CONFORMATIONAL ANALYSIS OF 2-ACETAMIDO-1,3-PROPANEDIOL AS A MODEL OF 3-ACETAMIDO-3-DEOXYHEXOPYRANOSES

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For the four basic conformations of the 1,3-propanediol moiety of 2-acetamido-1,3-propanediol the minimal conformational energy in dependence on the angle Φ (which expresses the rotation around the bond linking the acetamido group to the 1,3-propanediol) and on the parameter $\Delta\omega$ (which expresses the pyramidal character of bonds on the nitrogen atom) was determined by EHT and CNDO/2 methods. Conformation of the acetamido moiety in 3-acetamido-3-deoxyhexopyranoses of *gluco*, *talo*, *galacto* and *manno* configuration (all with equatorial acetamido group) is discussed. The interaction between the nitrogen lone electron pair and the carbonyl group (which fixes the planar conformation of the amide) as well as the energy of the N atom (which stabilises the pyramidal arrangement on this atom) are considered.

The amide group as a structural unit of biologically active compounds is the object of numerous structural studies. The concept of the planar arrangement of the amide group is based on the Pauling's formulation[1]. Properties of the amide (peptide) group were theoretically as well as experimentally studied using several model systems (see ref.[2]). Its electronic structure was calculated by all-valence MO methods[3-5]. Although even Pauling himself did not exclude[6] that the amide group might deviate from planarity this eventuality was studied in some detail only by Ramachandran and coworkers, first on cyclopeptides with smaller rings[7,8]. Later, conformations of simple amides were calculated by quantum chemical methods and confronted with the results of three-dimensional X-ray structure analyses[9,10]. The authors[9,10] concluded that an amide group can assume a non-planar arrangement without increasing significally the potential energy of the molecule and that this arrangement is characterised by a pyramidal arrangement of bonds on the nitrogen atom. A virtually planar amide group was found in crystalline 2-acetamido-2-deoxy--α-D-glucose[11] and 2-acetamido-2-deoxy-α-D-galactose[12]. A *trans*-amide group was found by ^{1}H-NMR spectroscopy in 2-acetamido-2-deoxy derivatives of α-D-glucose, α-D-galactopyranose and β-D-mannopyranose[13]. In no case a contingent non-planarity of the N-acetyl group bonded to the saccharide skeleton was hitherto considered. The aim of our paper is to investigate the conformation of the equatorial N-acetyl

group on a pyranose ring. As a model compound for the quantum chemical calculations we used 2-acetamido-1,3-propanediol. This compound can reasonably simulate the substitution on the $C_{(3)}$ atom of 3-acetamido pyranoses which we have already studied using the CD spectroscopy[14]. Another objective of our present study is to answer — partially — some more general questions, *i.e* whether the non-planar arrangement could be an inherent property of the amide bond, what is the geometric character of the deviation involved, and what factors cause this deviation.

CALCULATIONS

Three conformations *I—III* of 2-acetamido-1,3-propanediol, together with the angles characterising the spacial arrangement, are shown in Fig. 1. One hydrogen atom of the methyl group is in all cases eclipsed with the carbonyl oxygen atom. The angle $\Phi = 180°$ characterises the planar *trans*-amide orientation, angles χ_1 and χ_2 are parameters of calculation and characterise the configuration of the vicinal hydroxyl groups on the hexopyranose ring. In the conformation *I* both OH groups are simulated as equatorial ($\chi_1 = 60°$, $\chi_2 = 300°$). This arrangement corresponds to the 3-CH_3CONH *gluco* configuration. In the form *II* the OH groups are simulated
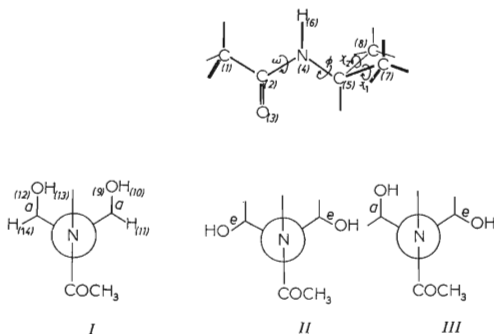

FIG. 1

Conformations of the 2-Acetamido-1,3-propanediol Molecule, Description of the Atoms and Torsion Angles and Newman Projections of the Three Orientations of the Hydroxyl Groups

I Fragment of *gluco* configuration, *II* fragment of *talo* configuration, *III* fragment of *galacto* configuration.

FIG. 2

Geometry of a Non-planar Amide Group

as axial ($\chi_1 = 300°$, $\chi_2 = 60°$), representing thus the 3-CH_3CONH *talo* configuration. The forms *III* and *IV* have one hydroxyl axial and the other equatorial; this situation corresponds to the respective 3-CH_3CONH *galacto* and *manno* configurations. When the rotation of the amide group around the $N_{(4)}$—$C_{(5)}$ bond was investigated, the torsion angle Φ was tabulated in steps of 20°, while in the proximity of minima or maxima the steps of 10° were used. The employed geometric parameters, listed in Table I, were taken from data for an amide in gas phase[15]. Bond lengths and bond angles were assumed to be constant during the rotation.

Next, the non-planarity of the amide group was examined. In order to describe the deviation from planarity, symbols $\Delta\omega$ and $\Delta\omega'$ are employed in this paper (Fig. 2),* $\Delta\omega$ being the torsion angle $O_{(3)}$—$C_{(2)}$—$N_{(4)}$—$C_{(5)}$ and $\Delta\omega'$, the angle $C_{(1)}$—$C_{(2)}$—$N_{(4)}$—$H_{(6)}$. In a pyramidal arrangement without torsion around the $C_{(2)}$—$N_{(4)}$ bond in a regular pyramid, both angles are equal, $\Delta\omega = \Delta\omega'$. The bond angles on the N atom were corrected for the degree of the pyramidicity (see Table I).

The calculations were performed using the EHT and CNDO/2 methods[18-20]. The single components of the total energy of the system[20] were separated into one- and two-center terms ($E = E_A + E_{AB}$). For the one-center term we can write

$$E_A = E_A^V + E_A^J + E_A^K, \tag{1}$$

where E_A is the energy of the atom A given as the sum of the total (one-center) one-electron AO energy of the electrons on the atom A (E_A^V), of the electron repulsion on the atom A (E_A^J), and of the electron exchange interaction on the atom A (E_A^K). For the two-center terms we can use an analogous relationship:

$$E_{AB} = E_{AB}^R + E_{AB}^J + E_{AB}^K + E_{AB}^V + E_{AB}^N = E_{AB}^R + E_{AB}^E, \tag{2}$$

TABLE I

Geometric Parameters

Bond lengths, Å		Bond angles	
$C_{(1)}$—$C_{(2)}$	1·51	$O_{(3)}$—$C_{(2)}$—$C_{(1)}$	124°
$C_{(2)}$—$O_{(3)}$	1·22	$O_{(3)}$—$C_{(2)}$—$N_{(4)}$	124°
$C_{(2)}$—$N_{(4)}$	1·35	$C_{(2)}$—$N_{(4)}$—$C_{(5)}$	120° (pro $\Delta\omega = 0°$)
$N_{(4)}$—$H_{(6)}$	1·01	$C_{(2)}$—$N_{(4)}$—$H_{(6)}$	119·98° ($\Delta\omega = 10°$)
$N_{(4)}$—$C_{(5)}$	1·47		117·65° ($\Delta\omega = 15°$)
$C_{(7)}$—$H_{(11)}$	1·02		115·71° ($\Delta\omega = 20°$)
$C_{(7)}$—$O_{(9)}$	1·42		113·04° ($\Delta\omega = 25°$)
$O_{(9)}$—$H_{(10)}$	1·00		109·47° ($\Delta\omega = 30°$)

*   Two systems of descriptors were suggested[9,16,17]. In the present paper we apply the notation of Ramachandran[9]. Assuming a regular pyramid, the parameter Θ_N which characterises the pyramidicity of the nitrogen atom equals to $-2\,\Delta\omega$.

where E_{AB}^R is the sum of the resonance integrals relative to the energy of the bond A—B, E_{AB}^J is the repulsion of the electrons on the atoms A and B, E_{AB}^V is the potential energy of the electron on the atom A in the field of the nucleus B and reverse, and E_{AB}^N is the repulsion energy between the nuclei A and B. Since the term E_{AB}^R, obtained from the CNDO/2 calculation, is directly comparable with the Ruedenberg interference energy[21], is characteristic for the A—B bond.

RESULTS AND DISCUSSION

Planar Amide Group

Variation of the conformational energy as a function of the rotation around the $C_{(5)}$—$N_{(4)}$ bond, calculated by the EHT method for the cases $I-IV$, is given in Fig. 3. It follows from the overlap population between the atoms that the shape of the potential curves is determined mainly by the mutual interactions of the atoms $H_{(6)}$ and $O_{(3)}$ with substituents at $C_{(7)}$ and $C_{(8)}$. The extremely high barriers exhibited compel us to deduce that the EHT method is not suitable for the conformational analysis of these systems (see also[22]) although it determines satisfactorily the positions of the extrema. Further we shall analyse the results obtained by the CNDO/2 method. In the case of I-gluco arrangement the absolute minimum on the conformational energy map $E(\Phi)$ was found for $\Phi = 40°$ (or $320°$ in the equivalent enantiomeric conformation). This minimum energy conformation is evidently caused by the existence of a hydrogen bond between the atoms $O_{(3)}$ and $H_{(10)}$ as indicated by the almost identical values of the interaction energies E^R and E^E. The interaction manifests itself by a change in the electron distribution in the $O_{(9)}\text{---}H_{(10)}\text{---}O_{(3)}$ segment. The maximum conformational energy for $\Phi = 90°$ is due to a repulsive electrostatic interaction, E^J, between the atoms $O_{(3)}$ and $O_{(9)}$. The high energy values for $\Phi = 140°$ are probably connected not only with an interaction of the atom $O_{(3)}$ with substituent
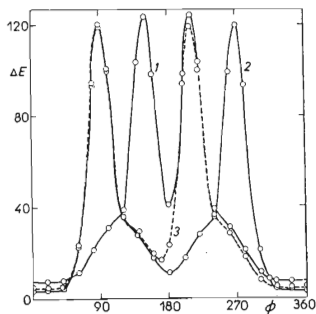

Fig. 3

Energy Change due to Rotation of Planar Acetamide Group around the $N_{(4)}$—$C_{(5)}$ Bond, as Calculated by the EHT Method

1 For *I-gluco* arrangement, *2* for *II-talo* arrangement, *3* for *III-galacto* arrangement. ΔE in kcal mol^{-1}.

at $C_{(7)}$ but also with repulsive interactions of the carbonyl carbon atom with the propane skeleton. The local minimum at $\Phi = 180°$ is caused by attractive interactions of the atom $O_{(3)}$ with the hydrogens $H_{(11)}$ and $H_{(14)}$, enabled by an advantageous orientation of the $C_{(2)}$—$N_{(4)}$ bond relative to the propane chain. The interactions of the $H_{(6)}$ atom with the 1,3-propanediol moiety are substantially less dependent on the orientation of the $C_{(2)}$—$N_{(4)}$ bond and contribute less to the energy changes.

Transfer of the OH groups at $C_{(7)}$ and $C_{(8)}$ into positions characterising the diaxial conformation (model *II-talo*, Fig. 4) leads to a change in interactions of the atom $O_{(3)}$ with substituents at $C_{(7)}$ and $C_{(8)}$. The absolute minimum for $\Phi = 50°$ (or $310°$) is caused by the interaction of $O_{(3)}$ with $H_{(11)}$ and of $H_{(6)}$ with $O_{(12)}$. Similarly to the *gluco* model, the maximum for $\Phi = 140°$ (or $220°$) is caused by a repulsive interaction between the atoms $O_{(3)}$ and $O_{(9)}$. The hydrogen bonds between $H_{(6)}$ and $O_{(12)}$ or $O_{(9)}$ give rise to local minima at $\Phi = 165°$ and $195°$. Also in this case, the interactions of the carbonyl group with the propane skeleton operate in the region of the torsion angles $\Phi = 80° - 120°$. In the region of the angles $\Phi = 165° - 195°$ the system is stabilised by the interaction between the π-orbital of the carbonyl group and the lone electron pairs (*p*-type) of the atoms $O_{(9)}$ and $O_{(12)}$; in this conformation this interaction has the greatest value.
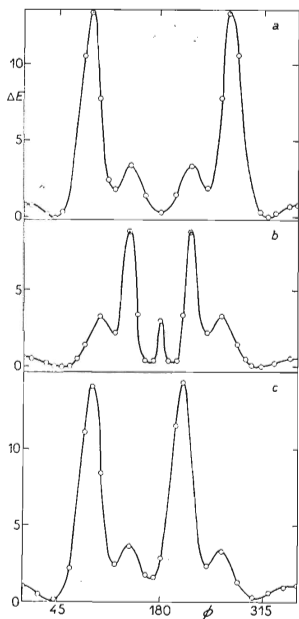

Fig. 4

Energy Variation in the Rotation of Planar Acetamido Group around the $N_{(4)}$—$C_{(5)}$ Bond, as Calculated by CNDO/2 Method

a For *I-gluco* arrangement, *b* for *II-talo* arrangement, *c* for *III-galacto* arrangement. ΔE in kcal mol^{-1}.

Finally, let us consider models of the enantiomeric *III-galacto* and *IV-manno* arrangements. The energy curve for *IV* can be divided into two parts: In the region $\Phi = 0° - 180°$ it is similar to the curve for the *gluco* arrangement (equatorial orientation of the OH group at $C_{(7)}$), whereas in the region $\Phi = 180° - 360°$ it reminds the curve for the *talo* arrangement (axial orientation of the OH group at $C_{(8)}$). In the proximity of $\Phi = 180°$ the effects of both the halves of the 1,3-propanediol grouping mutually overlap. In the maximum at $\Phi = 210°$ the higher conformational energy for the *galacto* than for the *talo* arrangement is probably the result of a smaller possibility of delocalisation of the $O_{(3)}$ lone electron pairs caused by the absence of the second OH group in the axial position. This explanation is supported also by the value of the contribution E^R which is considerably lower for the *galacto* than for the *talo* arrangement. By reason of symmetry, a similar interpretation holds also for the *manno* isomer.

NON-PLANAR AMIDE GROUP

The effect of non-planarity of the amide group on the energy of the studied models was investigated in the proximity of the most stable arrangements calculated for the planar amide group. We studied the conformational energy surface, $E(\Phi, \Delta\omega)$, in the ranges $\Phi \langle 50°, -50° \rangle$ and $\Delta\omega \langle 30°, -30° \rangle$ and tabulated the values of the angles Φ and $\Delta\omega$ in steps of $5°$. The complete conformational energy map for the *I-gluco* arrangement is given in Fig. 5. The absolute energy minimum is located at $\Phi = 30°$ and $\Delta\omega = 25°$. The corresponding energy is by 2·9 kcal mol^{-1} lower than the energy of the most stable conformer with a planar amide group $(\Phi = 40°)$.
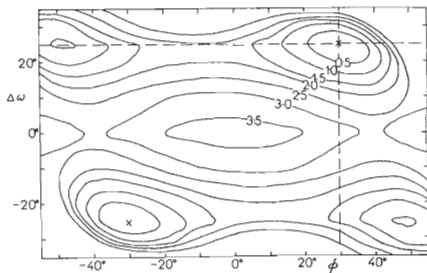

Fig. 5

Conformational Map $E(\Phi, \Delta\omega)$ for *I-gluco* Arrangement, Showing the Effect of Pyramidicity of the Nitrogen Atom

For the same pyramidicity ($\Delta\omega = 25°$) a local minimum was found for $\Phi = -50°$, its energy being by 0·4 kcal mol^{-1} higher than the energy of the absolute minimum. In the *II talo* arrangement the situation is similar. The absolute minimum $\Phi = 40°$, $\Delta\omega = 25°$ is by 2·02 kcal mol^{-1} more stable than the most planar arrangement. The second minimum is at $\Phi = -50°$ and $\Delta\omega = 25°$, and has the energy by 0·26 kcal mol^{-1} higher than the absolute minimum. Owing to the symmetry of both the *gluco* and *talo* arrangements, all the minima are doubled.

The cases of *III-galacto* or *IV-manno* are more complicated. The absolute energy minimum was found for $\Phi = -50°$, $\Delta\omega = 25°$, and it is by 4·7 kcal mol^{-1} energetically more advantageous than the optimum arrangement of *III* with a planar amide group. The energy of the local minima for $\Phi = 40°$, $-30°$ and $50°$ (for pyramidicity $\Delta\omega = -25°$) is higher than the energy of the absolute minimum by 0·2, 0·8 and 1·5 kcal mol^{-1}, respectively. In the case of *IV-manno* the position and the character of the energetic minima are analogous to those found for *III*. The intersections of the conformational maps in Figs 6 and 7 show the character of the energy changes in the proximity of the absolute minimum of the dependence $E(\Phi, \Delta\omega)$.

The separation of the total energy E into one-center and two-center terms was successfully used in the interpretation of barriers to internal rotation of molecules[23].
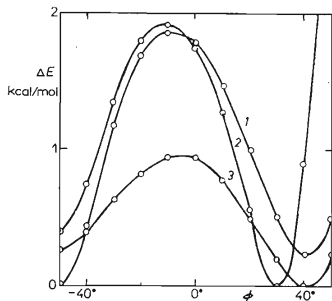

Fig. 6

Intersection of the Conformational Map $E(\Phi, \Delta\omega)$, Depicting the Dependence of the Energy on the Magnitude of Nitrogen Pyramidicity in the Proximity of Absolute Minima

1 For *I-gluco* arrangement, *2* for *II-talo* arrangement, *3* for *III-galacto* arrangement.
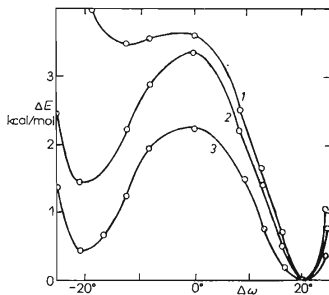
Fig. 7

Intersections of the Conformational Maps $E(\Phi, \Delta\omega)$, Depicting the Dependence of the Energy on the Torsion of a Non-planar Acetamido Group around the $C_{(2)}-N_{(4)}$ Bond in the Proximity of Absolute Minima

1 For *I-gluco* arrangement, *2* for *II-talo* arrangement, *3* for *III-galacto* arrangement.

In the present case we tried to make use of the single energy terms in the equations (1) and (2) in order to find the reasons for the greater stability of the non-planar arrangement of the amide group. Comparison of the values of the two-center terms for the planar with those for the non-planar arrangements shows that the sum E_{AB} increases with the increasing non-planarity, *i.e.* it has a destabilising effect on the total energy of the molecule. On the contrary, the sum of the one-electron contributions decreases with the increasing pyramidicity, stabilising thus non-planar arrangements. It follows from the detailed analysis of the contributions of the single interactions to the sum of the two-center part of the energy E_{AB} (Table II) that the most important contribution which determines the increasing destabilising effect of the sum E_{AB} with the increasing non-planarity are the interactions between the atoms $C_{(2)}$ and $N_{(4)}$. First of all, there is a change in the resonance interaction of the p_z orbital of $N_{(4)}$ with the p_z orbital of $C_{(2)}$ which characterises a diminished conjugation of the lone electron pair of $N_{(4)}$ with the π-bond of the carbonyl group. (The wave function of the lone electron pair has the form $\psi_{LP}(N) = p + \lambda s$, where the coefficient λ characterising the hybridisation is determined by the pyramidicity of the bonds on the nitrogen atom). The destabilisation of the system by an increasing non-planarity of the amide group can thus be explained by lowering the delocalisation of the nitrogen lone electron pair. An increasing deviation from planarity increases the contribution

TABLE II

Differences between Energy Contributions for Non-planar and the Most Stable Planar Arrangements (kcal mol^{-1})

Model $\Phi, \Delta\omega$		E_T	E_A	E_{AB}	E_+	$E_{2,4}$	$E_{2,4}^R$	$E_{2,3}$	$E_{2,3}^R$
gluco									
30°	25°	−2·92	−35·58	32·66	−32·53	27·62	21·78	−4·82	−2·79
−50°	25°	−2·53	−34·87	32·34	−31·71	27·99	22·17	−4·70	−1·94
talo									
40°	25°	−2·02	−36·64	34·06	−31·56	28·74	22·18	−4·55	−2·90
−50°	25°	−1·76	−35·54	33·78	−32·37	27·90	22·36	−4·64	−2·90
galacto									
−50°	25°	−4·70	−34·73	32·93	−31·91	27·55	22·04	−3·65	−1·84
40°	25°	−4·47	−38·29	33·83	−31·56	27·99	21·65	−4·16	−2·72
−30°	−25°	−3·90	−36·63	32·73	−31·62	28·18	21·72	−4·16	−2·77
50°	−25°	−3·22	−37·58	34·36	−31·17	27·68	21·62	−3·99	−2·63

of the nitrogen s atomic orbital to its lone electron pair which then obtains partially a character of an sp lone electron pair as compared with the "pure" p-type lone electron pair in the planar arrangement. Since the contribution of the nitrogen p-orbital in the lone electron pair decreases with an increasing contribution of the s orbital, and since there is no overlap between the s atomic orbital of the nitrogen and the π-orbital of the carbonyl, the value of this interaction must decrease. A greater s contribution lowers the energy of the lone electron pair of the nitrogen atom and simultaneously increases its local dipole moment. This is oriented in the direction of the lone electron pair and its value is the greatest for the sp^3 hybridisation.

The mentioned destabilisation is outweighed by the stabilising character of the energy change of the atoms. The energy change of nitrogen represents the decisive contribution to this stabilisation. The energy decrease of this atom is caused by the tendency to exist in the most advantageous electron configuration with a pyramidal arrangement of substituents. The energy gain in the transition from a planar into a non-planar conformation can be compared with the barrier to inversion of an ammonia molecule where the energy maximum corresponds to the planar arrangement (barrier height $5\cdot8$ kcal mol^{-1})[24]. The differences between the values of the particular contributions and the corresponding contributions for the planar arrangement are given for the absolute minima in Table II. According to the CNDO/2 calculation the greater stability of a non-planar amide group can be explained mainly by the tendency to achieve a more stable hybridisation of the nitrogen atom. This effect is partly compensated by lowering the conjugation of the nitrogen lone electron pair with the carbonyl group. The same reason for the stabilisation of a non-planar conformation of the amide group can be deduced also from very similar contributions of the single interactions in all cases studied. The different energy values of the particular minima are probably due to a different magnitude of the mutual interactions which is caused by different orientations of the CH_3CONH group relative to the propanediol skeleton.

All the calculations were carried out under assumption of a regular pyramide $(\Delta\omega = \Delta\omega')$. We investigated also the possible effect of twisting the regular pyramide around the bond $C_{(2)}$—$N_{(4)}$. The calculations revealed that this skewed pyramide $(\Delta\omega \neq \Delta\omega')$ leads invariably to energetically less advantageous conformers. The lower stability of these conformers is caused by lessening of the sp conjugation of the nitrogen lone electron pair with C=O bond.

The conclusion that the deformation of the amide bond has mainly the character of a regular pyramidal arrangement was achieved also by calculations[25] of the 4-azatricyclo[4,4,0,0^{3,8}]decan-5-one molecule in which the amide group has the *cis*-conformation. Also calculations of conformational maps for formamide, acetamide, N-methylacetamide and N-ethylacetamide have shown[9,10] that a deviation from planarity involves formation of a regular pyramide at the nitrogen atom.

This assumption was proved experimentally by a number of X-ray data, evaluated by Ramachandran and coworkers[10,11].

From the mentioned results it follows that the amide group can be considered as an inherently chiral formation, the chirality of which is caused by the pyramidicity of the nitrogen atom. Of course, the degree of the pyramidicity and the possible following torsion around the CO—N bond is strongly influenced by interactions with other parts of the molecule. In a chiral environment, such as in the studied 3-acetamido-3-deoxyhexopyranoses[15], the population of both possible enantiomeric arrangements is not equal or even only one of these arrangements is present. An experimental proof of the assumption that the non-planarity of the amide group is its inherent property should be sought in simple conformationally mobile amides in which the deviation from planarity cannot be caused either by a rigid skeleton, as *e.g.* in the case of 4-azatricyclo[4,4,0,0^{3,8}]decan-5-one[25] and 9-nonanelactam[17], or by packing in the crystal lattice, as in the peptides studied by X-ray diffraction[26]. The simplest model compound — formamide — was studied by microwave spectroscopy. An older study[27] found a non-planar arrangement of a skewed pyramide type whereas a more recent investigation[15] found a planar arrangement. If we consider the fact that the inversion barrier between the two enantiomeric pyramides at the nitrogen atom is very low and that the gaseous state enables an extremely rapid conversion of both energetically equivalent states, we cannot exclude that the found planar structure[15] reflects an averaged state of two pyramidal structures.

REFERENCES

1. Pauling L.: *The Nature of the Chemical Bond*, 2. edition, p. 207. Cornell University Press Ithaca, N.Y. 1945.
2. Smolíková J., Bláha K.: Chem. Listy *69*, 1009 (1975).
3. Yan J. F., Momany F. A., Hoffmann R., Scheraga H. A.: J. Phys. Chem. *74*, 420 (1970).
4. Popov E. M., Zheltova V. N.: Zh. Prikl. Spektrosk. *14*, 121 (1971).
5. Murthy A. S. N., Rao K. G., Rao C. N. R.: J. Amer. Chem. Soc. *92*, 3544 (1970).
6. Pauling L., Corey R. B.: Proc. Nat. Acad. Sci.: U.S.A. *37*, 251 (1951).
7. Ramachandran G. N.: Biopolymers *6*, 1494 (1968).
8. Ramachandran G. N., Chandrasekaran R., Kopple K. D.: Biopolymers *10*, 2113 (1971).
9. Ramachandran G. N., Lakshminarayanan A. V., Kolaskar A. S.: Biochim. Biophys. Acta *303*, 8 (1973).
10. Kolaskar A. S., Lakshminarayanan A. V., Sarathy K. P., Sasisekharan V.: Acta Crystallogr. *14*, 1081 (1975).
11. Johnson L. N.: Acta Crystallogr. *21*, 885 (1966).

12. Neuman A., Gillier-Pandraud H., Longchambon F.: C. R. Acad. Sci., Ser. C *277*, 455 (1973).
13. Shamper T. J.: Carbohyd. Res. *36*, 233 (1974).
14. Bystrický S., Staněk J., Jarý J., Bláha K.: This Journal, in press.
15. Hirota E., Sugisaki R., Nielsen C. J., Sørensen G. O.: J. Mol. Spectrosc. *49*, 251 (1974).
16. Dunitz J. D., Winkler F. K.: Acta Crystallogr. Sect. B *31* 251 (1975).
17. Winkler F. K., Dunitz J. D.: J. Mol. Biol. *59*, 169 (1971).
18. Hoffmann R.: J. Chem. Phys. *39*, 1397 (1963).
19. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw-Hill, New York 1970.
20. Fischer H., Kollmar H.: Theor. Chim. Acta *16*, 163 (1970).
21. Ruedenberg K.: Rev. Mod. Phys. *34*, 326 (1962).
22. Herndon W. C., Fever J.: Tetrahedron Lett. *1968*, 2625.
23. Gordon M. S.: J. Amer. Chem. Soc. *91*, 3122 (1969).
24. Swalen J. D., Ibers J. D.: J. Chem. Phys. *36*, 1014 (1962).
25. Maloň P., Bláha K.: This Journal, *42*, 687 (1977).
26. Ramachandran G. N., Kolaskar A. S.: Biochim. Biophys. Acta *303*, 385 (1973).
27. Costain G. C., Dowling J. M.: J. Chem. Phys. *32*, 158 (1960).

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