

MO Studies of the Barrier to Internal Rotation in *o*-Chloronitrobenzene and *o*-Dinitrobenzene

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The barriers to internal rotation in *o*-chloronitrobenzene and *o*-dinitrobenzene have been investigated by modified Pariser-Parr-Pople (PPP) and complete neglect of differential overlap (CNDO) approximations.

In a previous paper¹ the electronic structures of the molecules *o*-chloronitrobenzene and *o*-dinitrobenzene have been studied. Both of them were assumed to be planar. As is well known, however, steric effects are expected to be of importance in molecules of this kind. It would accordingly be of some interest to study the influence on the electronic structures from a rotation of the nitro-groups.

In this paper we have investigated these effects by performing calculations both within a modified PPP-approximation² for the π -electrons, and by a CNDO/2 study.⁴⁻⁶ The main purpose of the present investigation is to predict the most probable equilibrium conformation of the molecules and the barriers to rotation of the nitro-groups. The computational method applied for the π -electrons is similar to an approach used in corresponding studies previously.^{3,12} The gross features of this method may be characterized by a decomposition of the molecular energy into conjugation energy and non-bonded interactions. The total energy has been calculated for a number of conformations.

METHODS OF CALCULATIONS

(1) *The π -electronic study.* The total energy of the molecules has been assumed to be composed of conjugation energy and non-bonded interactions. The conjugation energy is furthermore considered as built up of the π -electron energy and the core-energy. The first of these terms were calculated within the zero differential overlap (ZDO) approximation, using a parametrization scheme previously introduced and discussed.²

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The one-electron parameter, W_μ , the core-resonance integrals, $\beta_{\mu\nu}$, and the two-electron two-center Coulomb integrals, $\gamma_{\mu\nu}$, between nearest neighbours have been taken from the literature.^{2,7-9} The two-electron integrals for non-nearest neighbours were estimated by a modified version of the uniformly charged sphere approximation designed for non-parallel p -orbitals.¹⁰ For the one-center two-electron integrals we have adopted values previously determined by one of us.¹¹

The core-resonance integral between nitrogen and the neighbouring carbon atom has been made dependent upon the rotational angle through the following relation

$$\beta_{\text{CN}}(\phi) = \beta_{\text{CN}}(0) \cdot |\cos\phi| \quad (1)$$

where ϕ is the angle of twist.

The corresponding two-electron repulsion integral has been treated in a way described in a similar study.³ The following expression is obtained

$$(\text{NN}|\text{CC})_\phi = \cos^2\phi(\text{N}_x\text{N}_x|\text{C}_x\text{C}_x) + \sin^2\phi(\text{N}_x\text{N}_x|\text{C}_y\text{C}_y) \quad (2)$$

For STO's the following expression is valid

$$(\text{N}_x\text{N}_x|\text{C}_y\text{C}_y) = (\text{N}_x\text{N}_x|\text{C}_x\text{C}_x) - 2(\text{N}_x\text{N}_y|\text{C}_x\text{C}_y) \quad (3)$$

The integral $(\text{N}_x\text{N}_x|\text{C}_x\text{C}_x)$ has been estimated by the procedure described in the parametrization scheme.² For the integral $(\text{N}_x\text{N}_y|\text{C}_x\text{C}_y)$, which is very small at the actual internuclear distances, we have adopted a theoretical value based on the orbital exponents of Duncanson and Coulson.¹³

The most realistic way of accounting for the repulsion between the positively charged core atoms is to represent it by the sum of the two-electron two-center integrals. This procedure has been followed here.

Several potential functions for the calculation of van der Waals interactions between non-bonded atoms have been suggested in the literature.¹² We have here applied the formula due to Hill¹⁴

$$\frac{E_{\text{nb}}}{\varepsilon} = - \left(\frac{2.25}{\alpha^6} \right) + 8.28 \times 10^5 \exp \left(- \frac{\alpha}{0.0736} \right) \quad (4)$$

where ε is a parameter which varies with the size of the atoms, $\alpha = r/(r_i^* + r_j^*)$, r being the interatomic distance and r_i^* and r_j^* the van der Waals radii of atoms i and j . The necessary parameters in eqn. (4) have been taken from different sources.¹⁵⁻¹⁷

The equilibrium conformations and the barriers to internal rotation were determined by considering the variation of the π -electron energy, the core energy and the non-bonded interactions as functions of the angle of rotation around the nitrogen-carbon bond.

During rotation all bond distances and valence angles were kept unchanged. The structure parameters for the *o*-chloronitrobenzene were chosen to correspond to the geometry of nitrobenzene,¹⁸ and to the C-Cl bond in chlorobenzene.¹⁹ For the dinitrobenzene the benzene structure of the ring together with the nitro group geometry from the nitrobenzene were assumed to be adequate.

(2) *The CNDO study.* The CNDO approximation applied here is the standard version CNDO/2.⁶ The parameters needed in this calculation were taken from the same paper.⁶

BARRIERS TO INTERNAL ROTATION

The energy term of importance in the π -electron study is, except from the non-bonded interactions, the sum of the E_π and the core-repulsion energy which is approximated by the two-electron integrals.

$$E = E_\pi + E^{\text{core}} = E_\pi + \sum_{i < j} Z_i Z_j \gamma_{ij} \quad (5)$$

In (5) Z_i and Z_j are formal charges of the core atoms.

As both E_π and E^{core} vary by changing conformations of the molecule, E given by (5) will be a function, $E(\phi)$, of the angle of rotation.

The conjugation energy is defined by the relation

$$E_{\text{conj.}}(\phi) = E(\phi) - E(90^\circ) \quad (6)$$

In Tables 1–4 the different energy contributions together with the total energy for each conformation are presented.

Considering the *o*-chloronitrobenzene we find that the calculation within the PPP-approximation predicts a planar structure with a rotational barrier of around 4 kcal/mol; see Table 1.

Table 1. Rotational energies for *o*-chloronitrobenzene calculated by the PPP approximation.

ϕ^a (degrees)	$E_{\text{conj.}} = E(\phi) - E(90^\circ)$ (kcal/mol)	$\Delta E^b_{\text{NBI}} = E\phi_{\text{NBI}} - E^{90^\circ}_{\text{NBI}}$ (kcal/mol)	$\Delta E_{\text{tot}} = E_{\text{conj.}} + \Delta E_{\text{NBI}}$ (kcal/mol)
0	-7.7805	3.8055	-3.9750
30	-5.6472	1.8040	-3.8432
45	-3.7020	0.7430	-2.9590
60	-1.8196	0.2197	-1.5999
90	0.0000	0.0000	0.0000

^a Rotation of the nitro group relative to the molecular plane.

^b Non-bonding interactions (NBI).

Spectral data²⁰ do indicate the most probable configuration to be described by an angle of twist of the nitro group in the region of 40 to 60 degrees from the planar form. Our results show, however, that the minimum is very shallow. As a matter of fact, the results indicate the existence of an approximately free rotation up to 45°.

For this molecule the results within the CNDO-approximation are approximately the same as revealed by Table 2. This approximation is, however, predicting a slightly higher barrier of 5 kcal/mol, and a steeper curve around

Table 2. Rotational energies for *o*-chloronitrobenzene calculated by the CNDO approximation.

ϕ^a (degrees)	$E = E(\phi) - E(90^\circ)$ (kcal/mol)
0	-5.3334
30	-2.5098
45	-0.8784
60	-0.1255
90	0.0000

^a Defined as in Table 1.

the minimum. The differences are, however, so small that they probably are within the uncertainties of the calculations.

The results for the *o*-dinitrobenzene are far more complex.

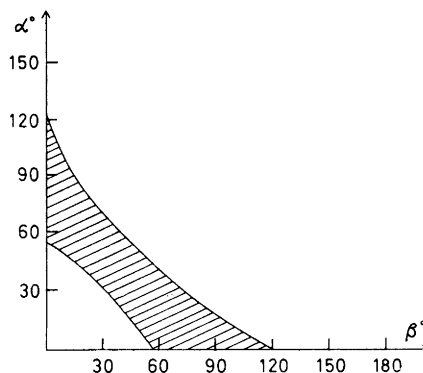
In Table 3 the results obtained by the PPP-method are given. The angles α and β in the table measure the amount of rotation of the nitro groups out of the planar form. Both groups are assumed to rotate in the same direction.

Table 3. Rotational energies for *o*-dinitrobenzene calculated by the PPP approximation. Both nitro groups rotated in the same direction. Values in kcal/mol. α and β indicate angles of rotation.

$\alpha \backslash \beta$		0	30	45	60	90	120	135	150
0	Total	12.8	-8.7	-17.1	-20.8	-22.8			
	NBI	34.3	12.4	4.3	1.4	0.6			
	Conj.	-21.5	-21.1	-21.3	-22.2	-23.4			
30			-20.2	-22.1	-22.1	-18.2	-13.5	-10.7	-6.8
			2.5	0.8	0.3	0.3	1.4	4.2	9.7
			-22.6	-22.8	-22.3	-18.4	-14.9	-14.9	-16.5
45				-21.7	-19.4	-12.5	-9.2	-9.6	
				0.2	0.1	0.1	0.6	2.0	
				-21.9	-19.5	-12.6	-9.9	-11.5	
60					-14.9	-6.3	-6.0		
					0	0	0.15		
					-14.9	-6.3	-6.2		
90						0			
						0			
						0			

As revealed by the table there are several configurations having energies grouped around -21 kcal/mol. This is illustrated in Fig. 1 where all the configurations having energies in the region -20 to -23 kcal/mol are within the hatched area. This area thus indicates a region of nearly free rotation.

Fig. 1. The hatched area embraces configurations of *o*-dinitrobenzene that have energies within -20 to -23 kcal/mol relative to a model with both nitro-groups orthogonal to the phenyl ring. The angles α and β indicate the amount of twist of the nitro-groups from a planar form.



In the cases where both the angles are small, the shortest oxygen - oxygen internuclear distances are in the region 1.6 to 2.0 Å. This rather short distance is critical both for the estimate of the non-bonded interactions, and for the application of the extended uniformly charged sphere approximation.

For the π -electron energy we have the following expression

$$E_{\pi} = \sum_{\mu} q_{\mu} \alpha_{\mu} + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta_{\mu\nu} + \frac{1}{4} \sum_{\mu} q_{\mu}^2 \gamma_{\mu\mu} + \sum_{\mu < \nu} (q_{\mu} q_{\nu} - \frac{1}{2} p_{\mu\nu}^2) \gamma_{\mu\nu} \quad (7)$$

and for the core-energy the term given by eqn. (5) is valid. By adding these terms together, and by splitting the α_{μ} 's in accordance with the Goeppert-Mayer Sklar formalism, we obtain the following expression for the total electronic energy

$$E = \sum_{\mu} q_{\mu} W_{\mu} + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta_{\mu\nu} + \frac{1}{4} \sum_{\mu} q_{\mu}^2 \gamma_{\mu\mu} + \sum_{\mu < \nu} (q_{\mu} q_{\nu} - \frac{1}{2} p_{\mu\nu}^2 - 2q_{\mu} Z_{\nu} + Z_{\mu} Z_{\nu}) \gamma_{\mu\nu} \quad (8)$$

The terms embraced by the parenthesis in (8) show that, when the system is unpolar, the conjugation energy should be rather unaffected by variations in $\gamma_{\mu\nu}$.

Table 4. Rotational energies for *o*-dinitrobenzene calculated by the CNDO approximation. Both nitro groups rotated in the same direction. Values in kcal/mol. α and β indicate angles of rotation.

$\alpha \backslash \beta$	0	30	45	60	90	120	135	150
0	10.8	1.5	1.5	0.8	-0.9			
30		0.8	0.3	-0.4	-0.4	0.7	0.3	0.2
45			-0.3	-0.6	-0.3	0.4	0.2	
60			-0.6	-0.6	-0.2	0.3		
90					0.0			

In our case, however, we have highly polar groups, and the choice of method for evaluating $\gamma_{\mu\nu}$ will certainly influence the result. This should indicate that the results are somewhat uncertain for small values of α and β .

The results given in Table 3 show a strong variation of the nonbonded interaction energy at small angles. For the conjugation energy the variation obtained by keeping one nitro group in the molecular plane and twisting the other, seems to be abnormal. This variation is hard to interpret, but may be partially related to some of the applied integral approximations.

The results of the CNDO calculations for this molecule presented in Table 4 are a little different from those of the π -electron study. These calculations are predicting an almost free rotation excluding only the planar case. The deviation from the PPP calculation is pronounced for large values of α and β . These conformations are forbidden in the PPP-approximation, but energetically favourable in the CNDO approximation.

From a physical point of view our results seem to be reasonable. Unfortunately no experimental information on the structures of these molecules seems to be available. X-Ray investigations^{21,22} on related compounds do, however, indicate that our results are reasonable.

Acknowledgement. This investigation has been supported by *Norges almenvitenskapelige forskningsråd*.

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Received November 14, 1970.