

Preferred conformers in 3-aminopropanol by the PCILO method

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Abstract. Preferred conformers in 3-aminopropanol have been determined by using the quantum-mechanical PCILO method. The results indicate two conformers for the molecule and both of them are stabilized due to intramolecular hydrogen bonding between O-H and N of the amino group. One of the conformers has been observed experimentally by microwave spectroscopy in excellent agreement with the theoretical prediction. The important implication of this result is that the preferred conformations of a molecule can be theoretically predetermined and transitions corresponding to the calculated conformers should be looked for in microwave spectroscopy. This will result in reducing the difficult and time-consuming efforts of scanning the microwave spectrum in wide frequency ranges.

Keywords. 3-aminopropanol ; PCILO ; preferred conformers.

1. Introduction

Recently we have investigated the preferred conformers in *n*-propanol (Saran and Chatterjee 1980) by using quantum-mechanical PCILO (perturbative configuration interaction using localized orbitals) method and the results have been compared with those observed experimentally from microwave spectroscopy in the gaseous state. The agreement between the theory and the experiment was excellent. This is due to the fact that the results of the theoretical computations are strictly valid for free and isolated molecules and in the gaseous state at low pressure, the molecules are far apart from each other and they can be very reasonably considered as free and isolated molecules. The situation, however, is not the same in solutions or in crystals where the environmental forces may cause the molecules to assume conformations other than those predicted by the theoretical calculations. The success in predicting correctly the preferred conformers in *n*-propanol (Saran and Chatterjee 1980) has prompted us to extend this study to 3-aminopropanol which has been recently investigated by McMahan *et al* (1979) using microwave spectroscopy and the results of our theoretical study are presented in this paper.

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2. Procedure

Figure 1 shows the schematic diagram of 3-aminopropanol with the torsion angles around the various single bonds. The torsion angles are defined as:

$$\Phi_{C1-C2} = O5 - C1 - C2 - C3$$

$$\Phi_{C2-C3} = C1 - C2 - C3 - N4$$

$$\Phi_{C3-N4} = C2 - C3 - N4 - H6$$

and $\Phi_{C1-O5} = C2 - C1 - O5 - H14$

with the *cis*-planar arrangement of the terminal bonds being taken as torsion angle equal to zero. The three classical staggered conformations, namely: *gauche*⁺ (*g*⁺), *trans* (*t*) and *gauche*⁻ (*g*⁻) correspond, respectively, to the values of torsion angle around 60°, 180° and 300°.

A general description of the PCILO method has been given in a review (Pullman and Saran 1976). The details of the method, however, can be found in original papers (Diner *et al* 1969; Jordan *et al* 1969). The bond lengths and the bond angles adopted for the construction of the molecule are: C1-O5 = 1.44 Å, C1-C2 = C2-C3 = 1.53 Å, C3-N4 = 1.48 Å, C-H = N-H = O-H = 1.09 Å, C-C-C = 112° and C-C-H = C-C-O = C-O-H = C-N-H = 109.47°. Conformational energy maps have been constructed as a function of two consecutive torsion angles by fixing the remaining two torsion angles in some preselected values. The computations of the energy have been carried out in 30° intervals of the torsion angles and the presentation of the results on the maps has been limited to the 5 kcal/mol isoenergy curves.

3. Results and discussion

3.1. The (Φ_{C3-N4} - Φ_{C2-C3}) conformational energy map

Figure 2 shows the conformational energy map which has been constructed for 3-aminopropanol as a function of torsion angles Φ_{C3-N4} and Φ_{C2-C3} by fixing the remaining two torsion angles $\Phi_{C1-O5} = \Phi_{C1-C2} = 180^\circ$ (*t*). The map shows two global minima: one at $\Phi_{C3-N4} = \Phi_{C2-C3} = 60^\circ$ (*g*⁺) and the other at $\Phi_{C3-N4} = 180^\circ$ (*t*) and $\Phi_{C2-C3} = 300^\circ$ (*g*⁻); both having exactly the same energy. There are two local minima about 0.5 kcal/mol higher in energy at $\Phi_{C3-N4} = 180^\circ$ (*t*) and $\Phi_{C2-C3} = 60^\circ$ (*g*⁺) and $\Phi_{C3-N4} = 60^\circ$ (*g*⁺) and $\Phi_{C2-C3} = 300^\circ$ (*g*⁻). In addition to these, there are low energy regions about 1 kcal/mol higher than the global minimum at $\Phi_{C3-N4} = 60^\circ$ (*g*⁺) and 180° (*t*) and both associated with the

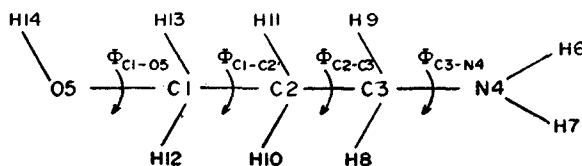


Figure 1. The schematic diagram of 3-aminopropanol with torsion angles.

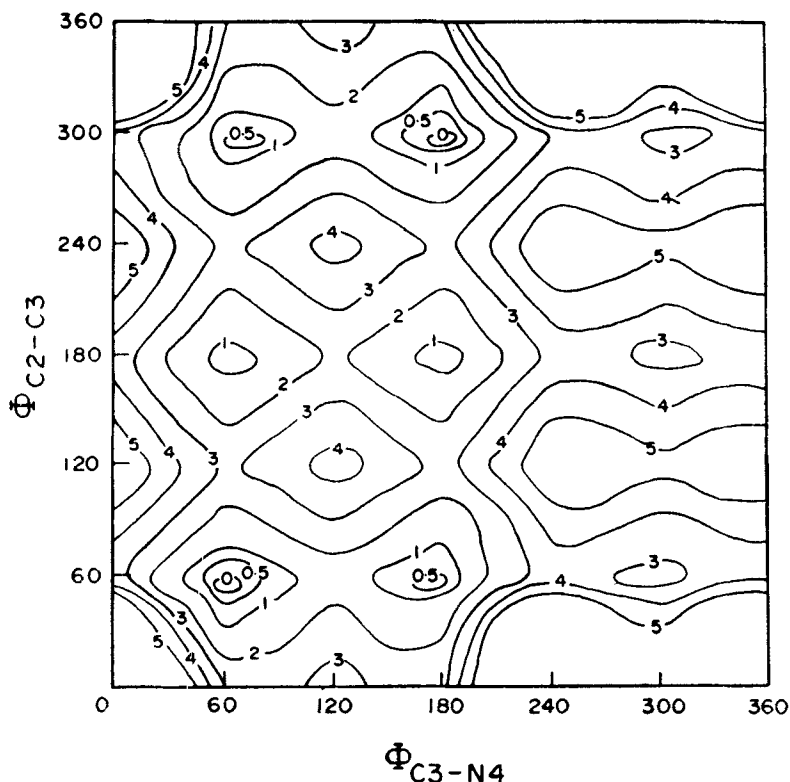


Figure 2. The $(\Phi_{C3-N4} - \Phi_{C2-C3})$ conformational energy map constructed with $\Phi_{C1-C2} = \Phi_{C1-O5} = 180^\circ$. Isoenergy curves in kcal/mol with the global minimum taken as energy zero.

same value of $\Phi_{C2-C3} = 180^\circ (t)$. It can also be seen from this map that the molecule is quite flexible.

3.2. The $(\Phi_{C2-C3} - \Phi_{C1-C2})$ conformational energy map

Figure 2 indicated two preferred values of $\Phi_{C3-C4} = 60^\circ (g^+)$ and $180^\circ (t)$ and for the construction of next conformational energy map these two values have been adopted. Figure 3 shows the $(\Phi_{C2-C3} - \Phi_{C1-C2})$ conformational energy with $\Phi_{C3-N4} = 60^\circ$ and $\Phi_{C1-O5} = 180^\circ$ and it can be seen that the global minimum occurs at $\Phi_{C2-C3} = 300^\circ (g^-)$ and $\Phi_{C1-C2} = 60^\circ (g^+)$. The map is again quite flexible similar to that shown in figure 2. There are three low energy regions about 1 kcal/mol lower than the global minimum. Two of these regions occur at $\Phi_{C2-C3} = 60^\circ (g^+)$ and $300^\circ (g^-)$ and both associated with $\Phi_{C1-C2} = 300^\circ (g^-)$ while the third occurs at $\Phi_{C2-C3} = \Phi_{C1-C2} = 60^\circ (g^+)$. The global minimum of this map is about 1 kcal/mol lower than that of the map shown in figure 2. The other map constructed with $\Phi_{C3-N4} = \Phi_{C1-O5} = 180^\circ$ is shown in figure 4. The global minimum in this map shifts to $\Phi_{C2-C3} = 60^\circ (g^+)$ and $\Phi_{C1-C2} = 300^\circ (g^-)$. Similar to the map in figure 3, this map is also quite flexible and shows three low-energy regions about 1 kcal/mol higher than the global minimum. These regions

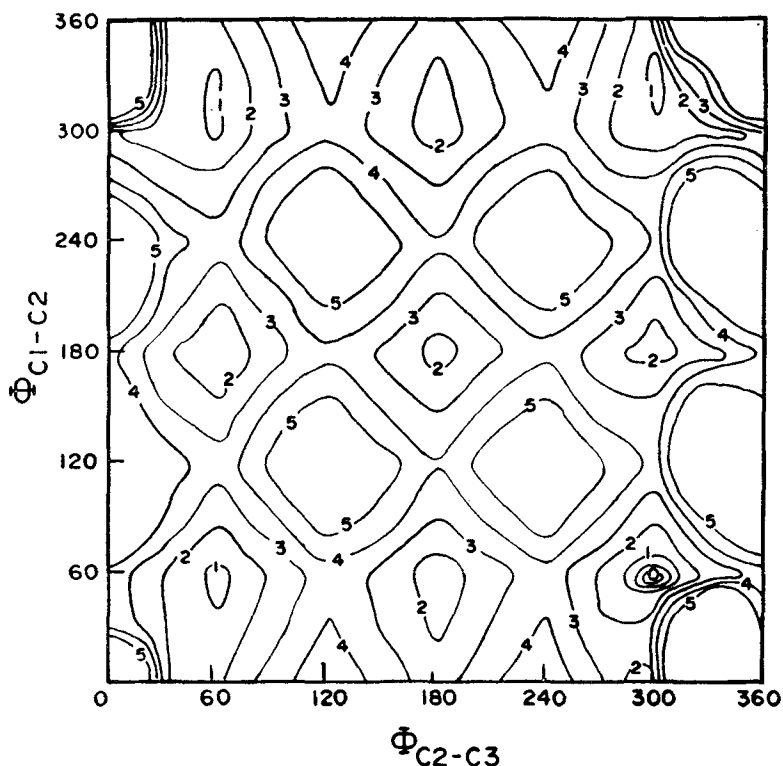


Figure 3. The $(\Phi_{C2-C3} - \Phi_{C1-C2})$ conformational energy constructed map with $\Phi_{C3-N4} = 60^\circ$ and $\Phi_{C1-O5} = 180^\circ$. Isoenergy curves in kcal/mol with the global minimum taken as energy zero.

occur at: $\Phi_{C2-C3} = 60^\circ (g^+)$ and $300^\circ (g^-)$ associated with $\Phi_{C1-C2} = 60^\circ (g^+)$ and $\Phi_{C2-C3} = \Phi_{C1-C2} = 300^\circ (g^-)$. The energy of the global minimum of this map is exactly the same as that of the map shown in figure 3. Thus, the global minimum of the maps in figures 3 and 4 are about 1 kcal/mol lower than that of the map in figure 2. From the above maps we get two preferred coupled values of Φ_{C3-N4} and Φ_{C2-C3} . These are: $\Phi_{C3-N4} = 60^\circ$ and $\Phi_{C2-C3} = 300^\circ$ and $\Phi_{C3-N4} = 180^\circ$ and $\Phi_{C2-C3} = 60^\circ$ and these values have been utilized for the construction of next conformational energy maps.

3.3. The $(\Phi_{C1-C2} \Phi_{C1-O5})$ conformational energy map

The conformational energy map constructed with $\Phi_{C3-N4} = 60^\circ$ and $\Phi_{C2-C3} = 300^\circ$ is shown in figure 5. It can be seen that the global minimum occurs at $\Phi_{C1-C2} = 60^\circ (g^+)$ and $\Phi_{C1-O5} = 180^\circ (t)$. The map is still quite flexible and there is one low energy region around $\Phi_{C1-C2} = 300^\circ (g^-)$ and $\Phi_{C1-O5} = 180^\circ (t)$ which is about 1 kcal/mol higher in energy than the global minimum. The other map constructed (figure 6) with $\Phi_{C3-N4} = 180^\circ$ and $\Phi_{C2-C3} = 60^\circ$ shows the global minimum at $\Phi_{C1-C2} = 300^\circ (g^-)$ and $\Phi_{C1-O5} = 180^\circ (t)$. In this map also there is one low energy region about 1 kcal/mol higher than the global minimum at

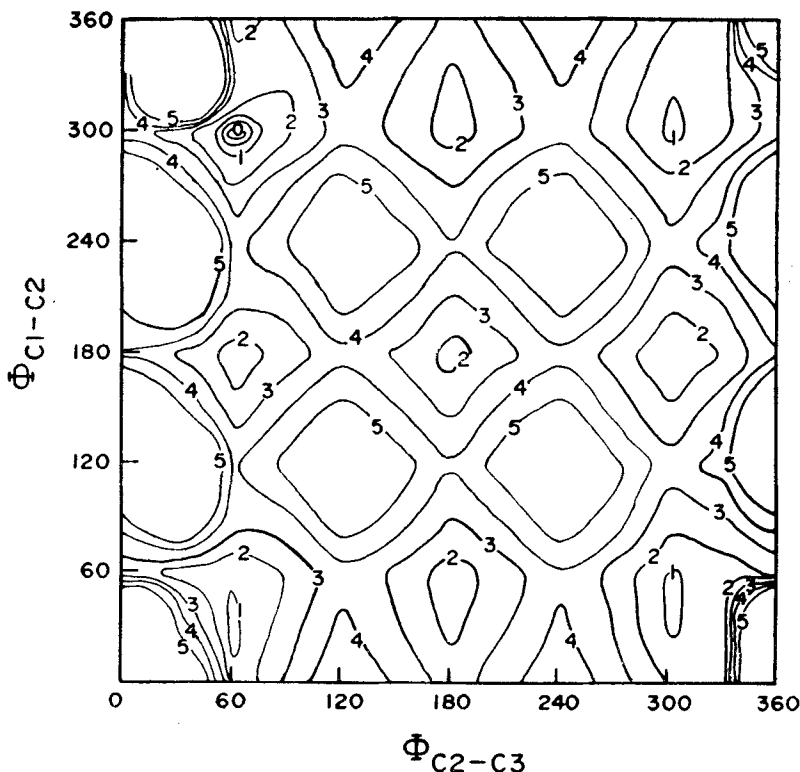


Figure 4. The ($\Phi_{C2-C3} - \Phi_{C1-C2}$) conformational energy map constructed with $\Phi_{C3-N4} = \Phi_{C1-O5} = 180^\circ$. Isoenergy curves in kcal/mol with the global minimum taken as energy zero.

$\Phi_{C1-C2} = 30^\circ$ (g^+) and $\Phi_{C1-O5} = 180^\circ$ (t). The global minimum of both the maps shown in figures 5 and 6 has exactly the same energy as that of the maps shown in figures 3 and 4, i.e. about 1 kcal/mol lower than that of the map shown in figure 2. From the maps shown in figures 5 and 6 we get two coupled values of Φ_{C2-C3} and Φ_{C1-C2} and these are: $\Phi_{C2-C3} = 300^\circ$ and $\Phi_{C1-C2} = 60^\circ$ and $\Phi_{C2-C3} = 60^\circ$ and $\Phi_{C1-C2} = 300^\circ$. These values have been, then, adopted for the construction of ($\Phi_{C1-O5} - \Phi_{C3-N4}$) map to obtain the preferred conformations of 3-aminopropanol.

3.4. The ($\Phi_{C1-O5} - \Phi_{C3-N4}$) conformational energy map

Finally, we have constructed two ($\Phi_{C1-O5} - \Phi_{C3-N4}$) conformational energy maps by fixing the coupled values of Φ_{C2-C3} and Φ_{C1-C2} as obtained in the previous maps. Figure 7 shows the map constructed with $\Phi_{C2-C3} = 300^\circ$ and $\Phi_{C1-C2} = 60^\circ$ and it shows a highly localized global minimum at $\Phi_{C1-O5} = 330^\circ$ and $\Phi_{C3-N4} = 150^\circ$. The energy of this global minimum is about 3.6 kcal/mol lower than that of the global minimum of the maps shown in figures 3-6 which is about 4.6 kcal/mol lower than the global minimum of the map in figure 2.

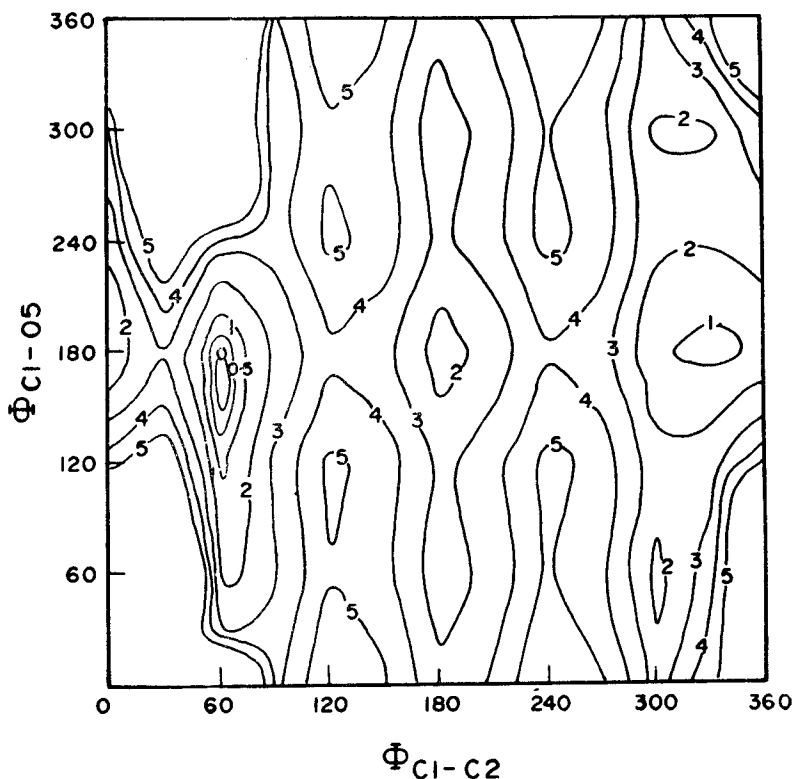


Figure 5. The $(\Phi_{C1-C2} - \Phi_{C1-O5})$ conformational energy map constructed with $\Phi_{C3-N4} = 60^\circ$ and $\Phi_{C2-C3} = 300^\circ$. Isoenergy curves in kcal/mol by taking the global minimum as energy zero.

The global minimum of the map shown in figure 7 is stabilized due to intramolecular hydrogen bonding between O5-H14 and N4. It can also be seen from figure 7 that except for the two 5 kcal/mol isoenergy curves, besides, the one encompassing the global minimum, the rest of the map is over 5 kcal/mol in energy. Figure 8 shows the conformational energy map constructed with $\Phi_{C2-C3} = 60^\circ$ and $\Phi_{C1-C2} = 300^\circ$. In this case again, similar to figure 7, a highly localized global minimum occurs at $\Phi_{C1-O5} = 30^\circ$ and $\Phi_{C3-N4} = 90^\circ$. This is again due to intramolecular hydrogen bonding between O5-N14 and N4 and the energy of this global minimum has exactly the same energy as that of the map in figure 7. Thus, the present theoretical investigations predict two most preferred conformers for 3-aminopropanol and both of them are stabilized due to intramolecular hydrogen bonding between O5-H14 and N4. These conformers have the torsion angles:

- (a) $\Phi_{C3-N4} = 150^\circ$ $\Phi_{C2-C3} = 300^\circ$
 $\Phi_{C1-C2} = 60^\circ$ and $\Phi_{C1-O5} = 330^\circ$
- (b) $\Phi_{C3-N4} = 90^\circ$ $\Phi_{C2-C3} = 60^\circ$
 $\Phi_{C1-C2} = 300^\circ$ and $\Phi_{C1-O5} = 30^\circ$

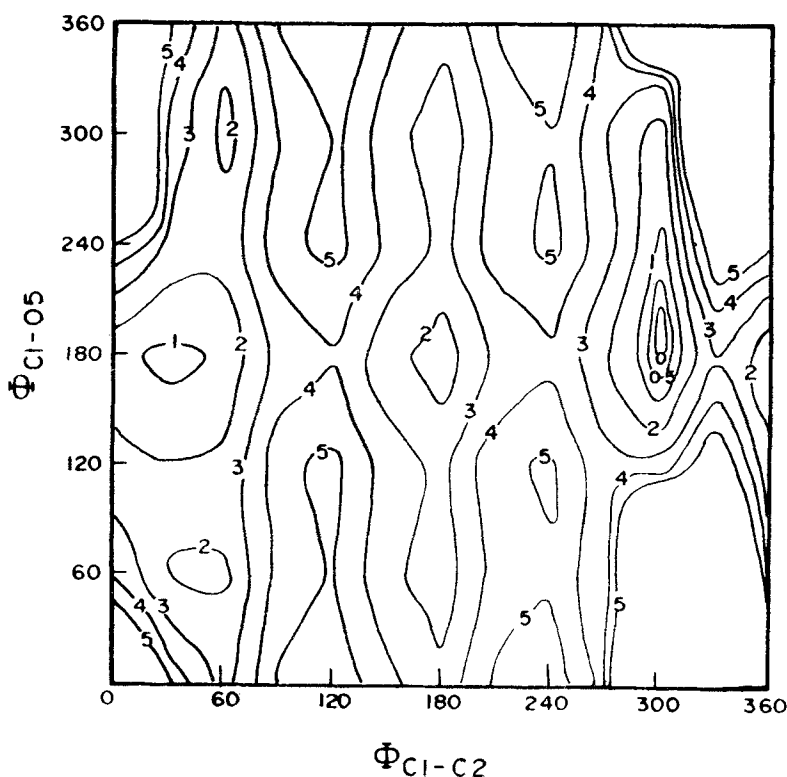


Figure 6. The $(\Phi_{C1-C2} - \Phi_{C1-O5})$ conformational energy map constructed with $\Phi_{C3-N4} = 180^\circ$ and $\Phi_{C2-C3} = 60^\circ$. Isoenergy curves in kcal/mol by taking the global minimum as energy zero.

Figure 9 shows the projection of 3-aminopropanol in conformation *b* with intramolecular hydrogen bonding shown by the dotted line. The distance between N4 and H14 is 1.58 Å and the hydrogen bond distance is 2.67 Å. The shorter distance than normally observed for linear hydrogen bonds (2.8 — 3.0 Å) is due to the angular nature of the hydrogen bond. A similar projection is obtained with the torsion angles of conformation *a*. It is quite unexpected to find two intramolecularly hydrogen bonded conformers with different torsional angles but of equal energy. Then what are these two conformers? In order to delineate this, we made models of these two conformers. The model building revealed that these two conformers are spatial conformers very similar to the two chair forms of cyclohexane ring. In conformation *a*, the central carbon atom is below the plane formed by the remaining two carbon atoms, the oxygen and the nitrogen atoms. The hydroxyl hydrogen atom which is hydrogen-bonded to nitrogen is above the plane of these four atoms. In conformation *b*, the central carbon atom is above the plane while the hydrogen-bonded hydrogen atom is below the plane. These two conformers are shown in figure 10.

McMahan *et al* (1979) have observed only one conformation for 3-aminopropanol from microwave spectroscopy in which there is an intramolecular hydrogen

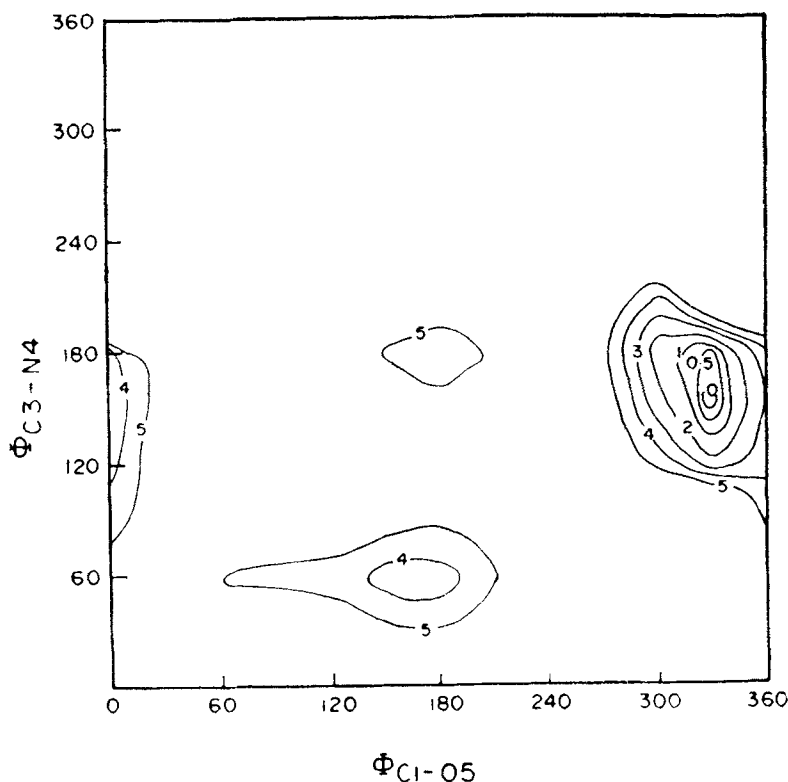


Figure 7. The $(\Phi_{C1-O5} - \Phi_{C3-N4})$ conformational energy map constructed with $\Phi_{C2-C3} = 300^\circ$ and $\Phi_{C1-C2} = 60^\circ$. Isoenergy curves in kcal/mol by taking the global minimum as energy zero.

bonding between O—H and N. Their experimental values of the various torsion angles:

$$\Phi_{C3-N4} = 66.5^\circ, \Phi_{C2-C3} = 68.5^\circ, \Phi_{C1-C2} = 283.5^\circ \text{ and}$$

$\Phi_{C1-O5} = 42^\circ$ are in excellent agreement with the present theoretically predicted conformation *b* for 3-aminopropanol. The conformer *a* is not observed experimentally because the two conformers have probably identical dipole moments and are in rapid equilibrium.

The present study, thus further corroborates the validity of theoretical prediction with the experimental results. As mentioned in our earlier paper (Saran and Chatterjee 1980), the above agreement has a very important implication. The preferred conformers in a molecule can be theoretically obtained before hand and only transitions corresponding to the calculated conformers should be looked for in microwave spectroscopy. This would result in reducing the difficult and time-consuming task of scanning the microwave spectrum in wide frequency ranges.

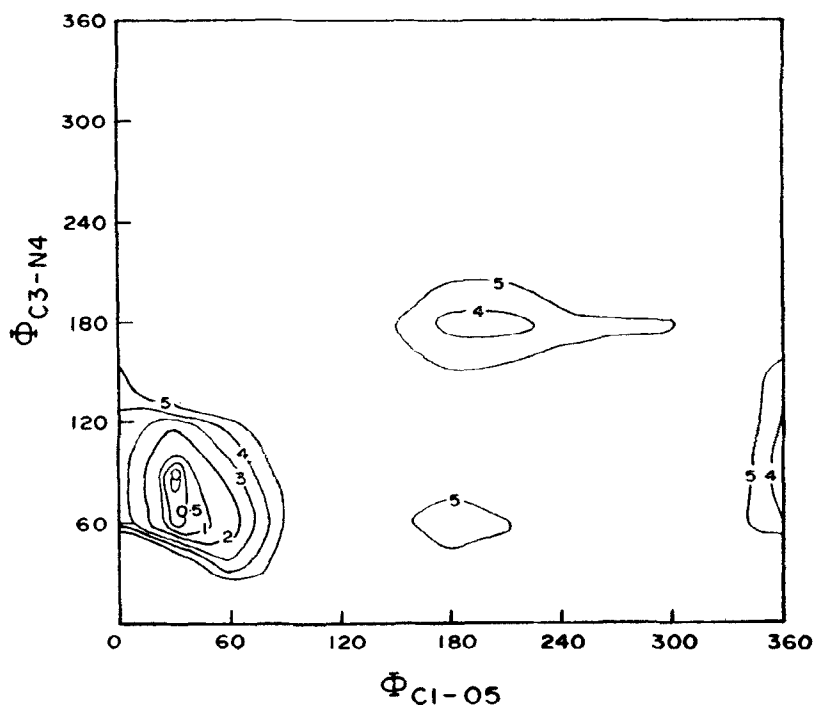


Figure 8. The ($\Phi_{C1-O5} - \Phi_{C3-N4}$) conformational energy map constructed with $\Phi_{C2-C3} = 60^\circ$ and $\Phi_{C1-C2} = 300^\circ$. Isoenergy curves in kcal/mol by taking the global minimum as energy zero.

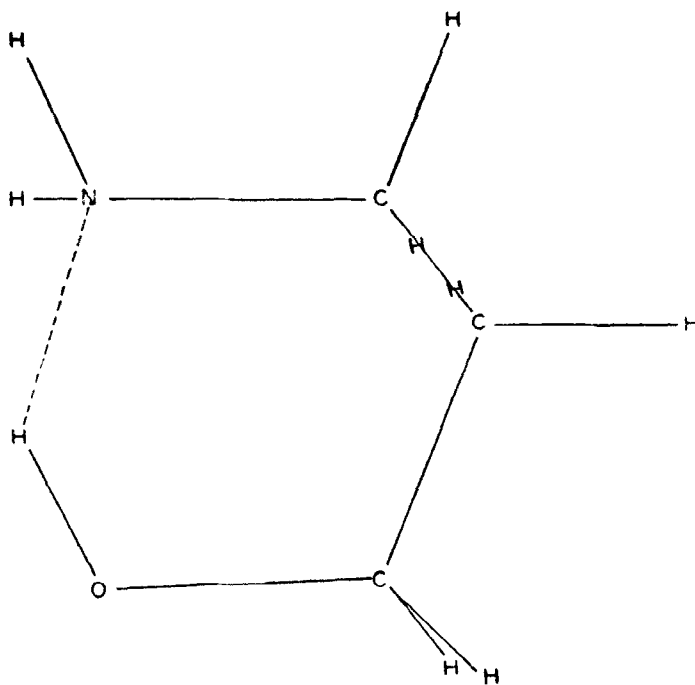


Figure 9. The projection of 3-aminopropanol in the conformer *b*.

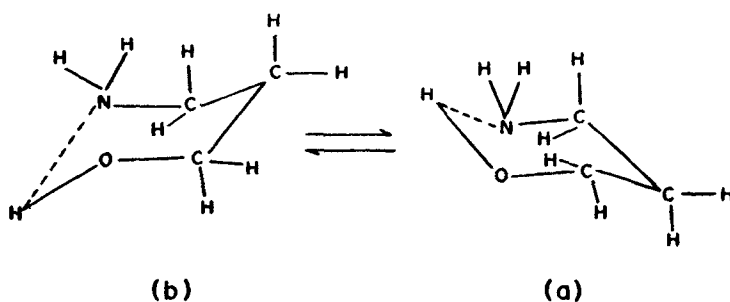


Figure 10. The diagram of 3-aminopropanol conformers in the chair form.

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