

Molecular Orbital Studies of the Barrier to Internal Rotation in Some Amides

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The barriers to internal rotation in the molecules formamide and benzamide have been estimated by a combined study of conjugation energy within the PPP-approximation and non-bonded interaction, and by CNDO/2 calculations. The latter method gave results which were in rather good agreement with available experimental information.

The barrier to rotation around the C-N bond in formamide has been the object of a series of both experimental and theoretical studies.¹⁻⁵ The stereochemistry around this bond is of great interest as the bond is an important link in the building up of large biological systems.

Accurate measurements⁶ on this molecule have demonstrated that all atoms apart from the amino-hydrogens are making a planar arrangement. Experimental studies of the barrier to rotation around the C-N bond in this molecule have led to a barrier height of about 18 kcal/mol.³ Advanced theoretical calculations of *ab initio* type using Gaussian basis sets, have reproduced the experimentally determined rotational barrier.⁵

The purpose of the present study is to investigate to which extent the simple MO methods based on the ZDO (zero differential overlap) approximation are able to account for the experimental findings.

We have applied two different methods. Firstly we have used the conventional PPP-approximation in an explicit study of the changes in the π -electron energy by rotation. This method includes a consideration of the changes in the core-energy and in the non-bonded interactions.

Secondly we have included all the electrons in the valence shell, treating them according to the standard version of the CNDO/2 approximation.^{7,8}

In order to obtain information about the influence of large, unsaturated substituents on the height of the rotational barrier, and on the equilibrium conformation around the C-N bond, we have included the molecule benzamide in our investigation.

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METHODS OF CALCULATION

In the study of the rotational barriers we have started from planar conformations. The deviations from these are determined by two rotational parameters, ϕ and θ . The first of these is defined as the angle of rotation around the bond C_2-N_3 , whereas the latter refers to rotation around C_2-C_4 in benzamide.

For labelling of atoms see Fig. 1.

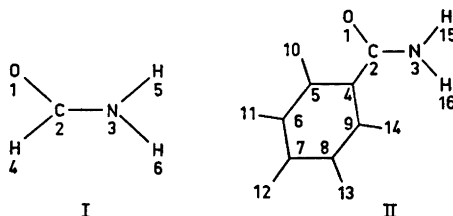


Fig. 1. Labelling of atoms in formamide (I), and benzamide (II).

A. The π -electron calculation

The calculational scheme applied in the present study has been used previously in similar investigations.⁹⁻¹² The total molecular energy is approximated by the sum of the π -electron energy and the non-bonded interactions. These two energy terms will be treated separately.

We have assumed the same length for corresponding bond distances in both molecules. This assumption is based on experimentally obtained structure data for formamide,^{6,13} benzamide,¹⁴ and related amides. Furthermore we have assumed all valence angles to be 120° . The assumed values for the bond distances are listed in Table I.

Table I. Assumed bond distances in the molecules formamide and benzamide. All values in Å. For labelling of atoms see Fig. 1.

Type of distance	Length
C-O	1.22
C_2-N	1.36
C_2-C_4	1.48
$(C-C)_{\text{phenyl}}$	1.40
C-H	1.09
N-H	1.02

(1) π -Electron energies. The energy of the π -electron systems has been calculated by the Pariser-Parr-Pople approximation. The parameter scheme

applied is one recently evaluated by Roos and Skancke.¹⁵ In this scheme the following relations are assumed:

$$\beta_{\mu\nu} = \beta_{\mu\nu}^{\circ} + \delta_{\mu\nu}^{\beta}(R_{\mu\nu} - R_{\mu\nu}^{\circ}) \quad (1)$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}^{\circ} + \delta_{\mu\nu}^{\gamma}(R_{\mu\nu} - R_{\mu\nu}^{\circ}) \quad (2)$$

$$W_{\mu} = W_{\mu}^{\circ} + \sum_{\nu=1}^3 n_{\nu} \Delta W_{\nu}(\nu) \quad (3)$$

and

$$\Delta W_{\mu}(\nu) = \Delta W_{\mu}^{\circ}(\nu) + \delta_{\mu\nu}^W(R_{\mu\nu} - R_{\mu\nu}^{\circ}) \quad (4)$$

In (1) and (2) $\beta_{\mu\nu}^{\circ}$ and $\gamma_{\mu\nu}^{\circ}$ are the values of the core-resonance and two-electron two-center integral for nearest neighbours at a chosen reference distance $R_{\mu\nu}^{\circ}$.

In (3) and (4) is given the expression for the one-electron one-centre integral with the necessary corrections due to the different types of neighbours to atom μ . The coefficient n_{ν} in (3) is equal to zero if the neighbouring atom to μ is hydrogen, otherwise it is equal to unity.

The parameter values used for the system studied here are presented in Table 2. For details concerning the evaluation of these parameters see Refs. 15–17.

The two-electron one-center integrals given in Table 2 are all invariant by the internal rotation. In the planar conformations the two-electron two-center integrals for nearest neighbours were determined by inserting the appropriate values from Table 2 in (2). For non-bonded distances the integrals

Table 2. Semi-empirical parameter values used in the calculation of the π -electron energies.

C–C bond ^a	C–O bond ^b	C–N bond ^c
$R_{CC}^{\circ} = 1.397 \text{ \AA}$	$R_{CO}^{\circ} = 1.22 \text{ \AA}$	$R_{CN}^{\circ} = 1.338 \text{ \AA}$
$\beta_{CC}^{\circ} = -2.42 \text{ eV}$	$\beta_{CO}^{\circ} = -2.46 \text{ eV}$	$\beta_{CN}^{\circ} = -2.25 \text{ eV}$
$\delta_{CC}^{\beta} = 3.05 \text{ eV/\AA}$		$\delta_{CN}^{\beta} = 2.6 \text{ eV/\AA}$
$\gamma_{CC}^{\circ} = 6.91 \text{ eV}$	$\gamma_{CO}^{\circ} = 9.33 \text{ eV}$	$\gamma_{CN}^{\circ} = 6.34 \text{ eV}$
$\delta_{CC}^{\gamma} = -3.99 \text{ eV/\AA}$		$\delta_{CN}^{\gamma} = -3.99 \text{ eV/\AA}$
$\gamma_{CC} = 11.97 \text{ eV}$	$\gamma_{OO} = 18.89 \text{ eV}$	$\gamma_{NN} = 15.44 \text{ eV}$
$W_C^{\circ} = -9.84 \text{ eV}$	$W_O = -19.60 \text{ eV}$	$W_N = -8.52 \text{ eV}$
$\Delta W_C^{\circ}(C) = 0.07 \text{ eV}$	$\Delta W_C^{\circ}(O) = -0.71 \text{ eV}$	$\Delta W_N^{\circ}(C) = 0.14 \text{ eV}$
		$\Delta W_C^{\circ}(N) = 0.03 \text{ eV}$
$\delta_{CC}^W = 9.22 \text{ eV/\AA}$		$\delta_{CN}^W = 5.6 \text{ eV/\AA}$

^a Ref. 15; ^b Ref. 16; ^c Ref. 17.

of this kind were evaluated by the uniformly charged sphere approximation¹⁸ based on the orbital exponents of Duncanson and Coulson.¹⁹

The two-electron integrals varying with the angle of rotation may be expressed in the following way:

$$\begin{aligned}
(\mu\mu|\nu\nu)\phi = & C_{xx}^{xx}(\mu_x\mu_x|\nu_x\nu_x) + C_{zz}^{zz}(\mu_z\mu_z|\nu_z\nu_z) + C_{yy}^{yy}(\mu_y\mu_y|\nu_y\nu_y) \\
& + C_{zx}^{zx}(\mu_x\mu_x|\nu_z\nu_z) + C_{xz}^{xz}(\mu_z\mu_z|\nu_x\nu_x) + C_{xy}^{xy}(\mu_x\mu_y|\nu_x\nu_y) \\
& + C_{yz}^{yz}(\mu_y\mu_z|\nu_y\nu_z)
\end{aligned} \quad (5)$$

where μ and ν represent $2p$ -orbitals centered at atoms μ and ν , respectively. The mutually orthogonal x - and y -axes are vertical to the z -axes which coincide with the straight line connecting the atoms during rotation. Furthermore, the x -axes are kept orthogonal to the planes through the molecular parts twisted relative to each other.

The coefficients, which are parameters determined by the molecular geometries, are functions of the angles of rotation, ϕ . For the planar molecules we have $C_{xx}^{xx} = 1$ and the remaining coefficients vanish identically.

In the same way as in a previous study recently carried through the integrals on the righthand side of (5) have been estimated by two principally different methods.¹¹

One of the methods represents a scaling of theoretical values based on Duncanson-Coulson orbital exponents by the following relation:

$$(\mu\mu|\nu\nu)_{\text{scaled}} = (\mu\mu|\nu\nu)_{\text{th}} \frac{(\mu_x\mu_x|\nu_x\nu_x)_{\text{ball}}}{(\mu_x\mu_x|\nu_x\nu_x)_{\text{th}}} \quad (6)$$

where $(\mu_x\mu_x|\nu_x\nu_x)_{\text{ball}}$ is the value of the pure π -component estimated by the uniformly charged sphere approximation.

The other method applied is a modified version of the uniformly charged sphere approximation valid for non-parallel p -orbitals.²⁰

A comparison of the values obtained by these two methods shows clearly that the results are in close agreement with each other. Accordingly we have chosen the simpler uniformly charged sphere approximation for the evaluation of these integrals.

The integrals $(33/22)\phi$ in both molecules and the integral $(44/33)\phi$ in (II) have been estimated in a particular way since the internuclear distances are too short to permit the use of the uniformly charged sphere approximation. These integrals may be decomposed in the following way by using a well-known relation valid for Slater-type orbitals:

$$(\mu\mu|\nu\nu)\phi = (\mu_x\mu_x|\nu_x\nu_x) - 2 \sin^2 \phi (\mu_x\mu_y|\nu_x\nu_y) \quad (7)$$

Here ϕ is the angle of rotation around the bond between atoms μ and ν . The first integral on the righthand side of (7) is the one valid for a planar molecule. The second one is so small at the actual distance that we have adopted a theoretical value based on the orbital exponents referred to above. This procedure has been applied in a similar study quite recently.¹¹

The integrals given by (1), (3), and (4) were evaluated numerically by using the values presented in Table 2. During rotation the core-resonance integrals β_{32} in both molecules and β_{34} in (II) were changed according to the relation

$$\beta_{\mu\nu}(\phi) = \beta_{\mu\nu}(0)|\cos \phi| \quad (8)$$

The remaining one-electron integrals were kept constant during rotation.

The most realistic way of accounting for the core repulsion is to represent it by the sum of the two-electron two-center integrals taking the formal charge of the core atoms properly into account. By this method inaccuracies in the values of the two-electron integrals will not influence the predicted value of the total electronic energy to any significant extent.

(2) *Non-bonded interactions.* The van der Waals interactions between non-bonded atoms will be of a varying degree of importance for the determination of the molecular equilibrium conformations. Several functions for the calculation of generalized van der Waals interactions between non-bonded atoms have been suggested in the literature. We have limited our choice of potentials to functions for which parameters cover all the types of interactions present in the molecules studied here.

One of the functions used was the one introduced by Hill:²¹

$$E_{\text{nb}} = \sum_{k < l} \left\{ 8.28 \times 10^5 \varepsilon_{kl} \exp [-r_{kl}/0.0736(R_k + R_l)] - 2.25 \varepsilon_{kl} \left[\frac{R_k + R_l}{r_{kl}} \right]^6 \right\} \quad (9)$$

where the sum is to be taken over all pairs of atoms k and l . R_k and R_l are the van der Waals radii for atoms k and l respectively, and ε_{kl} is a parameter specific to each atomic pair. The numerical values of these parameters and of the appropriate van der Waals radii were taken from a compilation by Eliel *et al.*²²

B. The CNDO/2 calculation

The CNDO studies of the molecules followed the standard scheme given by Pople *et al.*^{7,8}

In the approximations underlying this method the matrix elements of the Fock operator in the atomic orbital representation are given by

$$F_{\mu\mu} = U_{\mu\mu} + (2P_{AA} - P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} (2P_{BB} - Z_B)\gamma_{AB} \quad (10)$$

and

$$F_{\mu\nu} = \beta_{AB} S_{AB} - P_{\mu\nu} \gamma_{AB} \quad (11)$$

where

$$P_{\mu\nu} = \sum_j C_{j\mu} C_{j\nu} \quad (12)$$

The diagonal element $U_{\mu\mu}$ in (11) represents the binding energy of an electron in an atomic orbital X_μ , and may be expressed as

$$U_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) - (Z_A - \frac{1}{2})\gamma_{AA} \quad (13)$$

where I_μ and A_μ are ionization potential and electron affinity averaged over all the electronic states of atom A, and where Z_A is the effective nuclear charge of atom A.

The remaining symbols in the relations above have their standard meaning.

RESULTS AND DISCUSSION

In the following the equilibrium conformations and barriers to internal rotation predicted by the two different methods will be presented and discussed.

In the π -electron calculation the total π -electron energy is given by the relation

$$E_{\pi} = \sum_i [\varepsilon_i + \langle \psi_i | H^{\text{core}} | \psi_i \rangle] \quad (14)$$

where ε_i are the eigenvalues of the self-consistent Fock operator, and where $\langle \psi_i | H^{\text{core}} | \psi_i \rangle$ are matrix elements in the molecular orbital representation.

The energy term that is of importance in the present context is the sum of E_{π} and the core-repulsion energy, E^{core} . As both E_{π} and E^{core} vary by changing conformations of the molecules, their sum E will also be a function of the rotation angles.

The conjugation energy is estimated from the relation

$$E_{\text{conj.}}(\phi, \theta) = E(\phi, \theta) - E(90^{\circ}, 90^{\circ}) \quad (15)$$

In formamide only one rotational parameter appears.

The calculated variations in π -electron energy, in core-energy, in non-bonded interactions, and in total energy for the molecules studied are given in Tables 3 and 4.

Table 3. Formamide. The variation in π -electron energy, core-energy, non-bonded interactions, and total energies as functions of the angle of twist. Energies in kcal/mol.

ϕ°	PPP-calc.				CNDO-calc.
	ΔE_{π}	ΔE_{core}	ΔE_{nb}	ΔE_{tot}	ΔE_{tot}
0	-40.9	5.9	0.02	-35.0	-15.4
30	-32.3	4.5	0.01	-27.8	-11.7
60	-12.4	1.5	0	-10.9	-4.0
90	0	0	0	0	0

As revealed by the tables the non-bonded interactions make minor contributions to the variation of the total energies in the π -electron approximation. Thus in these calculations the variation in the π -electron and core-energies, as determined by the chosen semi-empirical parameters for the π -electrons is decisive both for the prediction of molecular equilibrium conformations and rotational barriers.

The results given in the tables demonstrate clearly that the equilibrium conformations as predicted by the π -electron approximation are planar for both molecules.

Table 4. Benzamide. The variation in π -electron energy, core-energy, non-bonded interactions, and total energies as functions of angles of twist. Energies in kcal/mol.

ϕ°	θ°	PPP-calc.				CNDO-calc.
		ΔE_π	ΔE_{core}	ΔE_{nb}	ΔE_{tot}	ΔE_{tot}
0	0	-33.7	-11.6	1.25	-44.1	-12.0
30	0	-29.9	-8.7	0.59	-38.0	-7.5
60	0	-20.5	-2.7	0.22	-23.0	-2.7
90	0	-14.0	0.3	0.21	-13.5	3.8
0	30	-30.3	-11.8	0.30	-41.8	-13.2
0	60	-23.5	-12.4	0.06	-35.8	-15.1
0	90	-20.2	-12.6	0.07	-32.7	-16.8
30	30	-26.5	-8.8	0.36	-34.9	-
60	30	-17.1	-2.6	0.12	-19.6	-
90	30	-10.6	0.4	0.08	-10.2	-
30	60	-19.6	-9.3	0.02	-28.9	-
60	60	-10.2	-3.0	-0.02	-13.2	-
90	60	-3.6	0.2	-0.01	-3.4	-
30	90	-16.2	-9.6	0.04	-25.8	-15.2
60	90	-6.6	-3.3	0.00	-9.9	-6.9
90	90	0	0	0	0	0

In formamide the experimental⁶ equilibrium conformation is planar apart from a small tilt of the hydrogen atoms out of the molecular plane.

In the case of benzamide an X-ray investigation¹⁴ of the crystal and molecular structure has led to the result that the phenyl group is twisted 26° out of the plane through the amide group. In the π -electron approximation the calculated energy difference between this conformation and a planar one is not more than around 2 kcal/mol, thus indicating that the observed non-planarity in the crystal might be due to intermolecular forces.

The barriers to rotation around the C-N bond as estimated by the π -electron calculations are 35.0 kcal/mol and 30.6 kcal/mol in formamide and benzamide, respectively. The corresponding values obtained by the CNDO calculations are 15.4 kcal/mol and 15.8 kcal/mol, respectively. The rotational barrier in formamide has been studied experimentally and values in the region 17 to 21 kcal/mol have been obtained. Experimental values for benzamide do not seem to be available. One should, however, expect the barrier for the C-N bond in this molecule to be roughly the same as the one in formamide.

From the above it is clear that the π -electron approximation gives barrier values that are far too high, whereas the CNDO calculations reproduce the experimental value for formamide with fair accuracy.

As is seen from Table 4 the π -electron calculations predict a barrier to rotation around the C_2-C_4 bond in benzamide of 11.4 kcal/mol. This value is

of the same order of magnitude as the one obtained by a similar study of the rotation of the aldehyde group in benzaldehyde.¹⁰ The CNDO calculations on benzamide give a barrier height of 3.8 kcal/mol, which compares nicely to an observed value of 4.7 kcal/mol obtained by a gas phase study of benzaldehyde.²⁴

The discrepancy between the sets of values predicted by the two methods is analyzed below.

In the PPP-calculations the π -electron energy may be expressed by the following relation

$$E_{\pi} = \sum_i \varepsilon_i + \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} \quad (16)$$

where ε_i are the eigenvalues of the π -electron Hamiltonian, $P_{\mu\nu}$ is an element of the charge-bond order matrix, and $H_{\mu\nu}^{\text{core}}$ is a matrix element of the core-Hamiltonian in the atomic orbital representation. The total energy considered in the studies of internal rotation may be expressed as

$$E_{\text{tot}}(\text{PPP}) = E_{\pi} + E_{\sigma} \quad (17)$$

where E_{π} is given by (16) and where E_{σ} is

$$E_{\sigma} = E^{\text{core}} + E_{\text{nb}} \quad (18)$$

In (18) E^{core} is the core-energy as expressed by the γ -integral approximation mentioned above, and E_{nb} is given by (9). This is a convenient way of decomposing the total energy.

All terms in (17) and (18) change their values during internal rotation. However, the only change occurring in E^{core} is the one given by the geometrical dependency of the two-electron two-center integrals over π -orbitals. This is due to the assumption of a fixed σ -electron distribution.

In the CNDO approximation the molecular electronic energy may be expressed by

$$E = E_{\pi'} + E_{\sigma'} + \sum_{\mu} \sum_{\lambda} P_{\mu\lambda} H_{\mu\lambda} \quad (19)$$

where $E_{\pi'}$ and $E_{\sigma'}$ are given by expressions analogous to (16) for the π - and σ -electrons, respectively, and where the summations over μ and λ in (19) extend over the π - and σ -electrons, respectively. The distinction between π - and σ -electrons is only valid for strictly planar systems. We have, however, chosen to label as π -electrons the electrons described by atomic orbitals orthogonal to the plane constituted by an atomic group during rotation. The last term in (19) represents the interaction between the π - and σ -electrons in the molecule.

The total molecular energy is given by

$$E_{\text{tot}}(\text{CNDO}) = E_{\pi'} + E_{\sigma''} \quad (20)$$

where $E_{\pi'}$ is the same as in (19), and where

$$E_{\sigma''} = E_{\sigma'} + \sum_{\mu} \sum_{\lambda} P_{\mu\lambda} H_{\mu\lambda} + \frac{1}{2} \sum_{A \neq B} \sum Z_A Z_B / R_{AB} \quad (21)$$

Table 5. Variations in the energy terms within the PPP- and CNDO-approximations, related to the total energy change $\Delta E = E(90^\circ) - E(0^\circ)$. Energies in kcal/mol.

Molecule	Bond of rotation	PPP		CNDO	
		ΔE_π	ΔE_σ	$\Delta E_{\pi'}$	$\Delta E_{\sigma''}$
Formamide	C ₂ -N	40.9	-5.9	33.9	-18.5
Benzamide	C ₂ -N	19.7	10.9	21.3	-5.5
	C ₂ -C ₄	13.5	-2.2	14.4	-19.2

The variations in the energy terms in (17) and (20) induced by a change in one of the rotational parameters from 0° to 90° while keeping the other at 0° , are given in Table 5.

As revealed by the table the changes ΔE_π and $\Delta E_{\pi'}$ are rather similar whereas the $\Delta E_{\sigma''}$ values are far more negative than the corresponding ΔE_σ values. This analysis thus indicates that the unreasonably high barriers predicted by the π -electron calculations are due to an improper treatment of the σ -electrons.

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