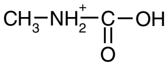
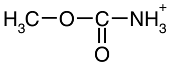
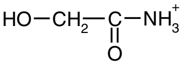
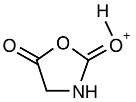
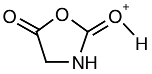
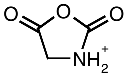
Chemical structure	E (kcal mol^{-1})
 $H_3\overset{+}{N}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$	0.0
 $CH_3{-}NH_2^+{-}\underset{\underset{O}{\|}}{C}{-}OH$	10.6
 $H_3C{-}O{-}\underset{\underset{O}{\|}}{C}{-}NH_3^+$	16.0
 $HO{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_3^+$	22.1

Table 4. *Relative energies (kcal mol^{-1}) of protonated glycine NCA at the B3LYP/6-311G** level of theory including zero-point energy corrections*

Chemical structure	E (kcal mol^{-1})
	0
	5.5
	18.5

(Devienne *et al.* 1998; Takano *et al.* 2004). However, the presence in space of the simplest of all amino acids still remains to be confirmed (Brown *et al.* 1979; Hollis *et al.* 1980, 2003a, b; Snyder *et al.* 1983, 2005; Berulis *et al.* 1985; Guelin & Cernicharo 1989; Combes *et al.* 1996; Ceccarelli *et al.* 2000; Kuan *et al.* 2003). It is also possible that molecular precursors of amino acids such as α-amino acids *N*-carboxyanhydrides (NCAs) were formed in the first place. In fact, these species were found to be activated building blocks that can yield polypeptides. Recently, it was reported that, in specific conditions, polymerization of racemic NCAs of hydrophobic α-amino acids may yield an enhanced abundance of homochiral oligopeptides (Blocher *et al.* 2001). NCAs were also shown to be the precursors of the mixed anhydrides amino acyladenylates (AA-AMP), as the usual activation of amino acids by adenosine triphosphate (ATP) is a very unlikely path for the first steps of prebiotic synthesis (Biron *et al.* 2004, 2005).

Given the difficulties in simulating the environmental conditions of interstellar space by laboratory experiment, quantum chemistry offers an alternative approach to this problem. In a previous investigation on prebiotic precursors (Chiaramello *et al.* 2005), we showed that state-of-the-art quantum simulation techniques make it possible to obtain reliable predictions of small energy separations between isomers or accurate values for spectroscopic data. Rotational constants, dipole moments and infrared signatures can be calculated with enough accuracy to carry out both laboratory experiments and spatial observations. In this paper, we report the main results obtained in a systematic investigation of glycine and the isomers that can possibly be formed together with the corresponding *N*-carboxyanhydride.

Computational methods

Density functional theory (DFT) was used throughout. For both geometry optimization and vibrational frequencies, we employed the standard split-valence polarized 6-311G** basis set of triple-zeta quality with the hybrid B3LYP method (Becke's (1993) three-parameter non-local exchange potential, coupled to the non-local correlation functional of Lee *et al.* (1988)). All the calculations were performed using the GAUSSIAN98 package (Frisch *et al.* 1998). For each molecule, several conformers were studied but only the characteristics of the most stable one are reported for comparison. Each structure, fully optimized, was verified to be a

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Table 5. *Computed and experimental rotational constants (GHz) and dipole moment (Debye) of glycine*

Method base	*A*	*B*	*C*	A_{calc}/A_{exp}	B_{calc}/B_{exp}	C_{calc}/C_{exp}	μ
$NH_2—CH_2—COOH$							
MP2/6-311G**	10.3030	3.8933	2.9185	0.9963	1.0044	1.0021	1.3
B3LYP/6-311G**	10.3603	3.8590	2.9037	1.0018	0.9956	0.9970	1.2
Experiment[a]	10.3418	3.8762	2.9123				

[a] Iijima *et al.* (1991).

Table 6. *Computed rotational constants (GHz) and dipole moments (Debye) of glycine isomers at the B3LYP/6-311G** level of theory*

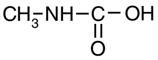
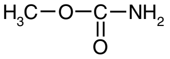
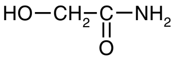
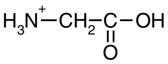
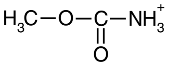
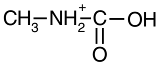
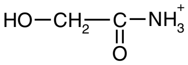
Chemical structure	*A*	*B*	*C*	A_{corr}	B_{corr}	C_{corr}	μ
 $CH_3{-}NH{-}\underset{\underset{O}{\|}}{C}{-}OH$	10.7337	4.0702	3.0072	10.7145	4.0883	3.0162	2.4
 $H_3C{-}O{-}\underset{\underset{O}{\|}}{C}{-}NH_2$	10.6840	4.3715	3.1663	10.4721	4.0575	2.9797	2.4
 $HO{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_2$	10.4909	4.0395	2.9708	10.6649	4.3910	3.1758	4.4

Table 7. *Computed rotational constants (GHz) and dipole moments (Debye) of protonated glycine isomers at the B3LYP/6-311G** level of theory*

Chemical structure	*A*	*B*	*C*	A_{corr}	B_{corr}	C_{corr}	μ
 $H_3\overset{+}{N}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$	10.2980	3.8988	2.9252	10.2795	3.9162	2.9339	5.6
 $H_3C{-}O{-}\underset{\underset{O}{\|}}{C}{-}NH_3^+$	9.8735	3.9352	2.9114	9.8558	3.9527	2.9201	5.2
 $CH_3{-}\overset{+}{N}H_2{-}\underset{\underset{O}{\|}}{C}{-}OH$	9.8645	3.9616	2.9229	9.8468	3.9793	2.9316	3.8
 $HO{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}NH_3^+$	8.3694	4.1807	2.8830	8.3544	4.1993	2.8916	3.4

stationary point by vibrational analysis. The geometrical parameters of neutral and protonated species are given in the form of a numerical appendix at the end of the paper.

Relative stabilities

The glycine isomers

There are 17 isomers of glycine. The relative energies of those we thought could have played an important role in prebiotic chemistry, and of glycine itself, are reported in Table 1, taking the most stable one as a reference. Structural data can be found in Tables A1–A3 in Appendix A.

It can be seen that the most stable structure is an amino acid, but it is not glycine. The next system on the energy scale is an amide ester. Glycine is only in third position, about ~ 10 kcal mol^{-1} higher than the most stable compound. The next one is an amide alcohol.

The fundamental result at this level of the study is that it is not the prebiotic α-amino acid that has the lowest energy of all the isomers. This may be a clue for understanding why glycine is so hard to observe in the gas phase in the interstellar medium: in conditions where the most stable molecule is the one that is formed, glycine does not satisfy the maximum stability requirement.

The protonated glycine isomers

The presence of glycine in space as a neutral compound remains doubtful, but, as with many molecules with heteroatoms, especially nitrogen or oxygen, it may exist under a protonated form. It is worth mentioning that all the cations detected in the interstellar medium (except for CO^+ and SO^+) are protonated species. Consequently, the same isomers were studied as before, first protonated on the acid group, then on the amine group.

Protonation on the OH part of the acid group does not produce a stable molecule: it leads to proton transfer on the amine group or to a dissociation of the molecule. On the

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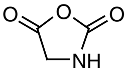
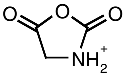
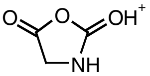
Table 8. *Computed rotational constants* (*GHz*) *and dipole moments* (*Debye*) *for neutral and protonated NCA at the B3LYP/6-311G** level of theory*

Chemical structure	A	B	C	A_{corr}	B_{corr}	C_{corr}	μ
	6.5650	2.3786	1.7655	6.5532	2.3892	1.7707	5.1
	5.8526	2.3214	1.6952	6.3843	2.3019	1.7105	7.4
	6.3958	2.2917	1.7054	5.8421	2.3317	1.7002	4.4

other hand, protonation on the C=O part of the acid group leads to the results reported in Table 2.

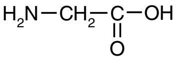
In such conditions, protonated glycine is the least-stable species. This can be explained by the fact that it is the only isomer that does not have its nitrogen bonded to the acid carbon. Consequently, there is no lone pair near the acid group to stabilize the molecule. However, when protonation occurs on the amine group, glycine becomes the most stable isomer (see Table 3). In this case, the fact that the $NH_3{}^+$ and C=O groups are far from each other contributes to the stability of protonated glycine. In the other isomers, where the two groups are linked together, the carbonyl group attracts the electrons, which destabilizes the protonated amine. Moreover, for glycine, it is possible to have an additional hydrogen bond between the $NH_3{}^+$ group and the oxygen of C=O, which gives a stabilized five-membered cycle. Therefore, protonated glycine becomes more stable than protonated N-methyl carbamate, which had the lowest energy of the neutral isomers. The other isomers have the same order of stability as in the neutral forms. Structural data can be found in Tables A1–A3 in Appendix A.

The N-carboxyanhydride of glycine and protonated isomers

As with glycine, neutral NCA and both N-protonated and O-protonated forms were considered. The results are reported in Table 4.

Protonation was studied only on the C=O group vicinal to the amine group because this oxygen is the more negatively charged, owing to the interaction with the nitrogen lone pair. Contrary to protonated glycine, NCA protonated on the C=O group is much more stable than NCA protonated on the amine group, the energy difference being ~18.5 kcal mol^{-1}. Two conformers of protonated NCA are found to be stable minima with an energy difference of ~5.5 kcal mol^{-1} owing to hydrogen bonding with the oxygen lone pairs. This is illustrated by the value of angle ∠HOC of the two conformers, i.e. 112.52° in the structure with a hydrogen bond versus 115.04° in the structure with no hydrogen bond. The complete set of geometrical parameters is given in Appendix A (Table A4).

Table 9. *Computed B3LYP/6-311G** infrared frequencies* (*cm*$^{-1}$) *and intensities* (*km mol*$^{-1}$) *of glycine compared with experimental data*

Assignment	Theory ν (I)	Experiment ν	$\nu_{\mathrm{expt}}/\nu_{\mathrm{theo}}$
 $H_2N{-}CH_2{-}\underset{\underset{O}{\Vert}}{C}{-}OH$			
OH str.	3743 (49)	3566	0.950
CH_2 sym. str.	3041 (18)		
C=O str.	1830 (282)	1781	0.973
NH_2 bend.	1682 (21)	1632	0.970
CH_2 wag.	1399 (19)	1385	0.990
C—N str. + C—O str.	1166 (141)	1131	0.970
C—N str. − C—O str.	1128 (159)	1101	0.976
CH_2 rock. + NH_2 twist.	929 (149)		
C—C str.	824 (82)	802	0.973
OH bend.	664 (96)	620	0.969
O—C=O bend.	509 (35)	501	0.984
C—C—O bend.	464 (31)	463	0.999
C—N tors.	222 (46)	260	1.173

Rotational constants

Looking for prebiotic species in space and principally for glycine was the main goal of a number of observation campaigns (Brown *et al.* 1979; Hollis *et al.* 1980, 2003a, b; Snyder *et al.* 1983, 2005; Berulis *et al.* 1985; Guelin & Cernicharo 1989; Combes *et al.* 1996; Ceccarelli *et al.* 2000; Kuan *et al.* 2003). The rotational constants of glycine are known in the literature (Iijima *et al.* 1991) but, to our knowledge, none were ever reported for the other isomers.

The calculation of rotational constants, by quantum-chemical methods alone, to a sufficient accuracy such that it can be used to support the identification of unknown molecules in space, is a difficult task. The main difficulty arises from the fact that the calculations are performed in the rigid rotor approximation leading to A_e, B_e and C_e at the equilibrium geometries, whereas the quantities needed to reproduce radio signatures A_0, B_0 and C_0 should take into account the motions of the nuclei. Some adjustment is then necessary to achieve an accuracy greater than ~0.3 %, which is usually the upper limit required for identification. Previous calculations on single species (Dimur *et al.* 2001) and molecular series of compounds (Cheikh & Pauzat 1999) showed the remarkable performance of DFT for the calculation of rotational constants when the B3LYP functional is coupled to the 6-311G** basis set.

The geometrical parameters obtained for neutral glycine are the same as the experimental ones and they are in agreement with those reported by Barone (1995) for conformer I of glycine, which is the most stable conformer. The corresponding rotational constants obtained at the B3LYP level of theory are reported in Table 5 together with those of the more standard *ab initio* MP2.

Both B3LYP and MP2 methods provide theoretical spectroscopic constants in almost perfect agreement with the values deduced from the experimental spectra with an

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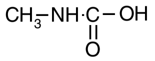
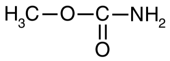
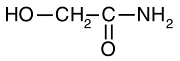
Table 10. *Best estimates of the infrared spectra of glycine isomers after scaling of the computed B3LYP/6-311G** infrared frequencies* (cm^{-1}) *and intensities* ($km\ mol^{-1}$)

Assignment	Theory ν (*I*)	Best estimates	Assignment	Theory ν (*I*)	Best estimates	Assignment	Theory ν (*I*)	Best estimates
 $CH_3-NH-C(=O)-OH$			 $H_3C-O-C(=O)-NH_2$			 $HO-CH_2-C(=O)-NH_2$		
OH str.	3814 (89)	3623	NH_2 asym. str.	3741 (52)	3554	NH_2 asym. str.	3722 (45)	3536
NH str.	3649 (39)	3467	NH_2 sym. str.	3612 (46)	3431	OH str.	3668 (96)	3485
CH_3 asym. str.	3070 (38)	2917	CH_3 asym. str.	3150 (20)	2993	NH_2 sym. str.	3593 (42)	3413
CH_3 sym. str.	3022 (59)	2871	CH_3 asym. str.	3116 (27)	2960	CH_2 asym. str.	2998 (42)	2848
C=O str.	1827 (430)	1778	CH_3 sym. str.	3046 (33)	2894	CH_2 sym. str.	2978 (49)	2829
C—N str.	1585 (210)	1542	C=O str.	1827 (401)	1778	C=O str.	1778 (301)	1730
CH_3 bend.	1504 (48)	1466	NH_2 bend.	1618 (138)	1578	NH_2 bend.	1627 (91)	1586
CH_3 bend.	1451 (22)	1415	CH_3 bend.	1478 (35)	1441	OH bend. + CH_2 wag.	1471 (47)	1434
C—N str. + C—O str.	1203 (293)	1171	N—C—O asym. str.	1357 (372)	1320	C—C—N asym. str.	1359 (229)	1322
C—N str. + C—O str.	1119 (117)	1089	C—O—C asym. str.	1122 (97)	1091	C—O str.	1128 (113)	1098
O—C=O wag.	777 (26)	769	+ N—C=O sym. str.			C—C str.	816 (17)	794
O—C=O bend.	515 (42)	510	C—O—C asym. str.	1089 (28)	1060	CH_2 rock. + NH_2 twist.	639 (25)	623
+ C—N—C bend.			+ N—C=O sym. str.			OH bend.	417 (86)	407
NH bend. + OH bend.	453 (210)	442	C—O—C sym. str.	871 (28)	847	C—C—O bend.	299 (20)	296
			O—C=O wag.	782 (23)	774	+ C—C—N bend.		
			NH_2 wag.	285 (258)	282	NH_2 wag.	199 (198)	197

average precision in the range of 0.3% as illustrated by the ratios of the calculated to the experimental constants close to unity. The B3LYP/6-311G** level of theory was used in the present study.

Predictions for glycine isomers

The A_{corr}, B_{corr} and C_{corr}, which are the best estimates of these constants, were obtained using the ratios A_{calc}/A_{exp}, B_{calc}/B_{exp} and C_{calc}/C_{exp} of Table 5. These values, reported in Table 6, should be accurate to within the 0.3% limit necessary to initiate observations in space or in the laboratory.

Before such an investigation can be conducted, another quantity has to be taken into account, i.e. the dipole moment of each molecule, as the intensity of the radio spectra scales with its square. Values between 2.4 and 4.4 Debye are large enough for such a purpose, but the dipole moment calculated for glycine (~1.2 Debye) might not be large enough for the radio spectra to be seen. This might be another reason, together with the complexity of the spectrum, why glycine is proving so hard to detect.

Predictions for protonated glycine isomers

Only the molecules protonated on the amine group are considered, as it is the only series in which glycine is the most stable species. The geometries of protonated glycine and its isomers are very similar to those of their neutral parents (see Tables A1–A3 in Appendix A). The geometrical parameters that are slightly changed are some angles involving the N atom and the N—H and C—N bond lengths; these bonds are longer in the protonated form because the charge increases repulsion between atoms. The only significant modification is found for the amide alcohol for which the most stable structure has a *cis* conformation for the neutral compound, but a *trans* conformation for the protonated one. Transferability of the correcting scheme is then reasonable and the ratios used to calculate A_{corr}, B_{corr} and C_{corr} reported in Table 7 are those used for the neutral compounds. The dipole moments of all the protonated molecules are large enough for the radio spectra to be seen.

Predictions for the N-carboxyanhydride of glycine and protonated isomers

Although the geometry of NCA is different from that of glycine in the sense that it is a cyclic molecule, both species have enough structural parameters in common to justify the use of the same scaling factors for the rotational constants. They are reported in Table 8 together with the corresponding dipole moments. Those are clearly large enough for the radio spectra to be detected.

Infrared frequencies

The recent detection of benzene by the Infrared Space Observatory (ISO) in the circumstellar medium in the direction of the proto-planetary nebula CRL 618 (Cernicharo *et al.* 2001) has lead to renewed interest for infrared signatures. The

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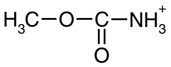
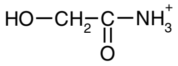
Table 11. *Best estimates of the infrared spectra of protonated glycine isomers after scaling of the computed* B3LYP/6-311G** *infrared frequencies* (cm^{-1}) *and intensities* ($km\ mol^{-1}$)

Assignment	Theory ν (*I*)	Best estimates
$\mathrm{H_3^+N{-}CH_2{-}COOH}$		
OH str.	3719 (181)	3533
NH_2 asym. str.	3504 (119)	3328
NH_2 sym. str.	3452 (117)	3279
NH str.	3124 (223)	2968
C=O str.	1829 (261)	1780
NH_3 bend.	1669 (40)	1627
NH_3 bend.	1652 (42)	1611
NH_3 bend. + CH_2 bend.	1505 (108)	1467
NH_3 bend. + CH_2 bend.	1472 (133)	1435
C—C str. + C—O str.	1440 (142)	1401
C—O str.	1200 (214)	1168
CH_2 wag. + NH_3 wag.	1105 (55)	1077
CH_2 rock. + NH_2 rock.	930 (21)	907
C—C str.	838 (62)	815
OH bend. + CH_2 rock.	676 (123)	659
OH bend + CH_2 rock.	517 (30)	504
O—C=O bend. + C—C—N bend.	480 (78)	475
O—C=O bend. + C—C—N bend.	309 (38)	306
 $\mathrm{H_3C{-}O{-}C({=}O){-}NH_3^+}$		
NH_3 asym. str.	3483 (138)	3309
NH_3 asym. str.	3467 (137)	3294
NH_3 sym. str.	3381 (90)	3212
C=O str.	1975 (391)	1922
NH_3 bend.	1636 (57)	1595
NH_3 bend.	1636 (62)	1595
CH_3 bend.	1484 (20)	1447
CH_3 bend.	1482 (22)	1445
CH_3 bend.	1475 (35)	1438
NH_3 bend.	1462 (166)	1425
C—O str.	1262 (364)	1228
CH_3 rock.	1188 (85)	1158
NH_3 rock.	1049 (26)	1023
NH_3 rock.	1032 (28)	1006
C—N str.	826 (122)	804
C—O—C bend.	243 (29)	241
O—C tors.	184 (24)	216
$\mathrm{CH_3{-}NH_2^+{-}COOH}$		
OH str.	3715 (241)	3529
NH_2 asym. str.	3439 (110)	3267
NH_2 sym. str.	3394 (81)	3224
C=O str.	1974 (341)	1921
NH_2 bend.	1631 (64)	1590
CH_3 bend.	1498 (39)	1461
CH_3 bend.	1491 (23)	1454
CH_3 bend.	1464 (17)	1427
NH_2 wag	1393 (130)	1358
OH bend.	1325 (42)	1292
C—O str.	1186 (204)	1154
NH_2 wag. + CH_3 wag.	1132 (46)	1104
NH_2 rock. + CH_3 rock.	863 (26)	841
N—C str.	737 (127)	717
NH2 rock. + OH bend.	649 (88)	633
NH_2 rock. + OH bend.	561 (74)	547
N—C—O bend.	471 (31)	466
 $\mathrm{HO{-}CH_2{-}C({=}O){-}NH_3^+}$		
O—H str.	3833 (151)	3641
NH_3 asym. str.	3488 (130)	3314
NH_3 asym. str.	3449 (193)	3277
NH_3 sym. str.	3329 (103)	3163
CH_2 sym. str.	3009 (13)	2859
C=O str.	1979 (196)	1926
NH_3 bend.	1644 (45)	1603
NH_3 bend.	1622 (32)	1581
CH_2 bend.	1481 (37)	1444
CH_2 wag. + NH_3 bend. + OH bend.	1438 (65)	1402
CH_2 wag. + NH_3 bend. + OH bend.	1402 (189)	1367
CH_2 wag. + OH bend.	1234 (52)	1203
O—C str. + C—C str. + C—N str.	1133 (155)	1102
C—O str.	1091 (72)	1062
CH_2 rock. + NH_3 rock.	883 (23)	861
NH_3 twist.	880 (46)	858
C—N str.	588 (62)	572
N—C—C bend. + O—C—C bend.	342 (49)	339
OH bend.	259 (162)	253
C—N tors.	101 (19)	118
C—C tors.	51 (22)	60

situation for these observables is similar to that of rotational constants and calibration is necessary to obtain accurate frequencies. In this study, appropriate scaling factors were determined per type of vibration (Sczcepanski *et al.* 1993) by adjusting the calculated spectra to the spectroscopic values of a representative molecule (glycine).

Test on glycine

The experimental spectrum of glycine taken as reference is that of Grenie *et al.* (1972). The important factors, namely the theoretical to experimental ratios of the infrared frequencies ν_{exp}/ν_{theory}, are given in Table 9. Only the frequencies with a calculated intensity larger than 15 km mol^{-1} ($\approx 5\%$ of the largest value) are reported.

Five high-frequency modes appear in the region 3800–1200 cm^{-1} of the vapour phase spectrum. Assignments made in the original study (Grenie *et al.* 1972) are confirmed here by the normal coordinate analysis except for the stretchings of the CH_2 group which were not detected in the original study. Below 1200 cm^{-1}, the spectrum is much more complex owing to combination bands. Assignments of experimental spectra in this region are obviously hard, and some bands at low frequencies could have been shifted as a result of the experimental conditions. The original assignment of some bands was revised in this study, using normal coordinate analysis, so as to reduce the variation of ν_{exp}/ν_{theory}. For example, the assignment of C—C stretching to the band 787 cm^{-1} was revised and associated with the 802 cm^{-1}

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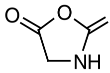
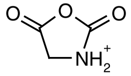
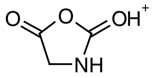
Table 12. *Best estimates of the infrared spectra of neutral and protonated glycine NCA after scaling of the computed B3LYP/6-311G** infrared frequencies* (cm^{-1}) *and intensities* ($km\ mol^{-1}$)

Assignment	Theory ν (*I*)	Best estimates	Assignment	Theory ν (*I*)	Best estimates	Assignment	Theory ν (*I*)	Best estimates
								
NH str.	3670 (64)	3487	NH_2 asym. str.	3459 (137)	3286	OH str.	3720 (325)	3534
C=O str.	1948 (250)	1895	NH_2 sym. str.	3406 (120)	3236	NH str.	3596 (209)	3416
C=O str.	1882 (789)	1831	C=O str.	2059 (135)	2003	C=O str.	2049 (241)	1994
N—C—O asym. str.	1350 (51)	1314	C=O str.	1979 (704)	1926	N—C=O asym. str.	1739 (440)	1692
C—N—C asym. str.	1285 (232)	1250	NH_2 bend.	1635 (69)	1594	N—C=O sym. str.	1574 (441)	1532
+C—C—O sym. Str			C=O—C str.	1181 (292)	1149	CH_2 wag. + NH bend.	1312 (57)	1279
C—N—C asym. str.	1105 (62)	1075	C—C—N str. + C—C—O str.	1052 (217)	1024	OH bend.	1192 (197)	1162
+C—C—O asym. Str			C—O str. + C—N str.	972 (96)	946	N—C—O str.	1107 (25)	1077
C—N—C sym. str.	1074 (94)	1045	C—O str. + C—N str.	858 (104)	835	C—C—O asym. str.	939 (54)	914
C—O—C asym. str.	934 (198)	909	C—O str. + O—C=O bend.	553 (62)	538	N—C—O wag.	763 (22)	755
C—N—C bend.	728 (40)	721	C—N str.	488 (36)	475	N—C—O bend.	758 (44)	750
NH bend.	416 (103)	406				N—C—O rock.	682 (142)	675
						C—C—N bend.	577 (118)	571
						OH bend. + NH bend.	515 (251)	502

frequency. All the ν_{exp}/ν_{theory} ratios are smaller than unity. The only frequency with a ratio much greater than unity is the lowest one, assigned to a torsion of the C—N bond, which is not surprising for a type of molecular motion outside the standard model of harmonic vibrations.

Predictions for glycine isomers, N-carboxyanhydride of glycine and protonated isomers

As the molecules for which we want to predict the infrared frequencies are isomers and derived anhydrides of the model molecule, no one-to-one mapping of the frequencies was attempted. However, the great similarity of the molecular fragments makes it possible to use one scaling factor per type of vibration, determined from the ν_{exp}/ν_{theory} obtained for glycine. For example, for double-bond stretching, the scaling factor used is 0.973. The corrected values of the theoretical calculations are presented in Tables 10–12. As previously mentioned, only frequencies with a calculated intensity greater than 5% of the largest value are reported for each molecule.

The most interesting molecules to consider with regards to the first steps of emerging life are N-protonated glycine and O-protonated NCA. The amine group of N-protonated glycine gives rise to three high-frequency modes that separate into two stretching vibrations of NH_2 (asymmetric at $3328\ cm^{-1}$ and symmetric at $3452\ cm^{-1}$) and a single stretching mode of NH at $3124\ cm^{-1}$. This is directly related to the two different bond lengths for N—H (1.023 and 1.046 Å) reported in Table A1 for the optimized structure. This can be explained by the fact that there is a H-bond between one of the H of the amine group and the oxygen of C=O (to give a five-membered ring). The local symmetry of the amine group is then broken; in fact, the H-bond makes the NH_3 group change from C_{3v} to C_s. Comparing the theoretical frequencies for NCA and its protonated forms shows that both neutral and N-protonated species have two intense bands assigned to C=O stretching vibrations. By contrast, O-protonated NCA has only one, as the bond between C and O is no longer a real double bond because of the interaction of the π lone pair on nitrogen with the $C{=}OH^+$ bond.

The accuracy of the estimation obtained here on infrared frequencies should be within a few percent of the real value.

Energy data

To complete this study, we calculated some energy data involving reactions of glycine and glycine NCA (Table 13). The enthalpies of the considered reactions were calculated as the differences between the energies of the products and those of the reactants, taking zero-point vibration energies into account. Only reactions between glycine or NCA and glycine, where at most only one of these molecules is protonated, were calculated. With regard to the protonated species, only N-protonated glycine and O-protonated NCA were considered, because these are the most stable ones. Moreover, the reaction implied is that between the amine group of the

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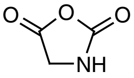
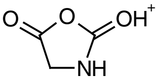
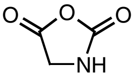
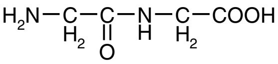
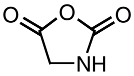
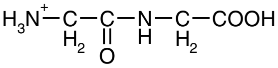
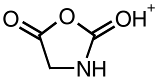
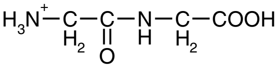
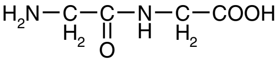
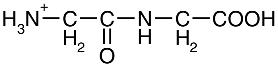
Table 13. *Computed enthalpies of formation of neutral and protonated glycine and diglycine at the B3LYP/6-311G** level of theory including zero-point energy corrections*

Reactants	Products	ΔH (kcal mol^{-1})
 + H_2O	$NH_2—CH_2—COOH + CO_2$	−18.95
 + H_2O	$NH_3^+—CH_2—COOH + CO_2$	−40.02
 + $NH_2–CH_2–COOH$	 $H_2N-\underset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H_2}{C}-COOH$ + CO_2	−18.43
 + $NH_3^+–CH_2–COOH$	 $H_3\overset{+}{N}-\underset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H_2}{C}-COOH$ + CO_2	−23.92
 + $NH_2–CH_2–COOH$	 $H_3\overset{+}{N}-\underset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H_2}{C}-COOH$ + CO_2	−44.98
$NH_2—CH_2—COOH + NH_2—CH_2—COOH$	 $H_2N-\underset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H_2}{C}-COOH$ + H_2O	0.52
$NH_2—CH_2—COOH + H_3N^+—CH_2—COOH$	 $H_3\overset{+}{N}-\underset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\underset{H}{N}-\underset{H_2}{C}-COOH$ + H_2O	−4.97

neutral form and the C═O group of the protonated one. The protonated amine no longer has a lone pair available, so its reactivity decreases, while that of protonated $C═OH^+$ increases.

Looking first at the reactions between neutral species, it is worth noting that, for the dimer of glycine, the geometry optimization predicts a twisting of the molecule similar to an α helix as in biological peptides. However, this reaction is the only one to have a positive energy difference, i.e. forming diglycine from its neutral monomers needs an energy supply. In addition, the reaction involving NCA and glycine is exothermic (∼ −18.5 kcal mol^{-1}) due to the hydrolysis of the anhydride function.

The other reactions studied, which involve one of the reactants in a protonated form, are all exothermic and, in this context, those involving protonated NCA are by far the most thermodynamically favoured.

Conclusion

The presence of amino acids in the interstellar medium remains doubtful, although complex amino acids are commonly found in carbonaceous chondrites collected on Earth. We have initiated a study in order to understand the stability of prebiotic species and this paper focuses on glycine, the simplest compound of the amino acid family, and its corresponding NCA.

Quantum-chemical simulations of the molecules with chemical formula $C_2H_5O_2N$ show that prebiotic glycine is not the most stable compound that can be formed: it is ∼10 kcal mol^{-1} higher in energy. The same argument of relative stability that explained why formamide $H_2N—HC═O$ (Chiaramello *et al.* 2005) was identified in the interstellar medium (rather than any of its isomers) provides here a rationalization of the permanent debate about the detection of glycine. It also suggests that a search for its more stable isomer $CH_3NHCOOH$ should be performed.

Since interstellar chemistry is known to rely on ion–molecule more than on neutral–neutral processes, a systematic investigation was then carried out on the protonated forms. Under these circumstances, the ion derived from the protonation of glycine on the amine group, $H_3N^+CH_2COOH$, is the most stable structure, approximately 10 kcal mol^{-1} below the protonated derivative of the molecule that is the most stable in the neutral form, $CH_3NH_2^+COOH$. This indicates that, if glycine currently detected in chondrites has an interstellar origin, it must have been synthetized as its protonated form by ion–molecule processes.

A preliminary screening of the enthalpy aspect of the problem shows that formation of a dipeptide is endothermic in a neutral process except if the anhydride derivative is used. By contrast, all reactions involving a protonated ion are feasible. This study suggests that the search for glycine may not be appropriate and should preferably be reoriented

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to the search of its protonated ion. To this end, rotational constants, dipole moments and infrared frequencies were calculated. The already excellent raw values of the rotational constants of glycine were used as a reference to derive correcting factors to be applied to the as yet unobserved compounds. These values together with the dipole moments should be sufficiently accurate to stimulate laboratory studies to further refine the spectra. The dipole moment of protonated glycine (~5.6 Debye) is large enough for a promising experiment.

The present simulations suggest that similar studies should be conducted on other amino acids to test whether all the amino acids present in meteorites may have been synthesized in a non-neutral form via interstellar ionic–neutral chemistry, and then incorporated in the solid where the hydration in the asteroid stage helped the formation of the more complex systems.

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Appendix A

Table A1. *Geometrical parameters for neutral and protonated glycine (angles are in degrees, bond lengths are in Å)*

Method base	B3LYP6-311G**	MP26-311G**	Experiment[a]	Method base	B3LYP6-311G**
NH_2—CH_2—COOH				H_3N^+—CH_2—COOH	
Bond lengths					
C—N	1.451	1.452	1.467	C—N	1.509
C—C	1.524	1.519	1.526	C—C	1.532
C═O	1.204	1.209	1.205	C═O	1.206
C—O	1.354	1.354	1.355	C—O	1.314
N—Ha	1.015	1.015	(1.001)	N—Ha	1.046
N—Hb	1.015	1.015	(1.001)	N—Hb	1.023
				N—Hc	1.023
C—Ha	1.095	1.094	(1.081)	C—Ha	1.089
C—Hb	1.095	1.095	(1.081)	C—Hb	1.089
O—H	0.969	0.967	(0.966)	O—H	0.973
Bond angles					
∠CCN	115.45	114.98	112.1	∠CCN	105.34
∠OCC	125.43	125.36	125.1	∠OCC	120.53
∠OhCC	111.52	111.25	111.6	∠OhCC	111.59
∠HaNC	109.60	108.52	(113.27)	∠HaNC	104.73
∠HbNC	109.59	108.53	(113.27)	∠HbNC	112.94
				∠HcNC	112.92
∠HaCC	110.05	110.00		∠HaCC	110.11
∠HbCC	110.07	110.00		∠HbCC	110.13
∠HOC	106.83	105.40	(112.28)	∠HOC	110.43
∠OCCN	0.44	0.28		∠OCCN	0.14
∠OhCCN	180.38	180.28		∠OhCCN	−179.86
∠HaNCC	57.77	56.76		∠HaNCC	−0.21
∠HbNCC	−57.52	−56.67		∠HbNCC	−118.73
				∠HcNCC	118.24
∠HaCNC	122.02	121.70		∠HaCNC	119.86
∠HbCNC	−122.11	−121.70		∠HbCNC	−119.95
∠HOCC	180.09	179.99		∠HOCC	180.05

[a] Iijima *et al.* (1991), the values in parentheses were assumed from low-level theoretical predictions (HF/4-21G).

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Table A2. *Computed B3LYP/6-311G** geometrical parameters for neutral and protonated glycine and isomers* (*angles are in degrees, bond lengths are in Å*)

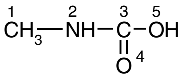
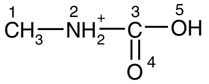
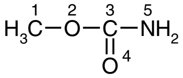
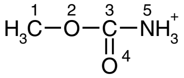
Method base	 $\overset{1}{CH_3}-\overset{2}{NH}-\overset{3}{C}(=\overset{4}{O})-\overset{5}{OH}$	 $\overset{1}{CH_3}-\overset{2}{NH_2^+}-\overset{3}{C}(=\overset{4}{O})-\overset{5}{OH}$	Method base	 $\overset{1}{H_3C}-\overset{2}{O}-\overset{3}{C}(=\overset{4}{O})-\overset{5}{NH_2}$	 $\overset{1}{H_3C}-\overset{2}{O}-\overset{3}{C}(=\overset{4}{O})-\overset{5}{NH_3^+}$
Bond lengths					
C^1—N^2	1.451	1.510	C^1—O^2	1.435	1.483
N^2—C^3	1.356	1.539	C^3—O^2	1.359	1.293
C^3═O^4	1.212	1.176	C^3═O^4	1.208	1.178
C^3—O^5	1.366	1.313	N^5—C^3	1.365	1.564
O^5—H	0.965	0.974	Ha—N^5	1.005	1.026
N^2—Ha	1.007	1.027	Hb—N^5	1.006	1.026
N^2—Hb		1.027	Hc—N^5		1.025
C^1—Ha	1.094	1.088	Ha—C^1	1.088	1.084
C^1—Hb	1.094	1.087	Hb—C^1	1.091	1.088
C^1—Hc	1.089	1.087	Hc—C^1	1.091	1.088
Bond angles					
$\angle C^3N^2C^1$	122.38	113.82	$\angle C^3O^2C^1$	114.87	116.80
$\angle O^4C^3N^2$	126.59	120.87	$\angle O^4C^3O^2$	124.54	135.44
$\angle O^5C^3N^2$	110.31	105.82	$\angle N^5C^3O^2$	109.88	105.79
$\angle HO^5C^3$	105.42	110.92	$\angle HaN^5C^3$	116.83	110.86
$\angle HaN^2C^3$	117.41	107.64	$\angle HbN^5C^3$	119.40	110.68
$\angle HbN^2C^3$		110.97	$\angle HcN^5C^3$		108.50
$\angle HaC^1N^2$	111.28	107.77	$\angle HaC^1O^2$	105.44	104.16
$\angle HbC^1N^2$	111.29	108.32	$\angle HbC^1O^2$	110.73	108.62
$\angle HcC^1N^2$	107.64	108.34	$\angle HcC^1O^2$	110.78	108.61
$\angle O^4C^3N^2C^1$	−0.03	1.26	$\angle O^4C^3O^2C^1$	−0.82	−0.06
$\angle O^5C^3N^2C^1$	179.98	181.13	$\angle N^5C^3O^2C^1$	177.85	179.87
$\angle HO^5C^3N^2$	179.99	180.05	$\angle HaN^5C^3O^2$	168.44	56.82
$\angle HaN^2C^3O^5$	0.00	57.82	$\angle HbN^5C^3O^4$	192.13	117.32
$\angle HbN^2C^3Ha$		58.61	$\angle HcN^5C^3O^4$		−2.75
$\angle HaC^1N^2C^3$	119.21	180.26	$\angle HaC^1O^2C^3$	180.01	179.98
$\angle HbC^1N^2C^3$	−119.12	−59.44	$\angle HbC^1O^2C^3$	−60.51	−60.71
$\angle HcC^1N^2C^3$	0.05	59.97	$\angle HcC^1O^2C^3$	60.48	60.67

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Table A3. *Computed B3LYP/6-311G** geometrical parameters for neutral and protonated glycine isomers* (*angles are in degrees, bond lengths are in Å*)

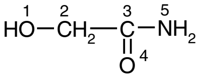
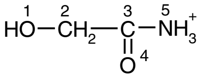
Method base	 $\overset{1}{HO}-\overset{2}{CH_2}-\overset{3}{C}(=\overset{4}{O})-\overset{5}{NH_2}$	 $\overset{1}{HO}-\overset{2}{CH_2}-\overset{3}{C}(=\overset{4}{O})-\overset{5}{NH_3^+}$
Bond lengths		
$C^2{-}O^1$	1.401	1.411
$C^2{-}C^3$	1.532	1.510
$C^3{=}O^4$	1.220	1.170
$N^5{-}C^3$	1.357	1.595
$H{-}O^1$	0.972	0.964
$Ha{-}C^2$	1.099	1.098
$Hb{-}C^2$	1.100	1.098
$Ha{-}N^5$	1.008	1.025
$Hb{-}N^5$	1.006	1.024
$Hc{-}N^5$		1.031
Bond angles		
$\angle C^3C^2O^1$	110.14	108.02
$\angle O^4C^3C^2$	119.95	130.89
$\angle N^5C^3C^2$	116.56	111.49
$\angle HO^1C^2$	104.77	111.21
$\angle HaC^2C^3$	108.71	106.70
$\angle HbC^2C^3$	108.69	106.68
$\angle HaN^5C^3$	118.76	109.36
$\angle HbN^5C^3$	122.29	109.46
$\angle HcN^5C^3$		108.60
$\angle O^4C^3C^2O^1$	0.08	178.82
$\angle N^5C^3C^2O^1$	180.09	−1.20
$\angle HO^1C^2C^3$	−0.10	182.30
$\angle HaC^2C^3O^4$	121.77	−59.00
$\angle HbC^2C^3O^4$	−121.60	56.52
$\angle HaN^5C^3C^2$	180.08	120.50
$\angle HbN^5C^3C^2$	−0.08	−121.37
$\angle HcN^5C^3C^2$		−0.22

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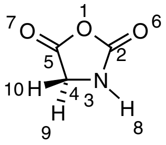
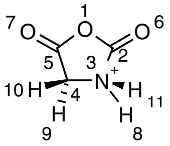
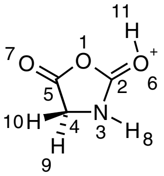
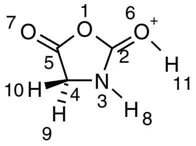
Table A4. *Computed B3LYP/6-311G** geometrical parameters for neutral and protonated forms of glycine NCA* (*angles are in degrees, bond lengths are in Å*)

Method base				
Bond lengths				
O^1-C^2	1.410	1.312	1.302	1.299
C^2-N^3	1.362	1.602	1.314	1.321
N^3-C^4	1.443	1.494	1.460	1.465
C^4-C^5	1.525	1.521	1.516	1.517
$C^2=O^6$	1.191	1.166	1.286	1.286
$C^5=O^7$	1.189	1.165	1.160	1.162
N^3-H^8	1.006	1.026	1.013	1.012
N^3-H^{11}		1.026		
C^4-H^9	1.094	1.090	1.093	1.093
C^4-H^{10}	1.094	1.090	1.093	1.093
O^6-H^{11}			0.974	0.971
Bond angles				
$\angle N^3C^2O^1$	107.01	106.15	114.92	114.43
$\angle C^4N^3C^2$	113.27	106.72	110.97	110.73
$\angle C^5C^4N^3$	101.17	104.10	102.31	101.91
$\angle O^6C^2O^1$	122.74	133.75	122.55	116.92
$\angle O^7C^5O^1$	123.81	121.69	120.52	120.94
$\angle H^8N^3C^2$	120.69	107.64	123.43	125.30
$\angle H^{11}N^3C^4$		113.88		
$\angle H^9C^4N^3$	113.68	111.31	112.34	112.17
$\angle H^{10}C^4N^3$	113.69	111.33	112.35	112.17
$\angle H^{11}O^6C^2$			112.52	115.04
$\angle C^4N^3C^2O^1$	0.05	−0.05	0.01	0.02
$\angle C^5C^4N^3C^2$	−0.07	0.06	0.00	0.01
$\angle O^6C^2O^1C^5$	180.00	180.02	179.98	179.94
$\angle O^7C^5O^1C^2$	180.00	180.02	180.01	180.04
$\angle H^8N^3C^2O^6$	−0.04	−57.43	0.03	−0.07
$\angle H^{11}N^3C^4C^5$		118.64		
$\angle H^9C^4N^3C^2$	−117.49	−118.67	−118.01	−118.00
$\angle H^{10}C^4N^3C^2$	117.35	118.81	118.03	118.02
			180.07	−0.11

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