

A theoretical study of the effects of polar substitution on the activation barriers for internal rotation around the C-N bond in *p*-substituted nitrosobenzenes: comparison of DFT and MP2 calculations

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The activation barriers for internal rotation around the C-N bond in *p*-substituted nitrosobenzenes were calculated using the density functional theory (DFT) and second-order Møller-Plesset (MP2) methods with the 6-31+g(d) basis set. The polarisable continuum model (PCM) was used to model the solvent effect. An explicit water molecule was also introduced to form a hydrogen bond with the nitroso group and its effect on the barrier was studied by DFT. The barriers were well-correlated with Hammett σ^+ rather than σ values, meaning a strong resonance effect on the transition state. The MP2 method produces better and comparable results with the few available experimental values.

Key Words: Para-substituted nitrosobenzenes, C-N bond rotation, polar substituent effect, molecular modelling DFT, MP2, PCM.

Introduction

It is very important to estimate the activation barrier of bond rotation in different systems in order to foresee, for example, the reactivity of one rotamer over the others and also their interaction with other molecules, particularly in molecular recognition.

The polar substituent effect is one of the most powerful tools in the elucidation of reaction mechanisms.^{1,2} This effect is observed in rates and equilibria, which is caused by the changes in the electronic structures going

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from reactant to transition states in rates or from reactant to product states in equilibria. Despite the successful application of polar substitution effects to rates and equilibria,³ very little is known about the effects on bond rotation.^{4–8}

The present work represents a theoretical approach to study the effect of polar substitution on the activation barriers of internal rotation of the C-N bond in *p*-substituted nitrosobenzene systems. Calculations were conducted using B3LYP density functional theory and MP2 Møller Plesset perturbation theory with the basis 6-31+g(d). PCM was used as the solvation model. Nitroso compounds are chosen for the sake of simplicity and the availability of experimental results for comparisons.^{7,8} Furthermore, it is known that the activation barrier is an indication of self-dimerisation tendencies in these compounds. The lower barrier means a greater tendency for dimerisation. It is also important to predict the structural properties of substituted nitrosobenzenes because of the great interest in them. The compounds included in the study are illustrated in Figure 1.

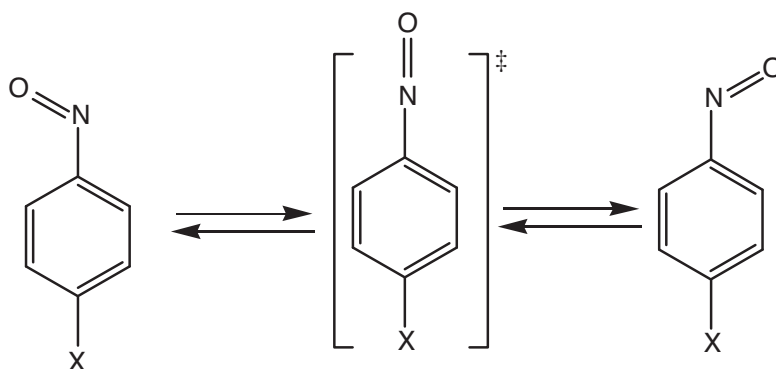


Figure 1. X=NO₂,CN, COMe (Ac), Cl, F, H, Me, MeO, OH and NH₂.

Methods

All calculations were performed by means of the GAUSSIAN 03 program⁹ using the B3LYP density functional theory and the perturbation theory (MP2) with the 6-31+G(d) basis (with 6 Cartesian d functions on non-hydrogen atoms), together with the PCM method for aqueous and chloroform solvation using $\epsilon = 78.4$ and 4.90 respectively, and UA0 (simple united atom topological model) for the molecular cavity. Convergence in the SCF procedure was typically achieved using geometry optimisations, which used default convergence criteria. TSs were located either by performing a transition state search on the geometry obtained from the highest energy point from scanning rotation around the C-N bond or fixing the torsional angle between the -NO group and phenyl-ring at 90° followed by opt = (ts,calcall). Some of them were also obtained from ts = QST2. All transition structures were characterised as possessing a single imaginary frequency corresponding to the transition vector (or reaction coordinate mode) for a particular chemical transformation, in contrast to energy minima with all-real vibrational frequencies. IRC calculations confirmed the identity of the energy minima adjacent to each saddle point.

Results and discussion

Nitrosobenzene is a planar molecule as indicated by NMR.⁷ Overlap between the phenyl pi-system and nitrogen's lone-pair electrons endows the planar forms (**I** and **III**) with greater stability than the nonplanar form (**II**). Structure **II** represents a transition state for rotation about the C-N bond as seen in Figure 2.

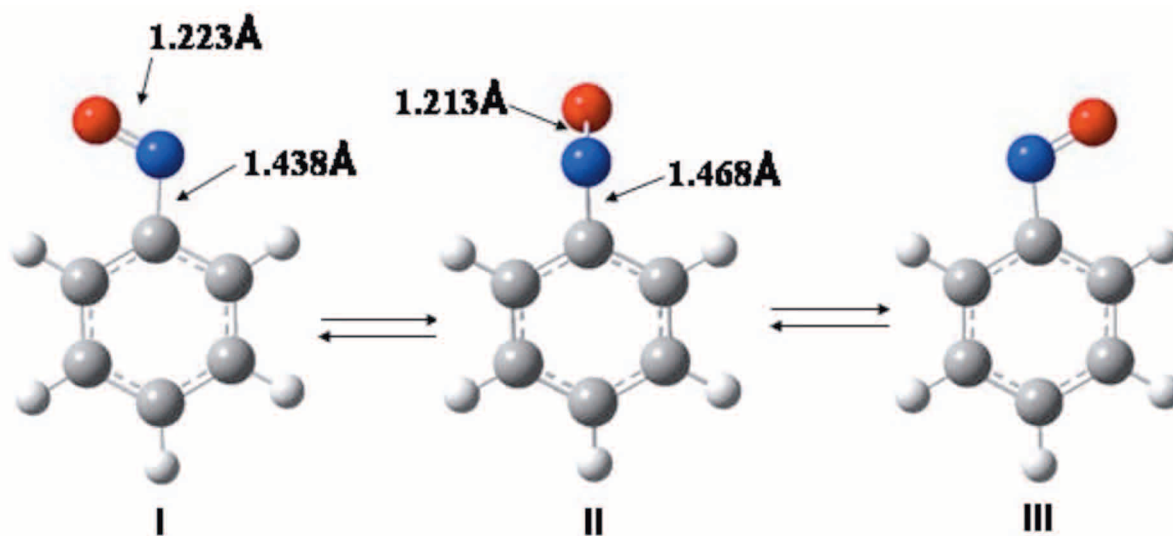


Figure 2. Structures of nitrosobenzene optimised by MP2/6-31+g(d) in chloroform. **I** and **III** are identical and correspond to the ground states and **II** corresponds to the transition state.

The difference in energy between these 2 forms will be denoted as ΔG^\ddagger and represents the barrier to rotation of the -NO group. The rotation barriers around C-N bonds in *p*-substituted nitrosobenzene were investigated by DFT and MP2 calculations using 6-31+g(d) basis set in vacuum and PCM solvents. The activation barriers are summarised in Table 1. The activation free energy barriers obtained from DFT calculations are in the ranges of 8-19 kcal/mol in water (PCM), 8-17 kcal/mol in chloroform (PCM), and 8-14 kcal/mol in vacuum. The barriers obtained from MP2 calculations are in the ranges of 7-11 kcal/mol in vacuum and 8-10 kcal/mol in chloroform (PCM). It is notable that reasonably good agreement was observed between the MP2 calculations and the few available experimental values with regard to the activation free energies for internal rotation barriers (see Table 1) within the limit of errors. It had previously been reported that MP2 somehow yields better values for the activation barriers for the internal rotation of C-O bond in substituted phenols.⁶ The activation barriers for closely related guanidinium compounds are in the range of 10-13 kcal/mol.⁴ B3LYP/6-311+g(d,p) level of theory was employed to calculate the activation barrier of *p*-methoxynitrosobenzene and it was unfortunately found that the value (16.46 kcal/mol) was even higher than the one obtained at B3LYP/6-31+g(d) level with reference to the experimental value (9.81 kcal/mol).^{7b} Therefore, it was decided that MP2 is the method of choice for predicting internal rotation barriers of substituted nitrosobenzenes.

Table 1. Activation free energies (ΔG^\ddagger)^a in kcal/mol calculated for *p*-substituted nitrosobenzenes by DFT and MP2 methods with 6-31+g(d) basis sets. Inputs in each column in the second row with a negative sign represent imaginary frequencies corresponding to the transition state of the respective transformation.

Substituents		ΔG^\ddagger B3LYP/6-31+g(d)				ΔG^\ddagger MP2/6-31+g(d)		
X	σ^b	Water ^c	Explicit ^d	GAS ^e	CHCl ₃ ^f	GAS ^g	CHCl ₃ ^h	exp ⁱ
NO ₂	0.778	7.99	7.52	8.07	8.02	8.25	5.82	
	(0.740)	-174.14	-180.56	-178.83	-176.94	-167.56	-171.24	
CN	0.660	8.02	j	8.66	8.72	8.59	8.27	
	(0.674)	-185.55		-188.73	-188.01	-171.71	-177.17	
Ac	0.502	9.04	8.50	8.71	8.97	7.67	7.51	
	(0.567)	-188.23	-186.37	-188.36	-189.96	-171.4	-177.05	
Cl	0.227	10.88	10.44	10.11	10.66	8.67	8.20	8.11 (7.51)
	(0.035)	-210.63	-211.12	-206.13	-210.87	-180.86	-189.39	
F	0.062	11.46	11.06	10.58	11.19	8.50	8.36	8.52
	(-0.247)	-217.12	-217.28	-211.82	-216.84	-183.92	-182.5	
H	0	10.76	9.48	9.64	10.44	7.94	8.13	8.21
		-212.9	-205.75	-202.94	-211.48	-180.2	-188.36	
Me	-0.170	12.96	10.31	10.14	9.81	7.99	8.65	8.54 (8.21)
	(-0.256)	-225.14	-215.73	-211.78	-222.72	-183.32	-194.27	
MeO	-0.268	14.23	12.69	12.25	13.63	9.73	10.03	9.81 (10.31)
	(-0.647)	-249.74	-242.96	-233.07	-246.85	-194.01	-205.31	
OH	-0.37	14.61	12.49	12.03	13.70	9.62	10.03	
	(-0.853)	-254.59	-240	-232.06	-248.5	-193.93	-202.29	
NH ₂	-0.66	18.66	14.77	13.77	17.13	9.94	11.19	
	(-1.111)	-291.12	-266.2	-250.84	-291.12	-199.43	-217.23	

^a ΔG^\ddagger corresponds to activation barriers, which are defined as the difference between energies reported as G_{TS} and G_{GS} , which are sums of electronic and thermal free energies of transition and ground states, which includes zero-point, thermal, and entropic terms at 298 K and 1 atm multiplied by 627.5. Those in solution (with non-electrostatic terms) include the total electronic energy polarised by the dielectric continuum together with the cavitation, dispersion, and repulsive terms within PCM.

^b σ_p values are taken from McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, 23, 420. The values within brackets correspond to σ_p^+ values and they are taken from Swain, C. G.; Lupton Jr, E.C. *J. Am. Chem. Soc.* **1968**, 90, 4328.

^cPCM in water

^dInvolving an explicit water in vacuum

^eIn vacuum

^fPCM in chloroform

^gIn vacuum

^hPCM in chloroform

ⁱExperimental values taken from reference 7b. Those within brackets are from Cox, R. H.; Hamada, M. *Org. Magn. Reson.* **1979**, 12, 322.

^jThe transition state could not be located.

Linear Free Energy Relationship: It was expected that electron-donating groups would increase the barrier of internal rotation of the C-N bond in nitrosobenzenes and this would be seen by the correlation of the activation barriers with polar substituted Hammett constants. It was indeed found that calculated activation barriers by DFT and MP2 methods for the internal rotation of the C-N bond in *p*-substituted nitrosobenzenes were well-correlated with polar Hammett sigma values. The correlation of Hammett sigma constants with the barrier to rotation about the C-N bond ΔG^\ddagger produces the following regression (Eqs. 1-12). It is quite obvious that all data fit comparably well with σ^+ rather than with σ , meaning that there is a strong resonance effect on the activation barriers.

B3LYP/6-31+g(d) in water

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-6.89 \pm 0.68) \times \sigma + 12.39 \pm 0.31 \quad r^2 = 0.93 \quad (1)$$

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-5.04 \pm 0.46) \times \sigma^+ + 11.31 \pm 0.29 \quad r^2 = 0.94 \quad (2)$$

B3LYP/6-31+g(d) in vacuum with explicit water

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-4.70 \pm 0.71) \times \sigma + 10.86 \pm 0.29 \quad r^2 = 0.86 \quad (3)$$

$$\Delta G_{rot}^\ddagger \text{ (kcal/mol)} = (-3.55 \pm 0.33) \times \sigma^+ + 10.11 \pm 0.20 \quad r^2 = 0.94 \quad (4)$$

B3LYP/6-31+g(d) in vacuum

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-3.98 \pm 0.45) \times \sigma + 10.96 \pm 0.20 \quad r^2 = 0.91 \quad (5)$$

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-2.74 \pm 0.23) \times \sigma^+ + 10.09 \pm 0.14 \quad r^2 = 0.95 \quad (6)$$

B3LYP/6-31+g(d) in chloroform

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-5.41 \pm 0.94) \times \sigma + 11.64 \pm 0.42 \quad r^2 = 0.81 \quad (7)$$

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-4.10 \pm 0.55) \times \sigma^+ + 10.78 \pm 0.34 \quad r^2 = 0.87 \quad (8)$$

MP2/6-31+g(d) in vacuum

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-1.15 \pm 0.45) \times \sigma + 8.78 \pm 0.20 \quad r^2 = 0.45 \quad (9)$$

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-0.97 \pm 0.28) \times \sigma^+ + 8.58 \pm 0.17 \quad r^2 = 0.60 \quad (10)$$

MP2/6-31+g(d) in chloroform

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-3.44 \pm 0.35) \times \sigma + 8.70 \pm 0.15 \quad r^2 = 0.93 \quad (11)$$

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-2.50 \pm 0.24) \times \sigma^+ + 8.17 \pm 0.15 \quad r^2 = 0.94 \quad (12)$$

MP2/6-31+g(d) in chloroform

(only electron donating groups, H, F, Cl, Me, MeO, OH and NH₂)

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-2.65 \pm 0.26) \times \sigma^+ + 8.06 \pm 0.15 \quad r^2 = 0.96 \quad (13)$$

MP2/6-31+g(d) in chloroform-experimental^{7b}

$$\Delta G^\ddagger \text{ (kcal/mol)} = (-2.67 \pm 0.07) \times \sigma^+ + 8.08 \pm 0.06 \quad r^2 = 0.99 \quad (14)$$

The magnitude of the slope in equations of the free energy relationships is basically an indication of the competition of interaction of the charge in the transition state between polar substituents and environment, namely solvents, when rates or equilibria are measured.³ The larger the slope the less interaction of the transition state with environment and hence the more pronounced the effect of substituents. The sign of the slope generally gives evidence about the type of the charge developed in transition state. The slope means positive charge development in going from ground state to transition state. The negative slopes calculated by DFT in different environments are -5.04, -4.10, -3.55, and -2.74 in water, chloroform, with explicit water in vacuum, and in vacuum alone. Similar results are computed by MP2. They are -1.15 and -2.50 in vacuum and in chloroform,

respectively. The question always arises as to whether the theoretical methods chosen would provide comparable results with those of experimental ones. A striking outcome produced from MP2 calculations is that they give a very similar free energy relationship with experimental results. The slope derived for just electron donating groups including parent nitrosobenzene (Eq. 13) has quite close parameters derived from experimental data (Eq. 14) where *para* substituents are H, Cl, Br, I, Me, MeO, NMe₂, and NEt₂.^{7b} This means that, as stated earlier, MP2 is the method to employ to predict the activation barrier of internal bond rotation at least for the C-N bond in substituted nitrosobenzenes.

The results, i.e. the magnitudes of the slopes, normally contradict the simple electrostatic interaction of solvent molecules with transition state structures involving charge developing where polar solvent like water reduces the effect of polar substituents. Therefore, the magnitude of the slope in polar solvents will be smaller than that in less polar ones. Thus it may be suggested that the slopes cannot be accounted for by charge changes in the effect of polar substituent on the internal rotation of the C-N bonds in substituted nitrosobenzenes. This was supported by the finding that calculated Mulliken charges on oxygen do not significantly change with polar Hammett constants (see Figure 3). So what could account for the strong dependency of activation barriers on Hammett sigma constants, namely the slopes of free energy relationships? This question will be answered in detail later in the text.

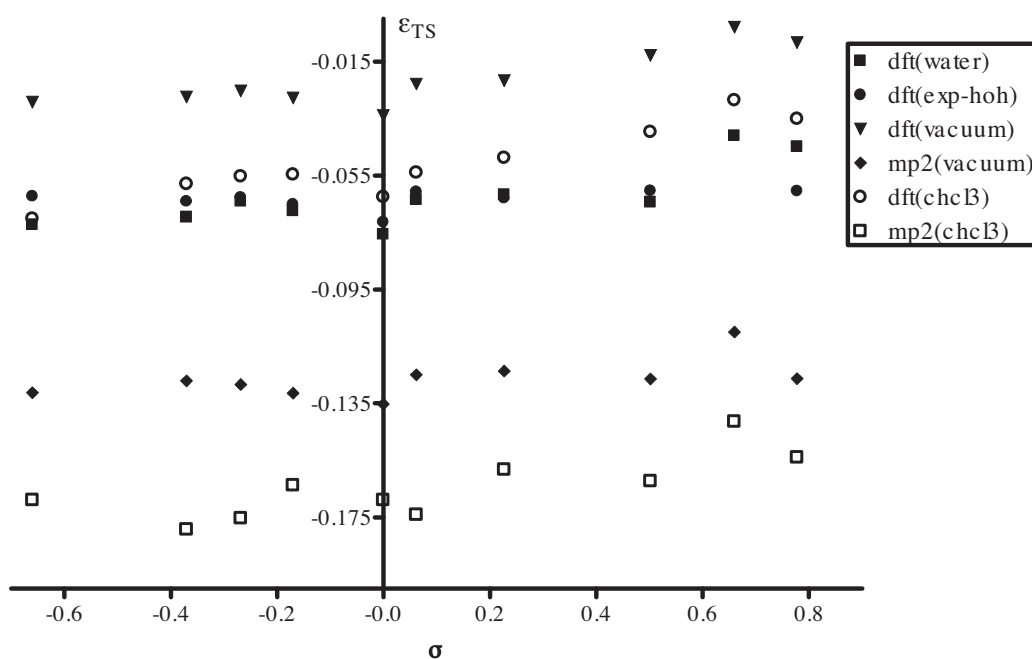


Figure 3. Dependence of Mulliken charges on oxygen atoms in the transition states of *p*-substituted nitrosobenzenes on polar Hammett constants calculated by DFT and MP2 methods at 6-31+g(d) level in different environments.

The other most important result gained from the slope derived from the linear free energy relationships, which indicates the bond changes going from ground state to transition state. The calculated C-N bond length changes, going from ground states to transition states, showed a strong correlation with the substituent Hammett constants as indicated by the regression statistics (Eqs. 15-26). The data are presented in Table 2. They show

that bond changes are rather correlated with Hammett σ^+ , meaning a strong resonance effect as seen in the dependency of activation free energies on Hammett constants. A similar trend in the magnitude of the slopes of dependency of bond changes on Hammett constants with the activation barriers was found, meaning that the more electron donating group has the shorter C-N bond length. This is consistent with the results obtained for the activation free energies. Thus it can be concluded that the strong dependence of activation barriers for internal rotation of the C-N bond on polar substituents is mainly due to the double bond character of the C-N bond in the ground state of the structure with more electron donating groups. For example, the calculated C-N bond length by MP2 in chloroform for *p*-nitronitrosobenzene in the ground state is 1.4399 Å, whereas this bond is 1.4111 Å for *p*-aminonitrosobenzene. Therefore, there is a 0.0288 Å difference between 2 bonds, which corresponds to 5.37 kcal/mol of difference in the activation free energies of 2 compounds.

Table 2. Calculated C-N bond lengths in ground (first row) and transition (second row) states for *p*-substituted nitrosobenzene by DFT and MP2 methods with 6-31+g(d) basis sets.

Substituents	B3LYP/6-31+g(d)			MP2/6-31+g(d)		
X	Water ^a	Explicit ^b	GAS ^c	CHCl ₃ ^d	GAS ^e	CHCl ₃ ^f
NO ₂	1.4366	1.4395	1.4486	1.4407	1.4461	1.4399
	1.4634	1.4645	1.4678	1.4644	1.4612	1.4592
CN	1.4322	1.4353	1.4450	1.4366	1.4458	1.4391
	1.4642		1.4686	1.4653	1.4610	1.4587
Ac	1.4290	1.4323	1.4429	1.4332	1.4433	1.4364
	1.4622	1.4626	1.4661	1.4632	1.4592	1.4570
Cl	1.4192	1.4254	1.4363	1.4244	1.4401	1.4319
	1.4649	1.4655	1.4696	1.4661	1.4601	1.4576
F	1.4167	1.4234	1.4345	1.4223	1.4398	1.4318
	1.4659	1.4665	1.4709	1.4672	1.4608	1.4579
H	1.4195	1.4274	1.4383	1.4254	1.4422	1.4334
	1.4634	1.4643	1.4684	1.4647	1.4595	1.4568
Me	1.4129	1.4216	1.4331	1.4191	1.4382	1.4288
	1.4627	1.4633	1.4675	1.4675	1.4585	1.4557
MeO	1.4013	1.4124	1.4242	1.4084	1.4309	1.4204
	1.4639	1.4645	1.4692	1.4692	1.4589	1.4560
OH	1.4001	1.4137	1.4256	1.4084	1.4330	1.4210
	1.4640	1.4654	1.4670	1.4654	1.4595	1.4562
NH ₂	1.3815	1.4037	1.4174	1.3929	1.4277	1.4111
	1.4626	1.4641	1.4691	1.4641	1.4584	1.4551

^aPCM in water, ^bInvolving an explicit water in vacuum, ^cIn vacuum, ^dPCM in chloroform

^eIn vacuum, ^fPCM in chloroform,

B3LYP/6-31+g(d) in water

$$\Delta\text{C-N } (\text{Å}) = (-0.0355 \pm 0.0030) \times \sigma + 0.0524 \pm 0.0014 \quad r^2 = 0.95 \quad (15)$$

$$\Delta\text{C-N } (\text{Å}) = (-0.0256 \pm 0.0018) \times \sigma^+ + 0.0463 \pm 0.0012 \quad r^2 = 0.97 \quad (16)$$

B3LYP/6-31+g(d) in vacuum with explicit water

$$\Delta\text{C-N } (\text{Å}) = (-0.0239 \pm 0.0028) \times \sigma + 0.0426 \pm 0.0012 \quad r^2 = 0.91 \quad (17)$$

$$\Delta\text{C-N } (\text{Å}) = (-0.0179 \pm 0.0011) \times \sigma^+ + 0.0389 \pm 0.0007 \quad r^2 = 0.98 \quad (18)$$

B3LYP/6-31+g(d) in vacuum

$$\Delta\text{C-N } (\text{Å}) = (-0.0209 \pm 0.0024) \times \sigma + 0.0354 \pm 0.0011 \quad r^2 = 0.90 \quad (19)$$

$$\Delta\text{C-N } (\text{Å}) = (-0.0157 \pm 0.0012) \times \sigma^+ + 0.0321 \pm 0.0008 \quad r^2 = 0.95 \quad (20)$$

B3LYP/6-31+g(d) in chloroform

$$\Delta\text{C-N } (\text{Å}) = (-0.0315 \pm 0.0029) \times \sigma + 0.0470 \pm 0.0013 \quad r^2 = 0.94 \quad (21)$$

$$\Delta\text{C-N } (\text{Å}) = (-0.0232 \pm 0.0016) \times \sigma^+ + 0.0420 \pm 0.0010 \quad r^2 = 0.97 \quad (22)$$

MP2/6-31+g(d) in vacuum

$$\Delta\text{C-N } (\text{Å}) = (-0.0109 \pm 0.0018) \times \sigma + 0.0218 \pm 0.0008 \quad r^2 = 0.82 \quad (23)$$

$$\Delta\text{C-N } (\text{Å}) = (-0.0084 \pm 0.0009) \times \sigma^+ + 0.0201 \pm 0.0006 \quad r^2 = 0.92 \quad (24)$$

MP2/6-31+g(d) in chloroform

$$\Delta\text{C-N } (\text{Å}) = (-0.0160 \pm 0.0024) \times \sigma + 0.0289 \pm 0.0011 \quad r^2 = 0.86 \quad (25)$$

$$\Delta\text{C-N } (\text{Å}) = (-0.0121 \pm 0.0014) \times \sigma^+ + 0.0263 \pm 0.0008 \quad r^2 = 0.91 \quad (26)$$

It would not be surprising to see the dependence of the force constant and imaginary frequency corresponding to the transition vector (or reaction coordinate mode) on polar Hammett constants since it would be expected that the force constant and thus the imaginary frequency is basically a measure of the strength of the C-N bond in the transition state. It was in fact found that the imaginary frequencies are well-correlated with Hammett constants as indicated in Eqs. 27-38. The data are reported in Table 1.

B3LYP/6-31+g(d) in water

$$\nu_i \text{ (cm}^{-1}\text{)} = (57.22 \pm 4.56) \sigma + -225.7 \pm 3.3 \quad r^2 = 0.93 \quad (27)$$

$$\nu_i \text{ (cm}^{-1}\text{)} = (77.62 \pm 7.747) \sigma^+ + -213.5 \pm 2.8 \quad r^2 = 0.96 \quad (28)$$

B3LYP/6-31+g(d) in vacuum with explicit water

$$\nu_i \text{ (cm}^{-1}\text{)} = (58.63 \pm 7.27) \sigma + -219.1 \pm 3.1 \quad r^2 = 0.90 \quad (29)$$

$$\nu_i \text{ (cm}^{-1}\text{)} = (44.08 \pm 3.32) \sigma^+ + -209.7 \pm 2.0 \quad r^2 = 0.96 \quad (30)$$

B3LYP/6-31+g(d) in vacuum

$$\nu_i \text{ (cm}^{-1}\text{)} = (49.07 \pm 5.26) \sigma + -213.4 \pm 2.2 \quad r^2 = 0.93 \quad (31)$$

$$\nu_i \text{ (cm}^{-1}\text{)} = (36.73 \pm 2.12) \sigma^+ + -205.6 \pm 1.3 \quad r^2 = 0.98 \quad (32)$$

B3LYP/6-31+g(d) in chloroform

$$\nu_i \text{ (cm}^{-1}\text{)} = (22.87 \pm 2.36) \sigma^+ + -184.1 \pm 1.0 \quad r^2 = 0.93 \quad (33)$$

$$\nu_i \text{ (cm}^{-1}\text{)} = (17.15 \pm 0.75) \sigma^+ + -180.4 \pm 0.5 \quad r^2 = 0.99 \quad (34)$$

MP2/6-31+g(d) in vacuum

$$\nu_i \text{ (cm}^{-1}\text{)} = (68.39 \pm 6.67) \sigma + -212.5 \pm 2.2 \quad r^2 = 0.94 \quad (35)$$

$$\nu_i \text{ (cm}^{-1}\text{)} = (50.55 \pm 3.62) \sigma^+ + -212.5 \pm 2.2 \quad r^2 = 0.97 \quad (36)$$

MP2/6-31+g(d) in chloroform

$$\nu_i (\text{cm}^{-1}) = (31.07 \pm 3.79) \sigma + -192.3 \pm 1.6 \quad r^2 = 0.91 \quad (37)$$

$$\nu_i (\text{cm}^{-1}) = (22.50 \pm 2.91) \sigma^+ + -187.5 \pm 1.8 \quad r^2 = 0.90 \quad (38)$$

Solvation: An explicit water molecule was deliberately introduced to form a hydrogen bond with the nitroso group in order to see the effect of solvation explicitly on the barrier. The structures of the ground, transition, and product states including the explicit water are illustrated in Figure 4 for the internal rotation of the C-N bond in nitrosobenzene. The results are shown in Table 1. It implies that the explicit water molecule increases the activation barrier of electron donating groups compared to that in vacuum. This is an accepted outcome since it would be expected that the solvent molecules would attract electrons from the nitroso group and consequently the nitroso group would draw relatively more electrons from the ring, thus increasing the barrier. In other words, the results hint that the electron withdrawing capacity of the nitroso group is enhanced with the explicit water. To rule out the possibility of the steric factor implemented by the solvent on the activation barrier, an explicit methanol molecule was also introduced in a similar manner but just for *p*-methoxynitrosobenzene by B3LYP. It was found that the explicit methanol produces results similar to those of water. This may be attributed to the fact that the water molecule, by forming a hydrogen bond with the nitroso group, causes more transmission of electrons from the ring. The C-N bond lengths produce supporting evidence for this explanation. Data in Table 2 show that C-N lengths with explicit water are quite close those in water (PCM) and much shorter than those in vacuum, implying the existence of an electronic effect.

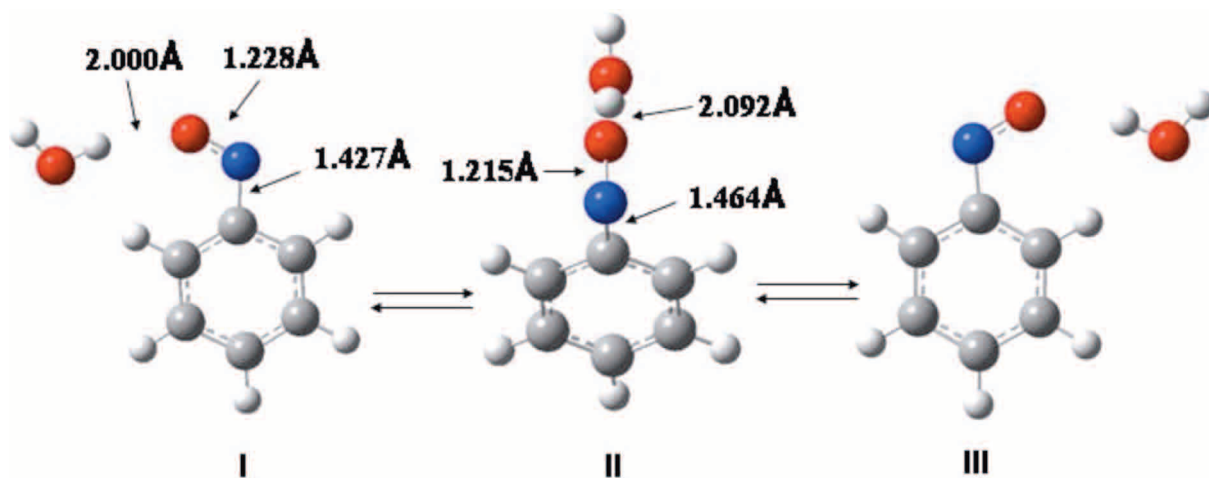


Figure 4. Structures of nitrosobenzene involving an explicit water molecule optimised by B3LYP/6-31+g(d) in vacuum. **I** and **III** are identical and correspond to the ground states and **II** corresponds to the transition state.

Steric Factors: Calculations were carried out by the MP2 method in vacuum to see the steric effect on the activation barrier by introducing methyl, ethyl, and methoxy groups at position 2. The structures are shown in Figure 5. Activation free energy barriers in kcal/mol are represented in Figure 6. Reverse reactions for the 3 systems all have lower activation energy barriers compared to forward reactions, which may be ascribed to the steric effect. On the other hand, the barriers for forward reactions of 2-methyl and 2-ethylnitrosobenzenes are similar but higher than that of 2-methoxynitrosobenzene. This means that introducing the methoxy group

at the *orto* position causes an inductive effect by withdrawing electrons from the ring instead of donating as in the case of *p*-substituted, thus leading to a longer C-N bond (1.4609 Å), and hence a lower activation barrier. The C-N bond length and activation barrier for *p*-methoxynitrosobenzene is 1.4589 Å (see Table 2) and 9.75 kcal/mol; so there is a difference of 2.03 kcal/mol between *orto* and *para* substituted methoxy.

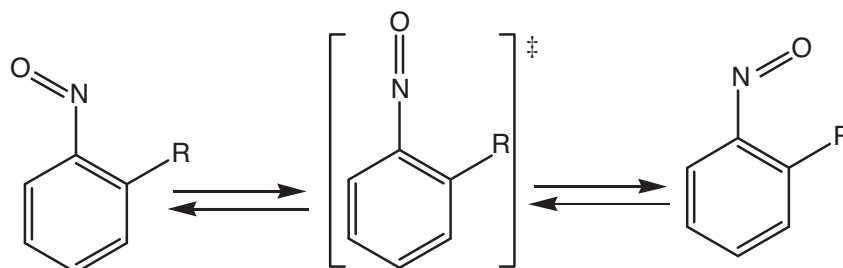


Figure 5. R=methyl (1); R=ethyl (2); R=methoxy (3).

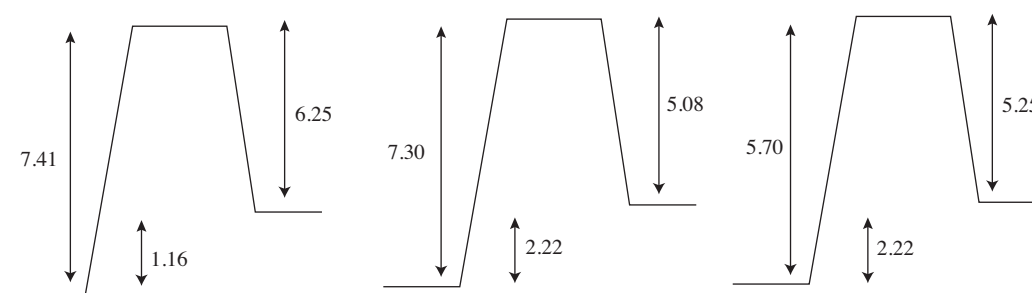


Figure 6. The values correspond to activation barriers (ΔG^\ddagger) in kcal/mol. Profile on the right corresponds to 2-methylnitrosobenzene; the one in the middle corresponds to 2-ethylnitrosobenzene, and the one on the left corresponds to 2-methoxynitrosobenzene. For each profile the values on the right correspond to the forward reaction and those on the left correspond to the reverse reaction.

Models: To see the individual contribution of resonance and inductive effects, several models were built and their rotation barriers were computed. The compounds chosen for this purpose are listed in Figure 7. The results are presented in Figure 8. They show that nitrosocyclohexane and nitrosoethane have a very similar and small activation barrier compared to nitrosoethene, whose activation barrier is close to those of aromatic ones, even larger than that of nitrosobenzene. This suggests that simple conjugation increases the barrier almost 8 times, corresponding to non-conjugated systems, basically due to the resonance effect.

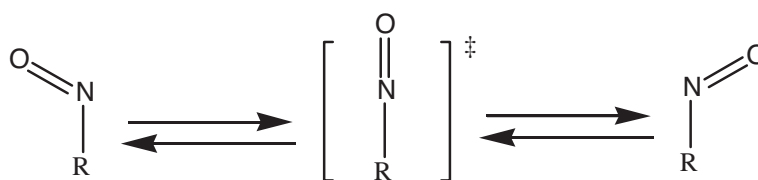


Figure 7. R=cyclohexyl (4); R=ethyl (5); R=vinyl (6).

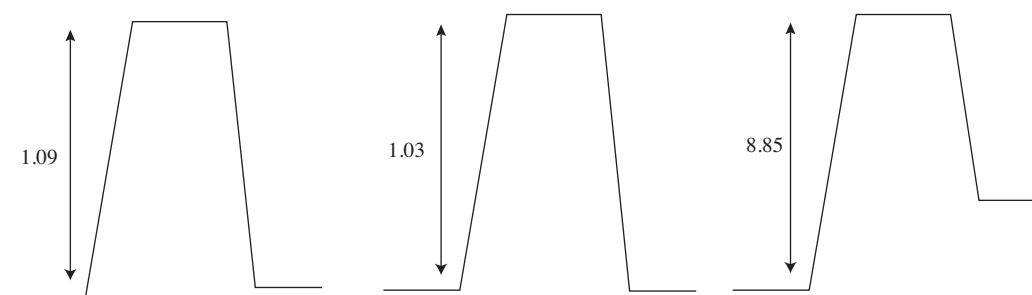


Figure 8. The values correspond to activation barriers (ΔG^\ddagger) in kcal/mol. The profile on the right corresponds to nitrosocyclohexane; the one in the middle corresponds to nitrosoethane, and the one on the left corresponds to nitrosoethene.

Conclusion

DFT and MP2 methods at 6-31+g(d) level of theory were used to predict the activation barriers for internal rotation of the C-N bond in *p*-substituted nitrosobenzenes. It was found that electron donating groups increase the barriers, which are well correlated with Hammett sigma σ^+ rather than σ , an indication of a strong resonance effect. The effect of solvation (PCM solvents) on the activation barrier including the introduction of an explicit water molecule was also studied. The result showed that the more polar the solvent the larger the barrier. This was ascribed to the interaction of the solvent molecule with the nitroso group; hence the electron donating groups will increase the barrier and consequently the slope will be larger in pure polar solvents. The results indicate that MP2 is the method of choice to predict the activation barriers for the internal rotation of the C-N bond, with results comparable with the few available experimental values.

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