# SEMIEMPIRICAL CALCULATION OF OPTICAL ROTATORY STRENGTH OF NON-PLANAR CONFORMATIONS OF FORMAMIDE

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Optimization of the molecular geometry of formamide by CNDO/2 and PCILO methods leads to a non-planar conformation with pronounced pyramidal arrangement of bonds on the nitrogen atom whereas the INDO method prefers the planar conformation. The optical rotatory strengths (CNDO/S calculation) of conformers with pyramidal nitrogen atom have opposite signs for the $n-\pi^*$ and $\pi-\pi^*$ electronic transitions. Deformation of the amide group by torsion around the C'—N bond leads to conformations with the same sign for rotatory strengths of both these transitions.

In spite of numerous quantum chemical calculations[1-4] of the optimum geometry of simple amides, there is still no satisfactory answer to the question whether the non-planarity of amide groups, experimentally found by diffraction methods, is an inherent property of this group or a consequence of intramolecular interactions between other parts of the amide molecule, or, finally, a result of intermolecular interactions in the crystal lattice. Diffraction analyses of amides and simple peptides[5] show that a non-planar deformation of an amide (peptide) group usually gives rise to a relatively regular pyramidal arrangement of bonds to the nitrogen atom, according to the Ramachandran relation[2] $\Theta_N = -2\,\Delta\omega$. The existing calculations relating the total molecular energy of simple amides[1-3] to the angles $\Delta\omega$ and $\Theta_N$ did not sufficiently take into account the changes of bond angles on the nitrogen atom which must necessarily take place in going from the planar to the pyramidal arrangement. In the present communication we tried to correct to some extent this oversimplification. A non-planar amide group represents an inherently chiral chromophore which could be detected by CD spectra[6,7]. Therefore, it might be useful to predict by calculation the relation between the sense of non-planarity of the amide group and its chiroptical manifestation.

CALCULATIONS

*Notation*: Non-planarity of a given amide group is expressed by two angular parameters: the angle $\omega(H\!-\!C\!-\!N\!-\!H^1)$ which, according to the convention[8], describes the torsion of the C—N bond, and the angle $\Theta_N$ introduced by Ramachandran[1] for the description of a pyramidal arrangement on a nitrogen atom (Fig. 1). The parameter $\Delta\omega$ (ref.[1]) is not satisfactory for an unequivocal description of the sense of non-planarity in a *cis*- as well as *trans*-amide group.

*Calculations of molecular geometry*: The CNDO/2 and INDO methods were used in the original parameterisation[9]. The molecular geometry of formamide was optimized in respect to all geometric parameters using the Murtagh-Sargent modification of the variable metric method[10]. The shape of the energy hypersurface was studied also by tabulation of the total molecular energy (calculated by the CNDO/2, INDO and PCILO methods) as a function of the anticipated most important geometric parameters (angle $\omega$ and length of the C—N bond). The studied problem — a partial change of $sp^2\text{-}sp^3$ hybridisation of the nitrogen atom — is not convenient for the PCILO method based on the concept of localized orbitals[11]. The PCILO calculations were therefore executed twice assuming the lone electron pair on the nitrogen to be of the $\pi$ or of the $\sigma$ type. The results obtained on the tabulation by the CNDO/2 method were analyzed by separation of the total energy into one- or two-center terms according to Fischer and Kollmar[12]. The starting geometry of formamide was derived mainly from the recommended geometric arrangement of an amide group in peptides[13] (bond lengths: C—N 0·135 nm, C=O 0·122 nm, C—H 0·110 nm, N—H 0·101 nm; bond angles: H—C—N 112°, O—C—N 125°). In contrast to the published calculations[1-3] we always assumed a regular pyramidal arrangement of bonds to the amide nitrogen $(\Theta_N = -2\,\Delta\omega)$ with the corrected bond angles $(\sphericalangle\ \text{C}\!-\!\text{N}\!-\!\text{H}^1 = \text{C}\!-\!\text{N}\!-\!\text{H}^2 = \text{H}^1\!-\!\text{N}\!-\!\text{H}^2)$ given in Table I. This Table lists also the values of the bond angle C—N—X which describes the position of a fictitious atom determining the orientation of the lone electron pair of the $\sigma$ type required for the PCILO calculation[11].
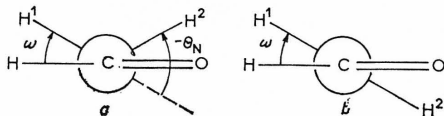


FIG. 1

Definition of the Angles Describing Non-planarity of an Amide Group

*a* Regular pyramidal arrangement of bonds on nitrogen, *b* torsion of the C—N bond.

*Calculation of the spectral parameters*: Wavelengths, oscillator strengths and optical rotatory strengths of the $n-\pi^*$ and $\pi-\pi^*$ transitions, as well as charge distributions of the excited states, were calculated for a non-planar arrangement of the formamide molecule by the direct procedure based on the CNDO/S wave function. We used the parameterisation according to Ellis and coworkers[14]. In the configuration interaction the calculation included 36 singly excited electronic configurations between the six highest occupied and the six lowest virtual molecular orbitals. As shown by test calculations, an acceptable stabilization of the rotatory strength values (for $\omega = 10°$, $\Theta_N = -20°$) is achieved using 15 configurations. The sign of the calculated rotatory strengths is not affected by the number of configurations used. The oscillator strengths and rotatory strengths were calculated using the gradient formalism[15], the wave functions being not subjected to deorthogonalisation[16,17]. The procedure employed differs from that used by us previously[7,18] in that each configuration is not transformed separately into the dipole length formalism. The optical rotatory strength was calculated according to the relationship[7]:

$$R_{0j} = -6.412 \cdot 10^{-37}(E_j - E_0)^{-1} \sum_{r,s} C_{\psi r} C_{\psi s} \langle \psi_0 \mid \vec{V} \mid \psi_r \rangle \langle \psi_s \mid \vec{r} \times \vec{V} \mid \psi_0 \rangle,$$

where $C_{\psi r}$, $C_{\psi s}$ are coefficients of the LCI series corresponding to singly excited configurations $r$ and $s$, and $(E_j - E_0)$ is the calculated LCI excitation energy in eV. The matrix elements of both the dipole operators are given in atomic units. For the optical rotatory strength we use the cgs units $(\text{esu}^2 \text{ cm}^2)$; 1 cgs unit $= 3.33564 \cdot 10^{-15} \text{ C}^2 \text{ m}^3 \text{ s}^{-1}$. In the calculations we used the optimized value of bond length

TABLE I

Bond Angles on the Nitrogen, Corresponding to a Regular Pyramid ($\sphericalangle$ C—N—H$^1$ = = C—N—H$^2$ = H$^1$—N—H$^2$; $\sphericalangle$ C—N—X describes the position of the $\sigma$-type lone electron pair — see PCILO calculations)

| $\omega$ | $\sphericalangle$ C—N—H$^1$ | $\sphericalangle$ C—N—X |
|---|---|---|
| 0° | 120·00° | 90·00° |
| 5° | 119·75° | 92·90° |
| 10° | 118·98° | 95·84° |
| 15° | 117·65° | 98·90° |
| 20° | 115·71° | 102·13° |
| 25° | 113·03° | 105·62° |
| 30° | 109·47° | 109·47° |
| 35° | 104·76° | 113·85° |

C—N (0·138 nm; *vide infra*), however, as shown by a test calculation, the use of the average value (0·135 nm) does not influence significantly the calculated values. The other geometric parameters were identical with the values used in the optimization of the molecular geometry of formamide by tabulation. The calculations were executed on CDC 3 300 and Siemens 4004/150 computers.

## RESULTS AND DISCUSSION

The geometric arrangements of the best planar and non-planar conformation of formamide, as obtained by optimization using the CNDO/2, method, are given in Table II. The non-planar structure is more stable by about 4·5 kcal mol$^{-1}$ and

TABLE II

Optimized Geometries of the Formamide Molecule

| Parameter | CNDO/2 non-planar structure | CNDO/2 planar structure | INDO planar structure |
|---|---|---|---|
| Energy, eV | −1 070·4287 | −1 070·2344 | −1 027·1555 |
| Bond lengths . 10, nm | | | |
| C—N | 1·378 | 1·360 | 1·359 |
| C=O | 1·262 | 1·265 | 1·267 |
| C—H | 1·121 | 1·120 | 1·124 |
| N—H$^1$ | 1·067 | 1·059 | 1·062 |
| N—H$^2$ | 1·068 | 1·060 | 1·064 |
| Bond angles | | | |
| H—C=O | 119·81° | 120·85° | 121·35° |
| H—C—N | 115·53° | 114·92° | 114·36° |
| O=C=N | 124·56° | 124·23° | 124·29° |
| C—N—H$^1$ | 110·28° | 122·77° | 123·26° |
| C—H—N$^2$ | 111·22° | 122·47° | 122·68° |
| H$^1$—N—H$^2$ | 107·51° | 114·76° | 114·05° |
| Torsion parameters | | | |
| $\omega$ | 36·14° | 0·00° | 0·00° |
| $\Theta_N$ | −60·71° | 0·00° | 0·00° |
| $\Theta_C$ | − 3·61° | 0·00° | 0·00° |

is characterized by a slightly twisted pyramid (Fig. 2) with extraordinarily high $\omega$ and $\Theta_N$ values. (For the equilibrium geometry of ammonia the angle $\omega$ equals 32·85; see ref.[19].) Also the inversion barrier is unrealistically high. Other geometric parameters are in accord with the expected data[13]. The INDO method affords the planar arrangement as the most stable one (Table II); no stable geometry with a non-planar amide group was found by this method. These results are in accord with the calculattions of Kolaskar and coworkers[2] who found the same discrepancy between the CNDO and INDO results. Calculations, executed by tabulation, agree qualitatively with the results of the total optimization. According to the CNDO/2 method, the regular pyramidal arrangement has an energy minimum characterized by $\omega = 30°$ and the C—N bond length 0·138 nm (Fig. 3), whereas the INDO method affords a broad minimum for the planar arrangement with identical C—N bond length (Fig. 4). In comparison with the maps reported by the Indian authors[2], our CNDO/2



Fig. 2

Projection of the Non-planar Amide Group in Formamide Molecule (CNDO/2 calculation — optimized geometry)
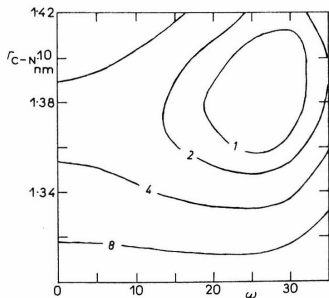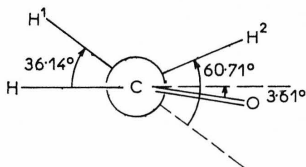


Fig. 3

Dependence of the Total Energy of Formamide Molecule (kcal mol$^{-1}$) on the Angle $\omega$ and C—N Bond Length ($\Theta_N = -2\,\Delta\omega$; CNDO/2 calculation)
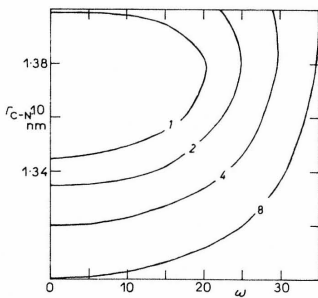


Fig. 4

Dependence of the Total Energy of Formamide Molecule (kcal mol$^{-1}$) on the Angle $\omega$ and C—N Bond Length ($\Theta_N = -2\,\Delta\omega$; INDO calculation)

calculations lead to a greater non-planarity and higher barrier to inversion; the minimum found by the INDO method is narrower. The results obtained by the PCILO method are very similar to the CNDO/2 results which is apparently due to the CNDO approximations in the integral calculations. The positions of the minima in the total energy map are identical for both the representations of the lone electron pair on nitrogen. The map, obtained for the $\pi$ type of the lone pair (Fig. 5) is shifted only for about $3.5$ kcal mol$^{-1}$ towards lower energies. The experimentally observed[20] increase of the optimum C—N bond length in the non-planar arrangement $(\omega \neq 0°)$ manifests itself only in the case of a complete optimization of geometry by the CNDO/2 method (Table II).

Decomposition of the total CNDO energy[12] into one- and two-center terms shows the found minimum for the non-planar arrangement to result from two competing effects: the decrease in the one-center energy of the nitrogen atom in a non-planar arrangement and the increase in the total two-center energy to which the energies C=O and C—N significantly contribute[21]. The extraordinarily high value of $\omega$-calculated by the CNDO/2 method, may be thus regarded as the result of underestimation of the conjugation energy at this level of approximation. It is known that the INDO method is better suited to calculate the barriers to inversion. Recent IEHT and *ab initio* STO-3 G calculations on N-methylacetamide, executed by tabulae tion, afforded results similar to those obtained by the INDO method[3]. On the other hand, Armbruster and Pullman[22], using the STO-3 G basis set, reported a completely optimized non-planar structure of formamide with a non-regular pyramide, of course
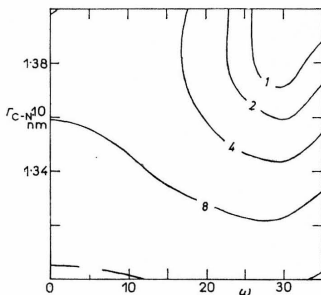


FIG. 5
Dependence of the Total Energy of Formamide Molecule (kcal mol$^{-1}$) on the Angle $\omega$ and C—N Bond Length ($\Theta_N = -2\,\Delta\omega$; PCILO calculation)

substantially more flattened than that resulting from the CNDO/2 calculations. We must therefore conclude, in accord with the Indian authors[2,3], that at least small deviations from planarity of the amide group, accompanied by formation of an approximately regular pyramidal arrangement of bonds on the nitrogen, do not require much energy. A recent paper of French authors[23] is interesting in this respect. They found, on the basis of IR spectra of N-methylacetamide in an argon matrix, that the nitrogen atom is pyramidal $(\Theta_N = 30°)$ and the barrier to inversion amounts to 2·5 kcal mol$^{-1}$.

As salient results of our study we can regard the calculated dependences of the spectral parameters on the angle $\omega$, either for species with a regular pyramide on nitrogen $(\omega = 0-35°; \Theta_N = -2\,\Delta\omega)$ or for forms where the planar amide group is deformed by torsion of the C—N bond $(\omega = 0-90°; \Theta_N = 0°)$. The method and parameterization (CNDO/S) used for this purpose afford, according to our previous experience[6,7,18], satisfactory values of rotatory and oscillator strengths. On the other hand, the energies of the transitions within the amide group are given very inaccurately, so that the shifts of $n-\pi^*$ and $\pi-\pi^*$ transitions are more reliable than the wavelength values. For the planar arrangement of formamide, the $n-\pi^*$ and $\pi-\pi^*$ transitions are calculated at 297 and 159 nm, respectively. In a pyramidal arrangement the $n-\pi^*$ transition exhibits a bathochromic shift whereas the $\pi-\pi^*$ transition shows a hypsochromic shift of approximately the same magnitude (for $\omega$ in the region $0-30°$ the shift is about 10 nm). On the contrary, when the amide group is deformed by torsion, both the transitions undergo a bathochromic shift; this is in accord with the previous results[24]. In this case, variation of $\omega$ within the range $0-90°$ shifts the $n-\pi^*$ and $\pi-\pi^*$ transitions by 15 nm and 35 nm, respectively. Both these types of non-planar deformation of the amide group in formamide bring about a significant decrease of the oscillator strength of both the transitions (Fig. 6 and 7).



Fig. 6

Oscillator Strength, $f$, (———) and Optical Rotatory Strength, $R$, (———) of the $n-\pi^*$ and $\pi-\pi^*$ Transitions of the Amide Group in a Formamide Molecule in Going from Planar to Regular Pyramidal Arrangement on the Nitrogen $(\Theta_N = -2\,\Delta\omega;$ CNDO/S calculation)

Values denoted X give rotatory strength of the CNDO/2-optimized non-planar geometric arrangement.
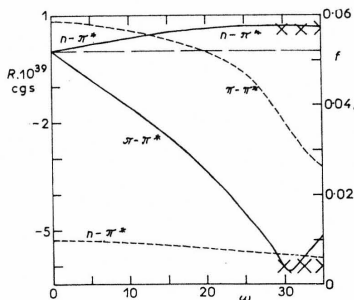
In accord with our previous finding[7], an out-of-plane deformation of the amide group manifests itself by a significant change in the excited states charge distribution (Fig. 8). In the planar arrangement, the $n-\pi^*$ excitation arises mainly from the $n$-orbitals of the oxygen atom, without any significant participation of the nitrogen lone electron pair: therefore, the charge densities on nitrogen in the ground and in the first excited singlet states are almost identical whereas there is a decrease of the negative charge on the oxygen atom during the $n-\pi^*$ excitation. This situation changes significantly already for small $\omega$ values, both for the formation of the pyramidal arrangement (Fig. 8) and for the deformation of the amide group by torsion. In this case, the $n-\pi^*$ transition is accompanied by a significant charge transfer from the nitrogen $n$-orbital to the antibonding $\pi^*$ orbital. A reverse trend occurs in the case of the $\pi-\pi^*$ transition. Rotatory strength calculations enable us to ascribe the signs of the Cotton effects to a defined sense of non-planarity of the amide group. We can say that an amide group with a pyramidal nitrogen atom, which is deformed in the sense shown in Fig. 1a, will exhibit a positive Cotton effect of the $n-\pi^*$ transition and an intense negative Cotton effect of the $\pi-\pi^*$ transition (Fig. 6). Contrary to our previous calculations[7], the intensity of the Cotton effect due to the $n-\pi^*$ transition is not enhanced. We can explain this fact by assuming that the rotatory
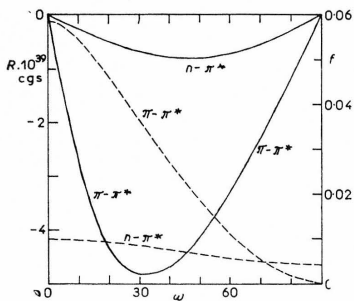


FIG. 7

Oscillator Strength, $f$, (— — —) and Optical Rotatory Strength, $R$, (———) of the $n-\pi^*$ $\pi-\pi^*$ Transitions of the Torsion-deformed Amide Group in Formamide Molecule ($\Theta_N = 0$; CNDO/S calculation)
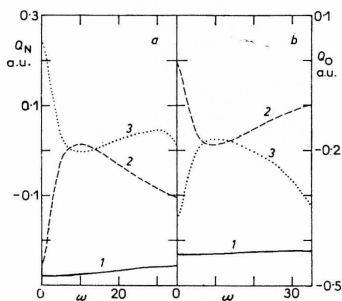
FIG. 8

Charge Alteration (atomic units) on $a$) Nitrogen ($Q_N$), $b$) Oxygen ($Q_O$) of the Amide Group in a Formamide Molecule in Going from Planar to Regular Pyramidal Arrangement (CNDO/S calculation)

*1* Ground state, *2* first excited singlet state, *3* second excited singlet state.

strength of the corresponding Cotton effect can be contributed to an enhanced extent by the vibronic interactions. These could cause the earlier observed[6] higher intensity of this CD band in optically active compounds containing rigid non-planar amide groups. The rotatory strengths of both transitions increase regularly till $\omega \sim 30°$. Fig. 6 shows a comparison of these results also with the optical rotatory strength of the optimized (CNDO/2) non-planar formamide structure. Since these values do not differ significantly from the results obtained for the corresponding values of $\omega$ using the averaged geometric parameters, we can infer that the optical rotatory strength is not very sensitive to small variations in bond lengths and valence angles in the studied molecule. If the amide group is deformed by torsion according to Fig. 1b, the calculated rotatory strength of both the transitions has the same, negative, sign (Fig. 7). In this case we found nodal planes for the values $\omega = 0°$ and $\omega = 90°$ whereas the greatest numerical values of rotatory strengths are calculated for $\omega = 45°$ ($n-\pi^*$ transition) and for $\omega = 30°$ ($\pi-\pi^*$ transition). Since most of the CD spectra of chiral lactams and amides exhibit mutually opposite signs of Cotton effects due to $n-\pi^*$ and $\pi-\pi^*$ transitions, we can assume (if our calculations are correct) that the deformations of amide groups by a mere torsion of the C—N bond are not common.

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