STRUCTURE AND RING INVERSION OF 2-PYRROLIDONE. SEMIEMPIRICAL QUANTUM CHEMICAL STUDY AND ANALYSIS OF X-RAY DATA

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The equilibrium structure and the ring inversion potential of the 2-pyrrolidone molecule has been studied by the semiempirical CNDO/2 and INDO methods. The calculated geometrical parameters are compared with experimental X-ray data and with earlier Consistent Force Field (CFF) results. The ring inversion is analyzed in terms of two types of puckering coordinates. The CNDO/2 method was found to yield a strongly nonplanar 2-pyrrolidone ring due to the overestimation of the amide pyramidality while INDO calculations led to a slightly nonplanar ring with an extremely low barrier of inversion.

Recently there is an increasing interest in the study of nonrigid (flexible) molecules, which exhibit large amplitude motions[1-3]. The most important types of large amplitude motions are the internal rotation, inversion (*e.g.* in the NH_3 molecule) and the out-of-plane motion of saturated or partly unsaturated *n*-membered rings.

n-Membered rings have $n - 3$ out-of-plane degrees of freedom. Here we are mainly concerned with the puckering motion of a five membered ring, the 2-pyrrolidone (Fig. 1). The two independent puckering coordinates can be defined in several alternative ways.

One definition, proposed by Cremer and Pople[4], is the generalization of the puckering coordinates introduced first by Kilpatrick, Pitzer and Spitzer[5] for the study of cyclopentane pseudorotation. This method is completely general and can be used for any *n*-membered ring. According to this method the distance, Z_j, of the *j*-th ring skeleton atom is measured from a properly defined mean plane. For five membered rings the displacements can be expressed as:

$$z_j = (2/5)^{1/2} q \cdot \cos(\phi + 4\pi(j - 1)/5), \quad j = 1, ..., 5, \qquad (1)$$

where q is the puckering amplitude, ϕ is the phase angle of pseudorotation.

An alternative definition of the puckering coordinates of five membered rings

can be given as appropriate linear combinations of the ring torsional angles $(\tau_1, \ldots, \tau_5)$:

$$\vartheta_1 = N_1[b(\tau_1 + \tau_5) + a(\tau_2 + \tau_4) + \tau_3], \tag{2}$$

$$\vartheta_2 = N_2[(a - b)(\tau_4 - \tau_2) + (1 - a)(\tau_5 - \tau_1)],$$

where $a = \cos 4\pi/5$, $b = \cos 2\pi/5$, $N_1 = (1 + 2a^2 + 2b^2)^{-1/2}$, $N_2 = [2(a - b)^2 + 2(1 - a)^2]^{-1/2}$ are normalization constants, τ_k are dihedral angles defined by the skeleton atoms $k - 1, k, k + 1, k + 2$. This set of coordinates has been proposed by Pulay and coworkers[6] for systematic vibrational analysis. ϑ_1 corresponds to the ring twisting, ϑ_2 to the ring bending mode (Fig. 2).

Any pair of puckering coordinates belongs to one of these two types: *a*) puckering amplitudes − phase angle (q, ϕ); *b*) ring twisting − ring bending coordinates, $(\vartheta_1, \vartheta_2)$. These two types of coordinates can be transformed into each other essentially by polar transformations, so they contain the same information. In the case of a regular pentagon the twisting and bending coordinates belong to a degenerate irreducible representation of the D_{5h} point group. If the potential barrier to pseudo-rotation is zero or low, the puckering amplitude and the pseudorotational phase angle describe two energetically different motions, so the $q - \phi$ set is the adequate
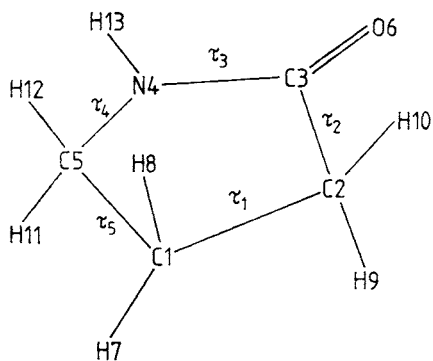

Fig. 1

Atom labeling of the 2-pyrrolidone molecule with the definition of ring torsional angles. Note that this numbering is different from the chemical one
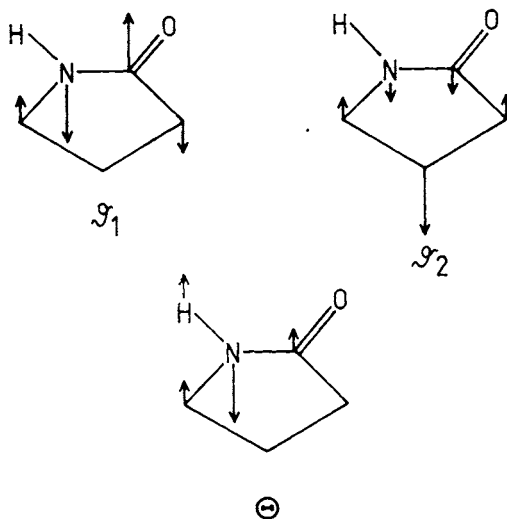
Fig. 2

Atomic displacements along the two puckering and the N—H out-of-plane coordinates constructed from the vibrational **B**-matrix in the 2-pyrrolidone molecule

coordinate pair. If, however, one of the two out-of-plane motions is strongly hindered (*e.g.* the ring twisting mode in the cyclopentene molecule), ϑ_1 and ϑ_2 will be markedly different in energy and the molecule behaves as a "pseudo-four-membered ring"[7].

As the 2-pyrrolidone molecule corresponds to an intermediate case between the above two extremes, it seemed worthwhile to use both types of coordinates in analyzing the ring inversion. The amide bond has a partial double bond character, so the rotation around it is hindered. Consequently ϑ_1 which involves the torsion around the amide bond (τ_3, see Fig. 1 and 2), is stiffer than the bending mode ϑ_2. In the 2-pyrrolidone molecule one has to consider a third large amplitude coordinate as well, the N—H out-of-plane bending mode (Θ) which is in strong kinetic coupling with the ring out-of-plane modes (Fig. 2).

Earlier studies of the title compound involve IR and Raman spectroscopy[8] and theoretical investigations on the equilibrium geometry and vibrational frequencies by the Consistent Force Field (CFF) method[9,10].

As no quantum chemical conformational analysis is available for the 2-pyrrolidone molecule, we have tried to investigate the equilibrium structure and the ring inversion potential of the molecule by quantum chemical methods. Since the small basis *ab initio* treatment of large amplitude motions is time consuming and does not give a quantitatively reliable potential, semiempirical methods have been chosen.

THEORETICAL

Methods

Geometry optimization of molecules containing several large amplitude degrees of freedom is a complicated task. Direct application of the force or gradient method[11] is inefficient, as the Cartesian components of the forces along the large amplitude coordinates are usually small. The Cartesian forces can be transformed into internal ones if the vibrational **B** matrix is known, so the geometry can be optimized with the internal force relaxation method using calculated or estimated force constants[12].

If the molecule contains "soft" coordinates (associated with large amplitude motions), even the internal force relaxation method can be inappropriate, since the small force constant values belonging to these coordinates render the optimization procedure oscillating with slow or no convergence. In such cases the so-called "geometry relaxation method" can be advocated. According to this the weakest coordinate, ξ (with the smallest quadratic force constant $F_{\xi\xi}$) is chosen and the molecule is distorted along ξ, with consequent optimization of all other internal degrees of freedom under the ξ = const. condition. The lowest energy point on this curved trajectory yields the absolute minimum and some restricted information is gained about the energy hypersurface.

In the case of the 2-pyrrolidone molecule the conformational analysis has been performed in terms of ϑ_1, ϑ_2 and Θ coordinates. This set of large amplitude coordinates has two advantages over q, ϕ, and $\Theta : 1)$ the force constants belonging to these coordinates can be easily calculated or estimated; $2)$ the molecule can be easily distorted along these coordinates using the algorithm given in ref.[6].

As shown by Combs and coworkers[13,14], among the various semiempirical methods INDO gives the best results for internal rotation and ring puckering motions. The INDO results are also far from quantitative, as far as the barrier heights are concerned, but they are much better than those given by the popular MINDO methods and are usually correct at a qualitative level (i.e. the geometry of the lowest energy conformer is acceptable).

The program used in our work is a modification of the CNDO/2 force program[15]. Calculations have been performed at both CNDO/2 and INDO levels.

X-Ray Data Retrieval

As no gas phase (microwave or electron diffraction) data are available for molecules containing the 2-pyrrolidone moiety, the Cambridge Crystallographic Data Files (CCDF) June 1983 version were used in order to get some experimental information about the structure of the 2-pyrrolidone ring. Although the large amplitude coordinates are sensitive to the state of aggregation, the tendencies are supposed to be unaltered in the solid phase.

The 2-pyrrolidone fragment has been retrieved in 107 entries of the SCONN connectivity file using the CONNSER program[16], corresponding to 113 bibliographic entries. In 22 cases no atom coordinates were given and 14 data sets, with R factor larger than 0·090, has been dropped. The remaining 77 structures have been analysed with the aid of the GEOM' 78 program[16]. Internal coordinates of the 2-pyrrolidone fragment (bond lengths, bond angles and torsional angles) and their averages were determined. The Cremer–Pople (q, ϕ) and the puckering parameters $(\vartheta_1, \vartheta_2)$[17] have been calculated for 89 occurrencies of the 2-pyrrolidone ring, including chemically or crystallographically different fragments.*

RESULTS AND DISCUSSION

Quantum Chemical Calculations

As indicated the equilibrium geometry of the molecule has been searched in the 3-dimensional large amplitude subspace of internal coordinates using the geometry relaxation method.

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* The listing of the CCDF refcodes with bibliographic data and with the internal and puckering coordinates are available from one of the authors (J.A.) upon request.

As ϑ_1 is considerably stiffer than ϑ_2 and Θ (the INDO force constants determined at the lowest energy conformer are $F_{\vartheta_1\vartheta_1} = 0.1651$ aJ/rad^2*, $F_{\vartheta_2\vartheta_2} = 0.0328$ aJ/rad^2, $F_{\Theta\Theta} = 0.0282$ aJ/rad^2) and it is in a strong coupling with the N—H out-of-plane mode $(F_{\vartheta_1\Theta} = -0.1367$ aJ/rad^2), the geometry optimization can be conveniently reduced to a two dimensional problem. The rigidities of ϑ_2 and Θ coordinates are comparable (see the force constant values given above) and the choice between them is arbitrary.

There is a continuing discussion about the planarity of the amide moiety. According to earlier investigations, CNDO/2 yields nonplanar[18,19] while INDO[18,19] in agreement with *ab initio* results (refs[20,21]) gives planar amide geometry. Since the CNDO/2 and INDO methods differ just in predicting the N—H out-of-plane coordinate[18], Θ has been chosen as relaxation coordinate. The coupling between ϑ_2 and Θ is positive in that sense that the energy decreases if both coordinates change in the same direction $(F_{\vartheta_2\Theta} = -0.0264$ aJ/rad^2), *i.e.* the minima occur in the $(+, +)$ and $(-, -)$ quadrants of the (ϑ_2, Θ) coordinate system. As the large amplitude vibrations are strongly anharmonic and the quadratic force constants depend on the actual value of the large amplitude coordinate, the existence of two further, energetically identical minima in the $(+, -)$ and $(-, +)$ quadrants cannot be excluded *a priori*. However, according to our calculations these secondary minima do not exist.

The zero level of the potential energy scale has been chosen as the energy of the molecule in the saddle-point of the ring inversion motion. In this geometry the puckering coordinates $(\vartheta_1$ and $\vartheta_2)$, the N—H out-of-plane coordinate (Θ) and the methylene rocking and twisting coordinates (for definition see ref.[12]) are all zero, and the molecule belongs to the C_s symmetry group. The optimization of this geometry was performed in the subspace of coordinates, which belong to the A' irreducible representation of the C_s point group. In this case the out-of-plane coordinates remain zero because of symmetry reasons.

The inversion potential has been calculated in two steps: *1)* starting from the saddle point geometry the molecule has been distorted along the Θ and ϑ_2 coordinates; *2)* the molecular geometry has been optimized under the $\Theta = $ const. condition. The potential curves obtained by the CNDO/2 and INDO methods are plotted on Fig. 3. In agreement with the earlier semiempirical calculations on aliphatic amides[18,19] CNDO/2 method predicts a strongly nonplanar amide geometry (which involves a nonplanar ring), while according to the INDO method the equilibrium geometry is nearly planar.

The INDO barrier is so small $(0.02$ kJ/mol or 1.7 cm^{-1}) that by inspection the potential curve seems to have its minimum at $\Theta = 0$. This value is much lower than the CNDO/2 barrier $(14.7$ kJ/mol) and significantly less than the thermal energy

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*   1 aJ $= 10^{-18}$ J.

at room temperature $(2\cdot4 \text{ kJ/mol})$. The calculated INDO barrier is in qualitative agreement with the reported CFF value: $0\cdot25 \text{ kJ/mol}$ $(21 \text{ cm}^{-1})^{10}$. According to Schellman and Lifson[10] the torsional energy provides the principal opposition to the planar structure and the barrier in pyrrolidone is essentially the balance between these two contributions. Similar delicate balance between ring strain and torsion can be found in other cyclic compounds, *e.g.* in the oxetane molecule[2,3]. Here the zero-point energy of the large amplitude motion is higher than the barrier, the geometry determined in the vibrational ground state is planar. The existence of the barrier shows up only in the far infrared spectra[2,3].* On the other hand CNDO/2 barrier is higher than the thermal or the zero-point energy, so 2-pyrrolidone is predicted to be strongly nonplanar in the vibrational ground state.

The equilibrium bond lengths and bond angles obtained by the CNDO/2 and INDO methods are compared to the CFF[9] and to the experimental (X-ray) data in Table I. As usually, the semiempirical methods shorten the C—C and C—N single bonds, while the C=O double bond and the amide C—N bond are slightly longer than the X-ray or CFF ones. The CNDO/2 C—N—C angle is far from the experimental or from the CFF value which is a consequence of the strong nonplanarity of the ring.

We have investigated if there is a direct relationship between the nonplanarity of the ring and the nonzero value of the N—H out-of-plane angle (Θ). Starting the restricted optimization from the $\Theta = 0$ and $\vartheta_2 = 0\cdot6$ rad values it has turned out that in the INDO approximation there exists a conditional minimum at $\Theta = 0$
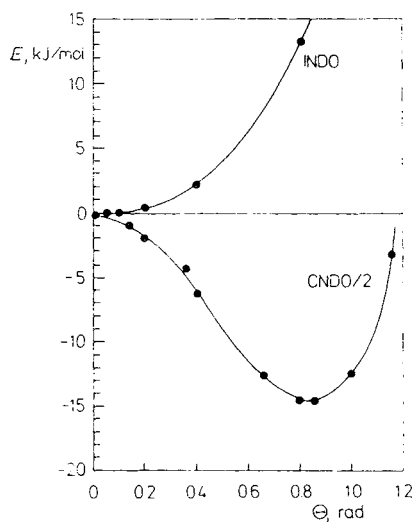

FIG. 3

Ring inversion potential function of the 2-pyrrolidone molecule *vs* the N—H out-of-plane angle (Θ) as calculated by CNDO/2 and INDO methods

* The calculated INDO barrier is even lower than the experimental barrier in the oxetane molecule, so the INDO ground state geometry can be regarded as planar.

TABLE I

Equilibrium bond lengths and bond angles calculated by CNDO/2 and INDO methods compared with averaged X-ray and CFF values

Parameter[a]	CNDO/2	INDO	CFF[b]	X-ray[c]
$r_{1,2}$	1·4807	1·4856	1·541	1·523 (0·031)
$r_{2,3}$	1·4666	1·4692	1·546	1·513 (0·025)
$r_{3,4}$	1·3997	1·3842	1·327	1·341 (0·024)
$r_{4,5}$	1·4233	1·4171	1·488	1·460 (0·015)
$r_{5,1}$	1·4811	1·4839	1·566	1·536 (0·020)
$r_{6,3}$	1·2719	1·2771	1·226	1·228 (0·014)
$\alpha_{5,1,2}$	104·23	107·11	103·0	104·19 (3·35)
$\alpha_{3,2,1}$	104·11	106·03	107·7	104·25 (1·59)
$\alpha_{2,3,4}$	110·47	107·62	108·4	108·29 (1·69)
$\alpha_{3,4,5}$	104·35	113·18	114·3	114·20 (1·88)
$\alpha_{4,5,1}$	106·31	105·19	106·4	103·15 (1·42)
$\alpha_{6,3,4}$	121·66	122·52	125·9	125·82 (1·49)

[a] Bond lengths in Å (10^{-10} m), bond angles in degrees. For atom labeling see Fig. 1. [b] From ref.[9]. [c] Values given in parentheses are the standard deviations.

TABLE II

Torsional angles, ϑ_1 and ϑ_2 puckering parameters and the N—H out-of-plane angle (Θ) in the optimal CNDO/2 and INDO geometries, and in the INDO conditional minimum ($\Theta = 0$) in comparison with the CFF values given in ref.[10]

Parameter[a]	CNDO/2 opt.	INDO opt.	INDO cond.	CFF
τ_1	—14·08	—9·01	—7·99	—7·6
τ_2	—5·86	5·51	5·84	6·1
τ_3	24·18	0·29	—1·39	—1·9
τ_4	—32·90	—5·94	—3·65	—3·1
τ_5	29·32	9·08	7·13	6·5
ϑ_1	0·6650	0·0073	—0·0378	—0·0515
ϑ_2	0·6311	0·2642	0·2203	0·2077
Θ	0·8545	0·0600	0	b

[a] Torsional angles in degrees, ϑ_1, ϑ_2 and Θ in radians. [b] Not given.

with a slightly higher energy than the absolute minimum. The torsional angles and the Θ coordinates in the CNDO/2 and INDO minima and in the INDO $\Theta = 0$ conditional minimum are compared to the CFF values[9] in Table II. There is an excellent agreement between the INDO and CFF results (especially in the $\Theta = 0$ conditional minimum), while CNDO/2 predicts a totally different equilibrium geometry. The CNDO/2 optimum geometry is distorted along both twisting (ϑ_1) and bending (ϑ_2) coordinates. This is very improbable due to the partial double bond character of the amide bond. The large ϑ_1 value is a direct consequence of the overestimation of the amide pyramidality and of the strong coupling between the ϑ_1 and Θ coordinates.

Let us investigate now the extent of the relaxation of various geometry parameters during the ring inversion motion. Table III summarizes the skeletal and amide bond lengths and bond angles together with their changes in three distorted geometries. The INDO bonds are slightly longer than the CNDO/2 ones (by about $1 - 3 \times 10^{-3}$ Å). Bond length changes are almost negligible (usually below 0.1%). The only exception is the amide C—N bond, where Δr reaches 1% at $\Theta = 0.8$ rad. The change of the C—N—C amide angle is also significant (about 6% at the largest distortion). Other bond angle changes are small, usually about 1°. The predicted bond length and bond angle changes are generally somewhat smaller using the INDO method as compared with CNDO/2.

Methylene angular parameters (scissoring, rocking, wagging, twisting) are not important in this context, but it is worth mentioning that similarly to other small ring compounds[2,3], the methylene twisting and rocking deformations couple with the ring puckering mode. Their normalized values may reach $2 - 3°$ in the distorted molecules.

The ring torsional angles and puckering parameters $(\vartheta_1$ and $\vartheta_2)$ calculated by CNDO/2 and INDO methods (Table IV) change similarly to each other, but here the differences between the two methods reach 3° or more.

The CNDO/2 and INDO net atomic charges differ considerably from each other, but their value is almost independent of the conformational state. This is encouraging from the point of view of CFF calculations[9,10], where usually constant net charges are used to estimate the electrostatic contribution to the potential energy.

X-Ray

According to the chemical intuition and theoretical (INDO and CFF) calculations[9,10], 2-pyrrolidone behaves as a pseudo-four-membered ring, *i.e.* the most populated are the envelope conformations, where the carbon atom opposite to the amide bond is above or below the ring plane. The scatterogram of Cremer–Pople puckering parameters (q, ϕ) calculated from the X-ray data displays a large number of ring conformations with $\phi \approx 0°$ and 180° (Fig. 4). The distribution of the puckering phase angle ϕ is illustrated on Fig. 5a. As the pyrrolidone ring is not a regular

TABLE III

Skeletal and amide bond lengths $(r_{i,j})$ and angles $(\alpha_{i,j,k})$ and their changes at three fixed values of the N—H out-of-plane coordinate. Upper values are calculated by CNDO/2, lower ones by INDO method

Parameter	Value[a]	Changes[b] at Θ (rad)		
		0·2	0·4	0·8
$r_{1,2}$	1·4828	− 7	−11	− 22
	1·4858	− 4	− 7	− 14
$r_{2,3}$	1·4655	0	+ 2	+ 11
	1·4692	+ 1	+ 2	+ 8
$r_{3,4}$	1·3829	+16	+50	+152
	1·3839	+12	+38	+128
$r_{4,5}$	1·4157	+ 7	+20	+ 65
	1·4170	+ 5	+16	+ 60
$r_{5,1}$	1·4818	− 5	− 7	− 7
	1·4840	− 3	− 4	− 2
$r_{3,6}$	1·2745	− 3	− 8	− 23
	1·2772	− 2	− 6	− 18
$r_{13,4}$	1·0625	+ 3	+15	+ 60
	1·0658	+ 4	+15	+ 58
$\alpha_{5,1,2}$	107·28	−0·77	− 1·32	−2·57
	107·37	−0·48	−0·90	−1·89
$\alpha_{3,2,1}$	106·25	−0·54	−0·87	−1·93
	106·25	−0·33	−0·61	−1·53
$\alpha_{4,3,2}$	107·91	+0·06	+0·63	+2·38
	107·68	+0·06	+0·44	+1·76
$\alpha_{5,4,3}$	112·96	−0·79	−2·34	−7·64
	113·32	−0·56	−1·79	−6·09
$\alpha_{4,5,1}$	105·60	−0·44	−0·33	+0·78
	105·38	−0·29	−0·28	+0·42
$\alpha_{6,3,4}$	122·53	−0·04	−0·25	−0·83
	122·52	−0·06	−0·21	−0·70
$\alpha_{13,4,3}$	124·66	−0·52	− 2·37	−9·97
	124·45	−0·60	− 2·52	−10·16

[a] Values are given for the saddle-point geometry with C_s symmetry; [b] changes are given in 10^{-4} Å and in degrees for the bond lengths and angles, respectively.

TABLE IV

Ring torsional angles and normalized puckering coordinates in three distorted geometries. All of these values are zero in the planar saddle-point geometry. Upper values are calculated by CNDO/2, lower ones by INDO method

Parameter[a]	Θ (rad)		
	0·2	0·4	0·8
τ_1	$-13\cdot69$	$-14\cdot82$	$-12\cdot85$
	$-10\cdot42$	$-11\cdot70$	$-10\cdot85$
τ_2	$+\ 6\cdot34$	$+\ 3\cdot54$	$-\ 5\cdot62$
	$+\ 4\cdot03$	$+\ 1\cdot52$	$-\ 5\cdot39$
τ_3	$-\ 3\cdot95$	$+\ 9\cdot91$	$+22\cdot61$
	$-\ 4\cdot37$	$+10\cdot03$	$+21\cdot23$
τ_4	$-12\cdot51$	$-19\cdot13$	$-30\cdot51$
	$-10\cdot84$	$-17\cdot23$	$-27\cdot76$
τ_5	$+15\cdot86$	$+20\cdot58$	$+26\cdot92$
	$+12\cdot79$	$+17\cdot38$	$+23\cdot62$
ϑ_1	$+0\cdot1061$	$+0\cdot2683$	$+0\cdot6202$
	$+0\cdot1171$	$+0\cdot2704$	$+0\cdot5739$
ϑ_2	$+0\cdot4352$	$+0\cdot5187$	$+0\cdot5790$
	$+0\cdot3401$	$+0\cdot4269$	$+0\cdot5070$

[a] Torsional angles in degrees, ϑ_1, ϑ_2 in radians.
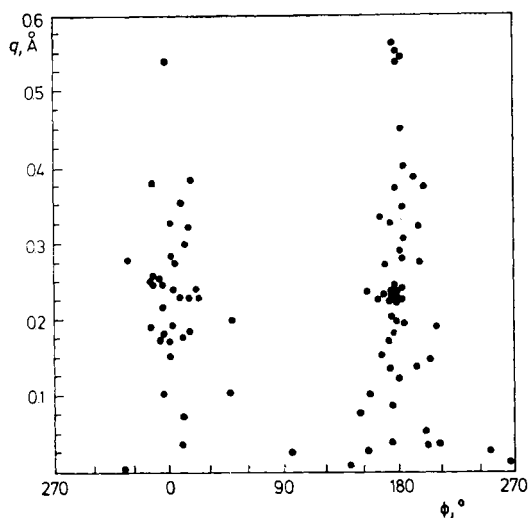

FIG. 4

Scatterogram of the Cremer–Pople parameters for 89 chemically or crystallographically different 2-pyrrolidone fragments

pentagon, the $\phi = 0 \pm 9°$, $36 \pm 9°$, ... regions have been regarded as envelope and the $\phi = 18 \pm 9°$, $54 \pm 9°$, ... regions as half-chair conformations (shaded and blank areas, respectively, in Fig. 5a). It is worth mentioning that twisted (half-chair) conformations in the neighborhood of the most populated envelope conformations are also relatively highly populated. While in the unsubstituted pyrrolidone ring the $\phi = 0°$ and $180°$ positions are energetically equivalent (they are enantio-meric), for substituted compounds this is not necessarily so: that is why the two maxima are not of equal height. The histogram of the puckering amplitude distribution (Fig. 5b) displays a maximum at about $0·2$ Å, indicating a slight, but significant nonplanarity of the pyrrolidone ring.

The alternative $(\vartheta_1, \vartheta_2)$ representation of the same set of X-ray data contains identical information in a less spectacular way (Fig. 6). Small values of the ϑ_1 (twisting) parameter and significant deviations from zero of the ϑ_2 (bending) parameter indicate that the pyrrolidone ring favours the bending type distortions from planarity. It is remarkable that in a certain number of rings both ϑ_1 and ϑ_2 are close to zero.

Calculating the polar coordinates belonging to the ϑ_1, ϑ_2 parameter set, the corresponding radial component R is found to be in good correlation with the Cremer-Pople puckering amplitude q:

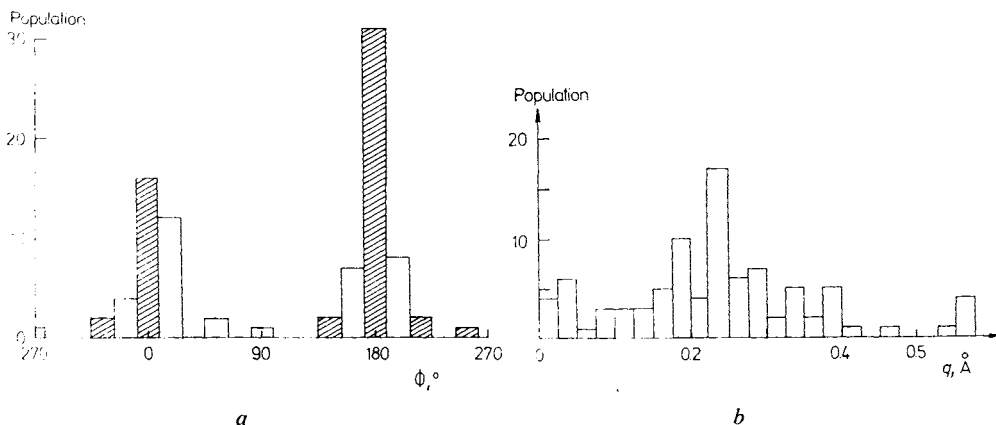$$R = 2·732q + 0·019 \quad (r^2 = 0·9964), \tag{3}$$

FIG. 5

Histograms illustrating a) the population of structures with various envelope (shaded bars) and half-chair (empty bars) conformations; b) the population of rings with puckering amplitude q(Å)

while the angular component ψ is essentially the negative of the Cremer–Pople pseudorotational phase angle ϕ:

$$\psi = -1 \cdot 002\phi + 361 \cdot 9 \quad (r^2 = 0 \cdot 9954). \tag{4}$$

In spite of the fact that the Cremer–Pople parameters are defined in a more general way (bond distances and bond angles are taken into account, while ϑ_1, ϑ_2 parameters depend solely on the ring torsional angles), it is evident from these correlation plots that in the case of a ring with fixed chemical structure the description of the puckered states by the two sets of parameters is practically equivalent.

The dihedral angles of some simple compounds containing the 2-pyrrolidone ring, including the 2-pyrrolidone–α-cyclodextrin complex and some compounds consisting of two pyrrolidone rings bound together by a spiro C-atom, are summarized in Table V. As only the relative sign of the torsional angles are important, τ_1 is chosen to be negative in all cases.

The main conclusions drawn from the analysis of the X-ray data are the following: *a*) the unsubstituted and some N-substituted rings are close to planarity; *b*) other substituted rings are usually nonplanar; *c*) the envelope (bent) conformations are more frequent than the half-chair (twisted) ones, *i.e.* ϑ_1 is stiffer than ϑ_2.
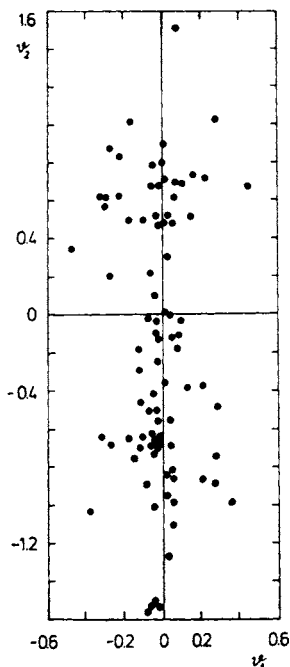

FIG. 6

Scatterogram of the $(\vartheta_1, \vartheta_2)$ puckering parameters for the same set of rings plotted on Fig. 4

TABLE V

Torsional angles and puckering parameters for some simple compounds containing the 2-pyrrolidone moiety determined by X-ray diffraction

Molecule	Ref.	Torsional angles (deg)					Puckering parameters (rad)	
		τ_1	τ_2	τ_3	τ_4	τ_5	ϑ_1	ϑ_2
I^a	22	− 7·7	+ 6·4	− 2·1	− 3·0	+ 6·7	−0·0570	+0·2122
II	23	−13·2	+ 7·3	+ 2·3	−10·4	+14·1	+0·0561	+0·4014
III	23	−19·8	+ 8·6	+ 7·4	−20·3	+23·5	+0·1988	+0·6421
IV	24	−22·3	+11·7	+ 4·8	−19·1	+24·6	+0·1269	+0·6922
V	25	−16·8	+10·8	0·0	−10·8	+16·4	−0·0014	+0·4887
VI^b	26	−23·9	+12·3	+ 5·3	−20·1	+26·1	+0·1357	+0·7351
		−23·9	+13·6	+ 3·1	−18·1	+25·1	+0·0785	+0·7201
VII^c	27	−23·5	+14·4	+ 1·5	−16·4	+23·7	+0·0351	+0·6954
		−27·9	+18·8	− 1·6	−16·4	+27·1	−0·0418	+0·8058
$VIII$	28	−22·5	+13·0	+ 2·7	−17·3	+23·9	+0·0730	+0·6837
IX	29	−30·9	+20·3	+ 0·1	−20·6	+31·1	+0·0045	+0·9163
X	30	−32·6	+27·2	−10·5	−10·7	+26·9	−0·2827	+0·8705
XI	31	−24·7	+23·2	−11·7	− 4·5	+18·5	−0·3173	+0·6332

^{a} 2-Pyrrolidone–β-cyclodextrin complex; ^{b} two crystallographically different rings; ^{c} two chemically different rings.

TABLE VI

Torsional angles and puckering parameters for 2-pyrrolidone and its substituted derivatives calculated by the CFF method[10]

Molecule	Parameters^a						
	τ_1	τ_2	τ_3	τ_4	τ_5	ϑ_1	ϑ_2
2-Pyrrolidone	− 7·6	+ 6·1	−1·9	−3·1	+ 6·5	−0·0515	+0·2077
3-Methyl-2-pyrrolidone	−18·3	+ 5·1	−4·8	−7·7	+15·8	−0·0383	+0·4410
4-Methyl-2-pyrrolidone	− 7·5	+14·0	−3·8	−7·7	+15·4	−0·0713	+0·3812
5-Methyl-2-pyrrolidone	−16·0	+13·0	−4·0	−6·4	+13·7	−0·1109	+0·4377

^{a} Torsional angles in degrees, ϑ_1, ϑ_2 in radians.

The substituent effects on the ring conformation are confirmed by the CFF calculations[10] (Table VI): the nonplanarity of the ring depends on the substitution.
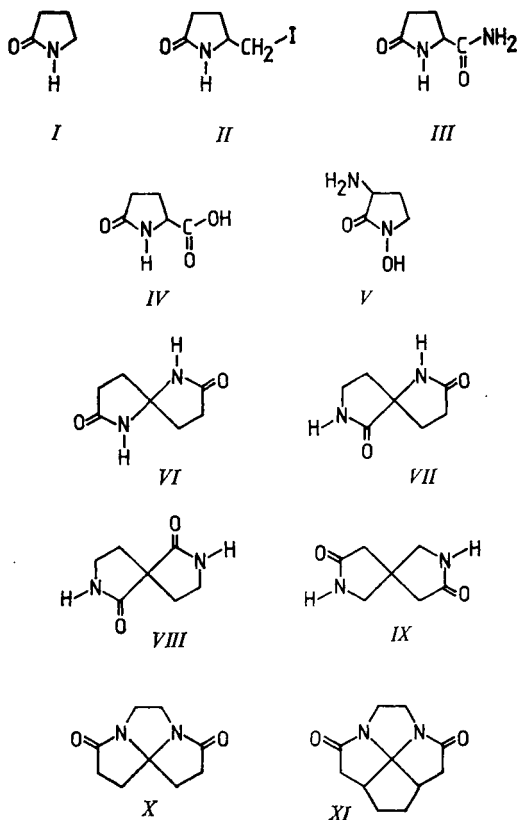
CONCLUSIONS

Comparison with X-ray and CFF data confirmed the quantum chemical results. Most of the substituted rings were found to be nonplanar, they are distorted along the ring bending (ϑ_2) coordinate. The main conclusion is that the ring twisting ϑ_1 coordinate is determined by the pyramidality of the amide N—H bond, while ϑ_2 is influenced by the substitution of the ring.

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