

Molecular Mechanics: The Conjugate Nitro Group Parameters in the MM2 Force Field.

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Abstract

The conjugated nitro group has been included in the π system calculation within the MM2 force field. New parameters have been estimated by a statistical process from X-ray molecular structures recorded in the C.S.D.S. Comparison of the corresponding results with those given by the MM2(91) force field parameters show a clear improvement for dihedral and bond angles. For N-O and C-N bond lengths a slight global improvement is also observed. A closer examination of the results for the latter bond shows that sometimes MM2(91) gives better results for six membered ring nitro compounds. By contrast the parameters proposed here are more adapted to five membered ring derivatives. The derived linear relations permit the study of molecules over a wider range of π indices. The introduction of a correction factor to the calculated molecular π dipole moment in conjunction with a necessary reestimation of some σ -bond dipole moments also leads to improved total molecular dipole moments.

Keywords : Molecular mechanics, MM2, nitro group

Introduction

Nitro compounds have a wide range of applications, ranging from explosives to drugs by way of solvents and compounds for non-linear optics.

In pharmacology, numerous compounds which exhibit an antimicrobial activity are aromatic or heterocyclic nitro-compounds, see, for example the biologically active molecules shown in Figure 1. While for valence saturated compounds the nitro group can be considered as a rather free rotor around the C-N bond, in biologically active molecules like those shown in Figure 1, the nitro group participates in the delocalized π bond system, exhibiting an important conjuga-

tion and leading to a substantial rotational barrier around the C-N bond.

Comprehension of the phenomena which rule the activity or inactivity of trypanocides of this type requires molecular modeling. For instance, Nifurtinox, Metronidazole and Megazole [see Figure 1] show an appreciable trypanocidal activity while some molecules of a similar nitro-imidazole series as are known to be inactive.

In an attempt to find the reasons for this, a structural study has been performed by both molecular mechanics (MM2) and semiempirical (AM1, PM3) methods [4].

We would like to report here a preliminary study which has led to molecular mechanics parameters for the conjugate nitro-group in the MM2 force field [5].

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Position of the question

Among "academic" force fields the MM2 force field is one of the most famous. It is widely distributed and still allows the widest choice of chemical functions, i.e. atom types. MM3 [6] and MM4 [7] are on the way to replace it, but certain parameters evaluated for MM2 can be considered as reasonable "first guesses" for MM3. In the present work, the MM2 force field version as it is handled in the MM2(87) program [8] (with the 1991 parameters [9]) has been used.

For aliphatic compounds the set of parameters for the unconjugated nitro group is complete and resident in the program. When the nitro group appears as a substituent in conjugate molecules, the parameters which are bond order dependent are attributed a median value and no PPP-SCF calculation explicitly includes the NO₂ group. Thus the parameters which permit the evolution of the "natural" C-N and N-O bond lengths and stretching constants (SSLOPE and TSLOPE) for instance are not present. In an attempt to improve the optimized geometries for this type of compound we have estimated the necessary modifications to the NO₂ group parameters so that this group can be fully included in the PPP-SCF and subsequent molecular mechanics calculations.

Unless otherwise stated, the determinations were based on 17 reference molecules (Figure 2) whose geometries in the crystalline solid state were found in the Cambridge Structural Data System [10]. Two of them, designated as YUVG0V and YUFGUB, whose X-ray structures were determined in our laboratory [10], have been collected in the C.S.D.S. very recently.

Modifications of the source-code

In the nitro group, the oxygen type number is 7 while the nitrogen one is 46. Atom type 7 is considered to be a π atom. Atom type 46 is not. Because it is not possible to indicate in the data that a new atom type is to be submitted for π quantum calculations, the source-code has had to be modified. This is easily done by replacing only atom type 46 by atom type 40 during the π calculation (Nitrogen atom contributing to the π system by an electron pair). Empirical quantum parameters for both types were thus assumed to be identical.

Further modification

As will be discussed below, π dipole moments calculated by the SCF or VESCF methods are overestimated. We thus have introduced a correction factor of 0.46. This factor plays a role only in the estimation of the molecular dipole moment and was implemented accordingly. As a consequence, several σ bond-dipole moments which were previously estimated so that combined with non-corrected π dipole moments they would fit the experimental ones, need to be reestimated. This has been done for some of them [11].

Non-bonding parameters

Van der Waals parameters and bond dipole moments interfere in the optimization process through electrostatic and non-bonding interactions. It was thus necessary before any estimation of stretching, bending and torsional parameters for

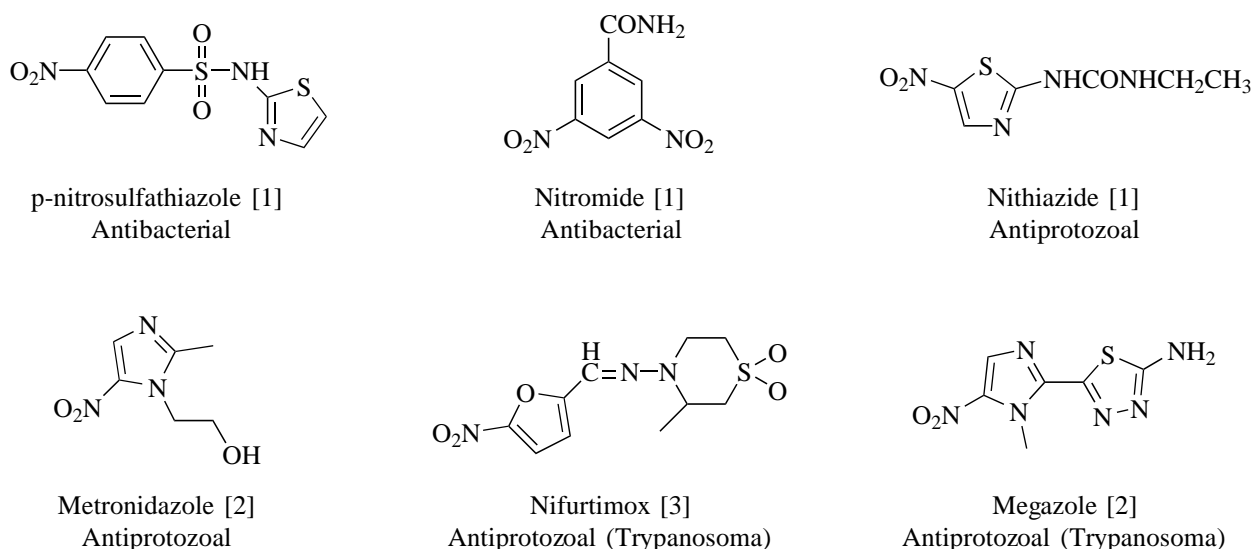


Figure 1. Some nitro derivatives known to be antimicrobial molecules.

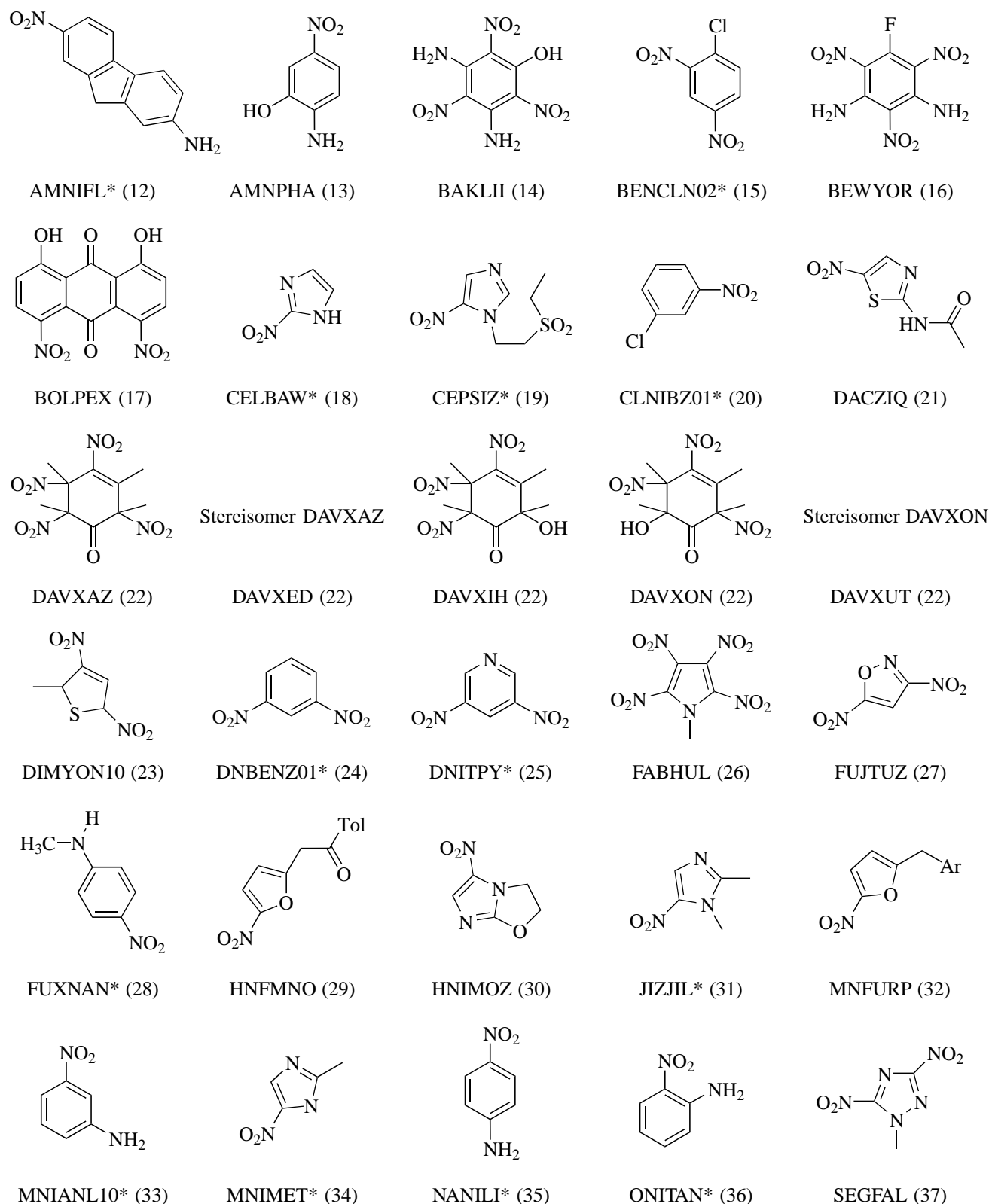
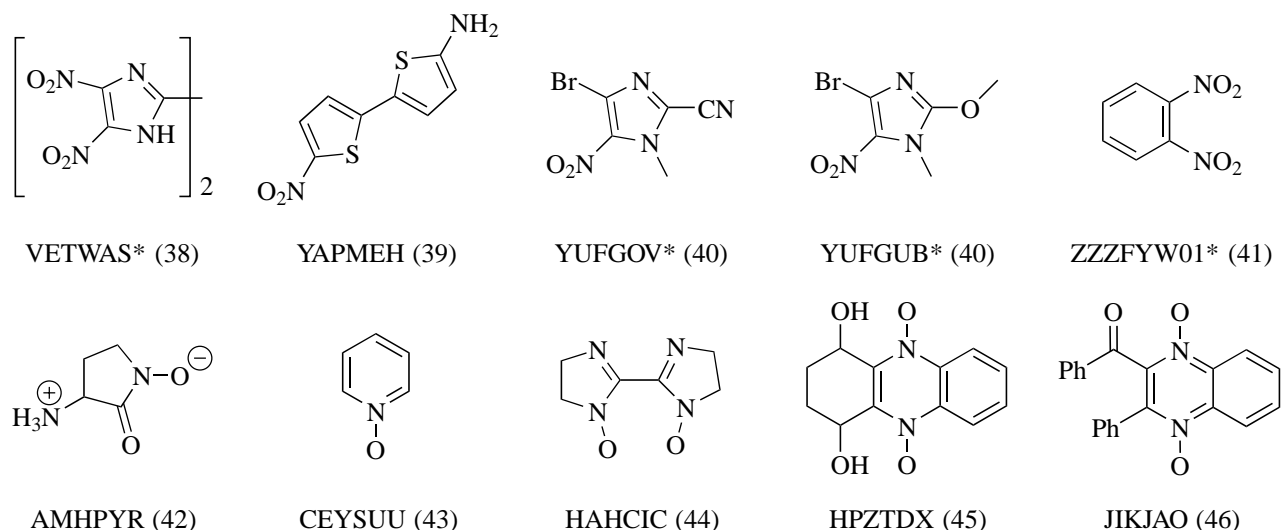


Figure 2 (continuous next page). Reference molecule formulas. Upper case letters correspond to the C.S.D. refcodes. References in parenthesis refer to the publication

of the crystalline structure. 17 molecules more commonly referred to are marked by an asterisk.

**Figure 2 (continued).**

the NO₂ group to estimate these non-bonding parameters. The only Van der Waals parameters missing were those of the type 46 nitrogen. They were attributed the same values as those for other nitrogen types.

Calculation of the C-N and N-O dipole moments.

The C-N and N-O bond moments proposed by Allinger et al. have been chosen to fit the experimental dipole moments of nitrobenzene and nitroethylene, but as the nitro group was not included in the π calculation, in fact, these dipole moments are total dipole moments, i.e. $\vec{\mu} = \vec{\mu}_{\pi} + \vec{\mu}_{\sigma}$.

Because we have introduced the nitro group in the calculation, we now have π charges on these atoms and thus the π dipole moments of the C-N and N-O bonds can be calculated and in fact are included in the total π dipole moment of the molecule. Keeping Allinger's values would result in taking the π dipole bond moments into account twice. It was thus necessary to evaluate for each bond the σ and π parts of the dipole moment.

The major difficulty which arises here is the validity of the π charges. Indeed it is known that a PPP type calculation overestimates these charges. In the case of the VESCF-PPP method used in MM3, Allinger has quantified this overestimation and the π moments are corrected by a 0.65 factor. For the SCF-PPP method used in MM2 the overestimation has not been quantified but is known to be even larger.

Use of overestimated π bond moments will lead to wrong σ moments and in some cases even the sign of $\vec{\mu}_{\sigma}$ could be wrong. In that respect, the example of nitrobenzene is illustrative. The π dipole moment calculated with MM2 for the whole molecule from the π charges without any correction is $\mu_{\pi} = 5.077\text{D}$ which is already larger than the experimental moment $\mu_{\text{exp}}^{\text{total}} = 4.00\text{D}$!

By use of the MM2 and MM3 programs and force-fields we have been able to estimate the correction factor for the SCF-PPP method (MM2). Nitrobenzene was chosen as the reference molecule.

For both methods and for the whole molecule :

$$\vec{\mu}_{\text{exp}} = \vec{\mu}_{\sigma} + \vec{\mu}_{\pi_{\text{corr}}} \quad \text{thus} \quad \vec{\mu}_{\sigma} = \vec{\mu}_{\text{exp}} - \vec{\mu}_{\pi_{\text{corr}}} \quad (1)$$

It was supposed that the correction factor in MM3 is valid and accurate, thus :

$$\vec{\mu}_{\pi_{\text{corr}}}^{\text{MM3}} = 0.65 \times \vec{\mu}_{\pi}^{\text{MM3}} \quad (2)$$

similarly

$$\vec{\mu}_{\pi_{\text{corr}}}^{\text{MM2}} = k \times \vec{\mu}_{\pi}^{\text{MM2}} \quad (3)$$

Thus the NO₂ group has been included in the VESCF-PPP calculation of MM3 to get $\mu_{\pi_{\text{corr}}}^{\text{MM3}}$ and the π charges on the N and O atoms. Supposing that both correction factors are valid and accurate

$$\vec{\mu}_{\pi_{\text{corr}}}^{\text{MM3}} = \vec{\mu}_{\pi_{\text{corr}}}^{\text{MM2}} \quad (4)$$

which leads to

$$k = 0.46 \quad (5)$$

and

$$\vec{\mu}_{\sigma}^{\text{MM2}} = 1.64\text{D} \quad (6)$$

We then had to divide the $\vec{\mu}_{\sigma}^{\text{MM2}}$ of the molecule into its different σ bond dipole contributions. For this it was assumed that:

- the C atoms of the phenyl group were not significantly contributing to the total σ dipole moment.
- and that $\mu_{\text{tot}}^{\text{NO}} = 2.53 \text{ D}$ (Allinger MM2)
From the geometry it was deduced :

$$\mu_{\sigma}^{\text{NO}} = 1.12 \text{ D} \quad (7)$$

$$\mu_{\sigma}^{\text{CN}} = 0.625 \text{ D} \quad (8)$$

Comparison with experimental values

Table 1 collects our results for 11 molecules (among which is nitrobenzene) for which the structure and the experimental dipole moment are known. Good agreement can be observed for the molecules either in the solid state or isolated in vacuum. Thus these new parameters were introduced into the MM2 force field and used in the determination of other unknown parameters.

Stretching parameters for delocalized C-N and N-O bonds.

It is well known that a bond length is a monotonously decreasing function of the π bond order. In MM2's philosophy the "natural" bond length l_0 is supposed to be a linear function of the π bond index P :

$$l_0 = (l_2 + \text{TSLOPE}) - \text{TSLOPE} \times P \quad (9)$$

or

$$l_0 = l_1 - \text{TSLOPE} \times P \quad (10)$$

l_2 and l_1 are respectively the extrapolated bond lengths for $P = 1$ (pure double bond) and $P = 0$ (pure single bond). In fact this linear relationship is good only within a definite range, so that l_2 and l_1 should not be confused with the experimental lengths of double and single bonds. The reason is that the graph of $l = f(P)$ shows curvature.

Eq. 9 uses parameters resident in the MM2 program for the already known delocalized bonds : l_2 and TSLOPE. Eq. 10, which is equivalent, but easier to handle, was used further.

We chose to extract statistically these bond parameters using crystallographic data from a much larger number of molecules (Figure 2) than the 17 already mentioned. These molecules, chosen from the C.S.D.S., had to satisfy the following criteria :

- be purely organic mono-or polynitro unsaturated compounds
- the R factor of the X-ray determination had to be less than 10%
- the compounds had to be closed-shell and the PPP-SCF calculation had to converge without any "trick".

The MM2 force field has been designed to reproduce room-temperature vibrationally averaged structures. MM2 is thus based on r_g bond lengths, ie on mean distances. X-ray structures from the CSDS give r_{α}^T bond lengths, ie distances between the mean positions of atoms at T temperature. The small difference between r_{α}^T and r_g structures has been neglected here because the experimental errors in room temperature X-ray data are probably several times the size of the correction from r_{α}^T to r_g which also is within the error limits of what can be expected from MM calculations.

32 molecules were thus selected, exhibiting 52 C-N bonds and 82 N-O bonds (Table 2). It will be seen in this table that a few nitroso compounds were also selected for the following reasons. It soon appeared that for N-O bonds, the bond lengths and π orders were confined in a narrow range and that it was almost impossible to find a best-fit straight line representative of $l_{\text{exp}} = f(P)$ with a good regression coefficient. It was necessary to extend the π range and we thus turned toward some nitroso compounds in which the nitrogen atom remains sp^2 hybridized and planar. The nitrogen atom here remains cross-conjugate as in the $Csp^2 - NO_2$ group but is linked to two sp^2 C and only one O and allows the N-O π bond order to reach smaller values.

For each molecule a PPP-SCF calculation, based on the crystalline coordinates, with no optimization of the geometry, was performed, thus giving for each bond a couple of values for l_{exp} (experimental bond length) and P_{exp} ("experimental") π bond-order. These values are recorded in Table 2 and plotted in Figure 3 and Figure 4. From these data the "best-fit" straight lines were found by least-squares and gave:

for C-N bonds :

$$l_{\text{exp}} = 1.514 - 0.240 \times P_{\text{exp}} \quad (11)$$

(r.coeff = -0.93122)

for N-O bonds :

$$l_{\text{exp}} = 1.422 - 0.301 \times P_{\text{exp}} \quad (12)$$

(r.coeff = -0.92215)

In the MM2 force field the stretching force constants of delocalized bonds also are supposed to be linear functions of π bond order :

$$k_0 = (k_2 - \text{SSLOPE}) + \text{SSLOPE} \times P \quad (13)$$

or

$$k_0 = k_1 - \text{SSLOPE} \times P \quad (14)$$

In this case, determination of the parameters k_1 or k_2 and SSLOPE cannot be based on a series of values of k_{exp} . Following various authors [48,49], Badger's rule [50] was used

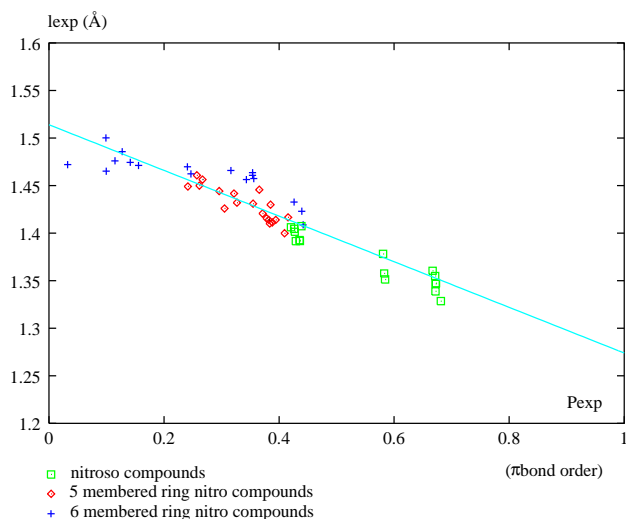


Figure 3. Plot of l_{exp} versus P_{exp} for the C - N bond.

to establish a relation between experimental bond length and stretching force constant. For atoms of the second period :

$$k_{exp} \times (l_{exp} - \xi)^3 = 1.86 \quad (15)$$

ξ is an adjustable parameter depending on the nature of the bond. ξ was found for the C-N bond by use of Allinger's 1991 parameters with $k = 5.05 \text{ mdyn} \cdot \text{\AA}^{-1}$ for $l = 1.463 \text{ \AA}$, leading to $\xi = 0.746$. If we substitute, in eq. 15, l_{exp} by the expression given in eq. 11, Badger's rule for that bond is expressed by :

$$k_{theor} = \frac{1.86}{(0.768 - 0.240P_{exp})^3} \quad (16)$$

Figure 5 shows the curve corresponding to eq. 16 as well as the k_0 values calculated from eq. 15 with $\xi = 0.746$. The "best-fit" straight line equation was found to be :

$$k_0 = 3.56 + 6.927 \times P \quad (17)$$

(r coeff = 0.92141)

For the N-O bond we had incomplete references for the determination of ξ . Allinger's 1991 parameters gave $k_0 = 7.5 \text{ mdyn} \cdot \text{\AA}^{-1}$ and $l_0 = 1.22 \text{ \AA}$ but, as above mentioned, not TSLOPE and SSLOPE, so that those k_0 and l_0 values can be considered as median values for which the corresponding π bond order is not given. The MMX force field [12] gives $k_2 = 9.13 \text{ mdyn} \cdot \text{\AA}^{-1}$ with $l_2 = 1.22 \text{ \AA}$. TSLOPE and SSLOPE are given but are of no use in the present case because they have been determined in the VESCF method context instead of the PPP-SCF. As a consequence ξ was modified step by step within the range 0.550 – 0.592. For all the N-O bonds and each value of ξ , k_{theor} and k_{exp} were calculated :

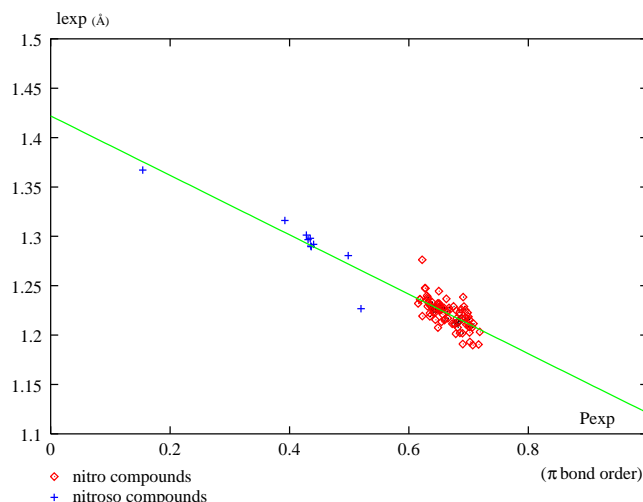


Figure 4. Plot of l_{exp} versus P_{exp} for the N - O bond.

$$k_{theor} = \frac{1.86}{(1.422 - 0.302P_{exp} - \xi)^3} \quad (18)$$

$$k_{exp} = \frac{1.86}{(l_{exp} - \xi)^3} \quad (19)$$

Each value of ξ gives a theoretical curve ($k_{theor} = f(P_{exp})$) and a cloud of dots ($k_{exp} = f(P_{exp})$) where P_{exp} is the value of P calculated from the experimental bond length. Five theoretical curves and the cloud of dots for $\xi = 0.570$ are represented in Figure 6. For each cloud of dots we also determined the best-fit straight line passing through and finally chose the value ξ which gives an extrapolated value of k_2 close to 9.13 and a k_{exp} close to 7.5 for a medium value of 0.67 for the π bond order of the nitro compounds. The best value of ξ found that way was 0.570 which led to $k_2 = 9.22$ and $k_{exp} = 6.78$ for $P_{exp,med} = 0.67$. The equation of the linear curve is thus :

$$k_0 = 1.832 + 7.388 \times P \quad (20)$$

(r.coef = 0.8809)

(Figure 7)

The question then was to find the "natural" bond lengths that would give calculated bond lengths l_{calc} closest to the experimental ones, i.e. to find for both bond types the best l_1 and TSLOPE values [see eq. 10]. Starting from the parameter values of eqs. 11 and 12, the calculated bond lengths were obtained by optimisation of the molecular geometries. In these calculations the atoms which do not belong to the NO_2 group were fixed in their crystalline positions in order to keep the intramolecular influence they have on the geometry of the C-NO₂ moiety in the crystalline conformation to

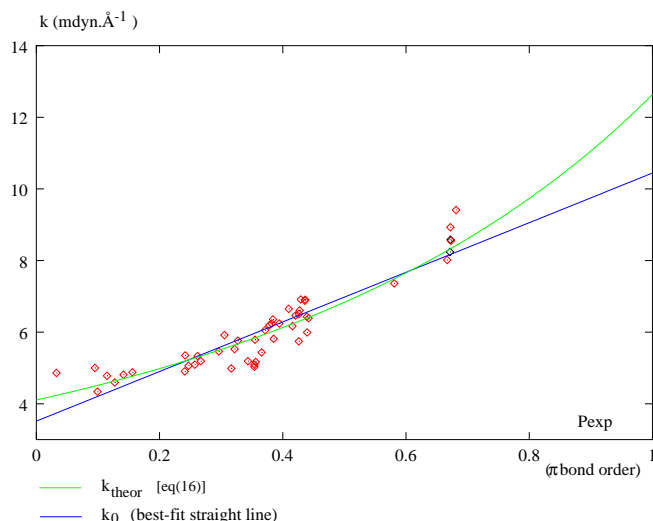


Figure 5. Plot of the C - N bond stretching force constant as a function of the π bond index (Nitro-plus nitroso-derivatives).

which the calculated conformation is compared. Refinements of the parameters for both bond types should be correlated because of the cross-conjugation of the N atom. In fact, as shown in Figure 8, the C-N and N-O π bond orders appear to be only slightly correlated and it seems that the C-N bond order is created mostly at the expenses of the free valence index of the N atom. The consequence is that we were able to refine separately the l_1 and TSLOPE parameters of each bond type. Refinements were made by trial and error and examination after each small change of the parameters of the plot of $l_{\text{calc}} = f(l_{\text{exp}})$. A linear correlation was found:

$$l_{\text{calc}}(l_1, \text{TSLOPE, surrounding}) = \alpha + \beta \times l_{\text{exp}} \quad (21)$$

and the further modifications of l_1 and TSLOPE were done in such a way that β tends to 1 and α to 0 with a minimal squared deviation.

The results are collected in Table 3 and illustrated by Figures 9 and 10. A better fit of the diagonal by the best-fit straight line would imply a fourth digit in the values of the parameters and would lead to an illusory precision.

Application of the parameters so determined (see Table 4) to the 17 reference molecules gave the results of Table 5 [available as supplementary material]. Comparison of the calculated C-N bond lengths with the experimental ones led to a mean unsigned difference of 0.021 Å (max : 0.054) and for the N-O bond lengths to 0.007 Å (max : 0.033).

Torsional parameters and out-of-plane bending

As mentioned above the torsional potential around a delocalized bond is a function of π bond order. In the MM2 force field it is the V2 coefficient in the expansion of the

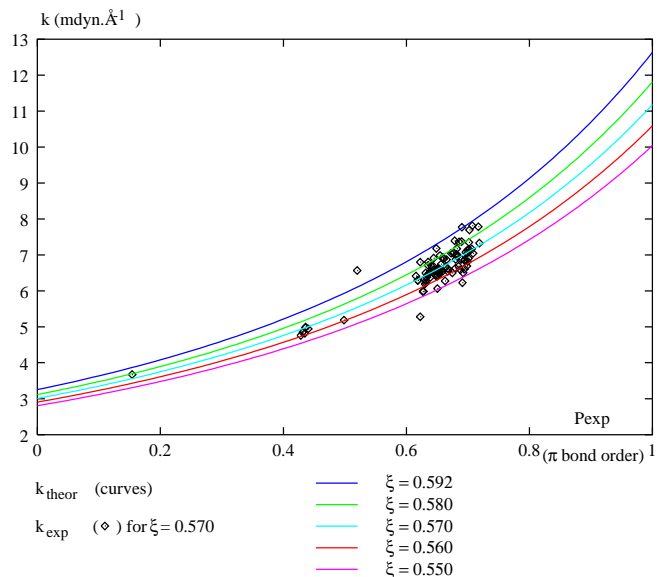


Figure 6. Plot of $k_{\text{theor}} = f(P_{\text{exp}})$ for the N - O bond for several values of ξ (see text).

torsional energy which is mostly a function of the π bond order of the hinge-bond of the concerned dihedrals [51]. In the last versions of MM2 [52] V2 is a function of the π bond order $P^{(0)}$ and the resonance integral $\beta^{(0)}$ of the hinge bond

$$V_2 = V_2(0) \times P^{(0)} \times \beta^{(0)} \quad (22)$$

The superscript (0) means that these quantities are calculated with the dihedral angle set to zero or 180°. In this case $V_2(0)$ is a function of the atom types. Because the type 46 N atom is now a π atom we had to adjust the $V_2(0)$ parameters for the dihedrals in which the (A)-C-N-(O) bond is involved. It was not necessary to modify the source code because as soon as the π atom is involved in the PPP-SCF calculation $P^{(0)}$ and $\beta^{(0)}$ for the concerned bonds are calculated and V2 modified accordingly. So by use of the 17 reference-molecules (Figure 2) containing all together 22 distinct nitro groups, we determined by trial and error three $V_2(0)$ constants (assuming $V_1 = V_3 = 0.0$) corresponding to three different types of dihedrals. The determination was based on 9 molecules (AMNIFL, BENCLN02, CELBAW, CEPISZ, JIZJIL, MNIMET, VETWAS, YUFGOV, YUFGUB) by the following procedure. Assuming for the three types of dihedrals an identical $V_2(0)$, the cumulative error was calculated for a set of values, ranging from 0 to 15. This cumulative error was the sum of the differences $|\Omega_{\text{calc}} - \Omega_{\text{exp}}|$ for a dihedral involving the NO_2 group in the molecules. The plot of the cumulative error against $V_2(0)$ (see Figure 11) revealed a minimum for $V_2(0) = 4.0$. Further full optimization of these molecules, using the newly found parameter, did not reveal any anomaly and the parameter was retained.

New parameters are collected in Table 4 and results concerning the reference molecules in Table 6.

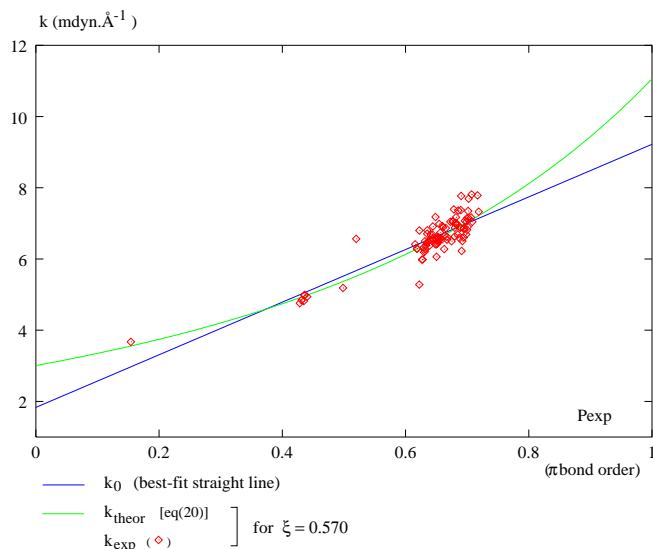


Figure 7. Plot of the best-fit straight line $k_o = f(P)$ corresponding to the values obtained by eq (10) with $\xi = 0.570$ for the experimental N - O bond lengths.

We explain the largest discrepancies, which occur for YUFGUB, by the following considerations. It is well known that dihedrals, among internal coordinates, are the most sensitive to intermolecular forces. As soon as one compares calculated dihedrals in an isolated molecule "in vacuum" with experimental dihedrals measured in the solid state, there is the possibility of observing large differences. The compound labeled YUFGUB, for which there is only one optimized calculated conformation, exhibits, 4 distinct geometries in the unit cell, which mostly differ in their dihedral angles. So the discrepancies were to be expected. Otherwise the results are very good either when the dihedrals are close to 0° or 180° or when the NO_2 group is tilted (Table 6 - VETWAS).

In relation to this, it is important to notice that the torsional angles, as they are defined, are functions not only of the tilt angle of the NO_2 group but also of the N atom pyramidalisation. The out of plane bonding energy is not corrected by the π bond order. It was found that the out of plane bonding constants for the type 46 N atom were too small and had to be increased as shown in Table 4.

Bending and other parameters

Bending force constants and "natural" values for the angles around the type 46 N atom were already given in the MM2(91) force field [9]. Most of them were kept unchanged. We nevertheless found it more accurate to increase the 7-46-7 force constant from 0.600 to 0.800 and decrease the corresponding θ_0 value from 128.6 to 124.6° (Table 4). Table 7 shows the good agreement of the calculated angles with the experimental ones. For the 22 distinct NO_2 groups of the 17 reference molecules the mean unsigned deviations for the O-N-O

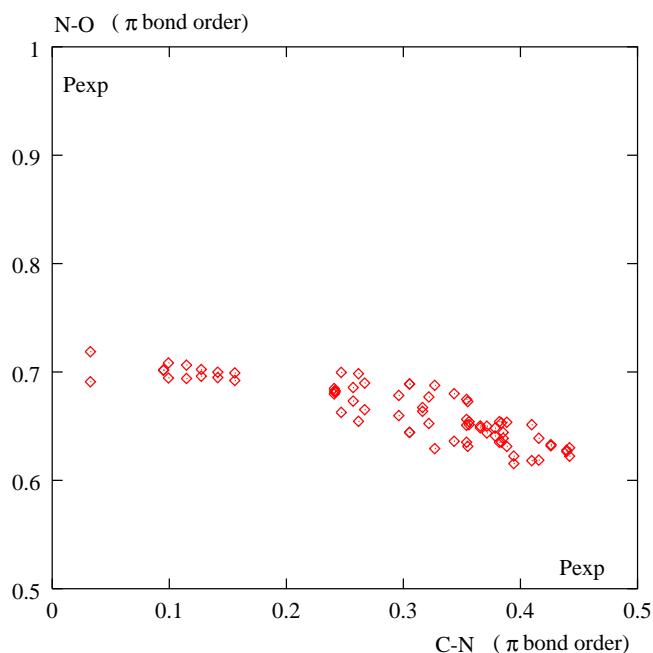


Figure 8. π bond orders of the N - O bonds versus the π bond order of the adjacent C - N bond (calculated from the experimental bond lengths) for the 32 reference molecules.

and O-N-C angles are : 0.98° and 0.73° respectively, the maximum observed being 3.4° .

Van der Waals parameters for the type 46 Nitrogen atom were present in the MM2(91) force field and were not modified.

Heats of formation were not calculated, the lack of experimental data preventing significant comparisons.

Discussion and conclusion

Though it is more satisfying, conceptually, to introduce the nitro group into the π system when it is conjugate, it is nonetheless of importance to verify if such a modification brings improvements in the results. To this end we compared results obtained to the present parameters with those obtained with the resident parameters of MM2(91), for the 17 reference molecules series. The choice is of course limited and arbitrary, but the selected molecules are rather varied. Tables 8, 9 and 10 collect the values of the unsigned differences between the experimental and calculated bond lengths, angles and dihedral angles involving the nitro group.

Generally speaking one can observe a slight improvement in lengths, consistency in angles and an important improvement in dihedral angles. In most cases the introduction of the correction factor to the π dipole moment in conjunction with the necessary re-estimation of the σ bond dipole moments did not damage the calculated molecular dipole moment and even substantially improved it.

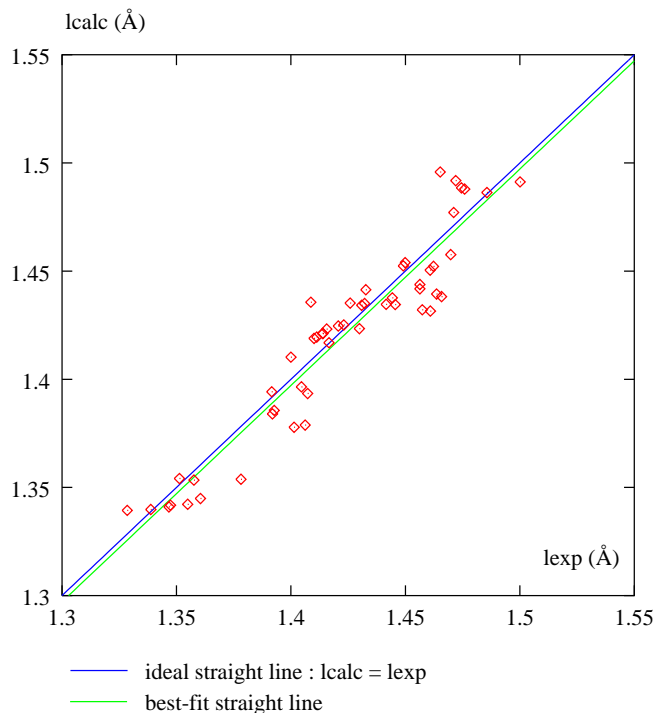


Figure 9. Correlation of the calculated C_{sp^2} - NO_2 bond lengths (MM2 - This work) with the experimental values (X-ray) - 52 values for 32 molecules.

The main effort in parametrization was carried out with respect to the C-N and N-O bond lengths parameters and, in that area, global results could appear somewhat deceiving. Our results require closer examination. Concerning the N-O bond, if we limit the discussion to the nitro compounds "stricto sensu", the π index of that bond has a very narrow variation domain (0.6 to 0.73) as shown in Figure 4.

Appropriate but constant values of the "natural" bond length and force constant were already rather good approximations, so that a spectacular improvement of the results was not to be expected-although a tendency for the experimental bond length to vary with the π bond index is visible. The addition of some nitroso compounds - for which the N atom remains sp^2 - in return expands the variation domain of the π index and linear expressions of the N-O bond parameters should work for compounds including a N-O bond of much smaller π index without damage to the nitro species.

As for the C-N bond, the π index range is much larger : 0 to 0.7 (0 to 0.45 if we omit the nitroso compounds). On Figure 3 three classes of compounds have been distinguished. The nitro derivatives which contain a five membered ring occupy, with a rather small dispersion, the 0.25 - 0.45 domain whereas the nitro derivatives containing a six membered ring show a more complex distribution. They occupy a larger π range (0 to 0.45) and the dispersion relative to the correlation straight line is larger. There are roughly two distinct regions. From 0 to 0.2 for the π index, most of the representative dots are below the line, while from 0.2 to 0.45 they all

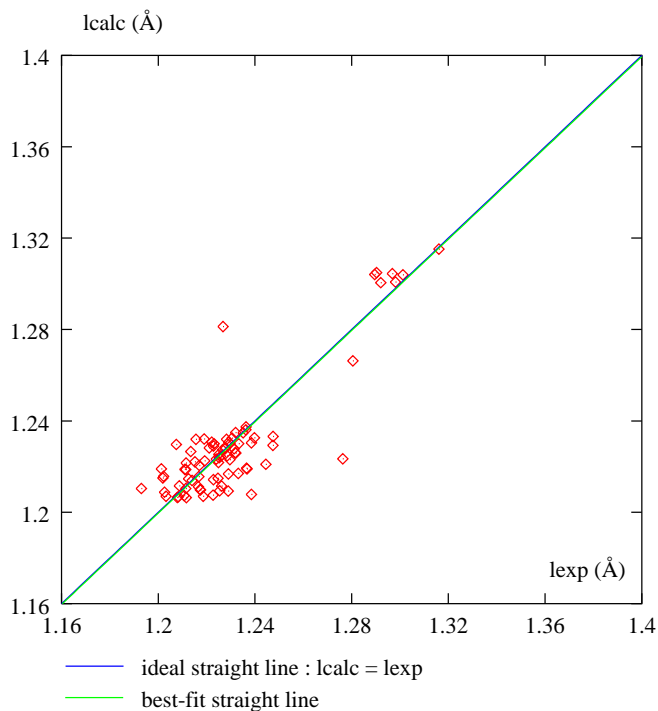


Figure 10. Correlation of the calculated N_{sp^2} - O bond lengths (MM2 - This work) with the experimental values (X-ray) - 82 values for 32 molecules.

are above. Were the study limited to the sole six membered ring derivatives, we could expect a correlation straight line with a lower slope, even horizontal, at least in the 0. - 0.4 domain. Indeed, if we consider the horizontal "ribbon" defined by 1.463 ± 0.015 Å (1.463 Å is the natural C- NO_2 bond length in MM2(91)), 12 among the 17 compounds are included. A "ribbon" of the same width along the correlation straight line includes only 9 compounds of that type so that better results were not to be expected for this type of derivative when the π index is taken into account. This is reflected by the comparison in Table 8. In return, the "MM2(91) ribbon" encloses only 4 five membered ring derivatives among 19 and no nitroso compound whereas our "correlation ribbon" contains 18 among the 19 five membered ring derivatives and also 11 among the 16 nitroso ones. This explains the better results for five membered ring derivatives, which was one of our goals, and the possible extension to the nitroso derivatives. It is also important to notice that the MM2(91) parameters for the C- NO_2 bond can be rather bad when the conjugation is strong (π bond index : 0.4 to 0.45) even for the 6 membered ring derivatives.

Thus the conclusion of the present study is that the introduction in to the π system of the nitro group, when it is conjugated, is conceptually and practically more satisfying. The proposed parameters improve the angles and dihedral angles. The introduction of a correction factor to the π dipole moment also improves calculated molecular dipole moments, provided that some σ bond dipole moments are reevaluated.

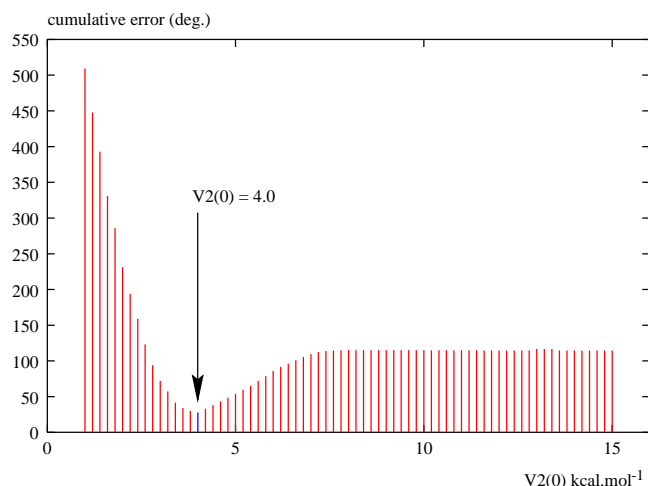


Figure 11. Determination of the $V_2(0)$ torsional constant around the C - N bond. Plot of the cumulative error for different values of $V_2(0)$ (see text).

Globally the bond lengths are also improved even if a lesser precision is evident in some cases for C-N bond, in six-membered ring derivatives. Nevertheless for that bond, the correlation of the "natural" length with the π index permits calculation for a wider range of π indices. Because the present parameters were determined on molecules in the solid state only, minor further refinements are to be expected.

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Table 1. Experimental and calculated dipole moments for 11 reference molecules.

Refcode [a]	μ_{exp} (D)	Ref.	$\mu_{\sigma}^{\text{MM2}}$ (D) [b]	μ_{π}^{MM2} (D) [b]	$\mu_{\text{tot}}^{\text{MM2}}$ (D) [c]	$\mu_{\text{tot-opt}}^{\text{MM2}}$ (D) [c]	$\mu_{\text{tot-opt}}^{\text{MM2(91)}}$ (D) [d]
nitro benzene	4.00	[9a]	1.63	2.34	4.00	4.23	
nitro ethylene	3.70	[9a]	1.62	1.98	3.56	3.77	
BENCLN02	3.00 - 3.31	[15], [47]	1.59	2.15	3.22	3.25	3.56
CLNIBZ01	3.44	[20], [47]	1.63	2.31	3.47	3.68	3.45
DNBENZ01	3.88	[24], [47]	1.67	1.95	3.62	3.92	3.93
DNITPY	1.11	[25], [47]	0.21	1.35	1.35	1.57	1.55
FUXNAN	6.66 - 6.82	[28], [47]	2.50	3.74	6.23	6.28	4.84
MNIANL10	4.68 - 5.04	[33], [47]	2.19	2.94	5.12	5.11	4.72
	4.90 [e]						
NANILI	6.14 - 6.37	[35], [47]	2.45	3.61	6.07	6.19	5.23
	6.29 [e]						
ONITAN	4.04 - 4.38	[36], [47]	1.52	2.70	4.22	4.32	3.59
ZZZFYW01	6.00	[41], [47]	2.76	3.29	6.05	6.16	6.29

[a] Upper case letters correspond to CSDS refcodes.

[b] Calculated for the crystalline geometry.

[c] After full optimization by MM2 with correction factor.

[d] After full optimization by MM2(91)

[e] Reported mean value (see ref).

Table 2a. Selected molecules for the determination of the stretching parameters, the refcode is the CSDS one (For formulas see Figure 2).

Refcode	C - N bond [a]			N - O bonds [a]		
	l_{exp} (Å)	k_{exp} (mdyn/Å)	P_{exp}	l_{exp} (Å)	k_{exp} (mdyn/Å)	P_{exp}
AMNIFL	1.4574	5.1662	0.3561	1.2314	6.4287	0.6515
				1.2277	6.5378	0.6542
AMNPHA	1.4609	5.0907	0.3539	1.2277	6.5378	0.6508
				1.2211	6.7386	0.6563
BAKLII	1.4087	6.3909	0.4419	1.2763	5.2789	0.6223
				1.2398	6.1898	0.6301
	1.4231	5.9918	0.4395	1.2474	5.9838	0.6278
				1.2475	5.9812	0.6266
	1.4623	5.0609	0.2469	1.2367	6.2766	0.6627
				1.2087	7.1388	0.6996
BENCLNO2	1.4698	4.9052	0.2408	1.2247	6.6281	0.6797
				1.2228	6.6861	0.6847
	1.4658	4.9875	0.3163	1.2249	6.6220	0.6672
				1.2240	6.6494	0.6637
BEWYOR	1.4636	5.0335	0.3539	1.2290	6.4992	0.6747
				1.2305	6.4550	0.6352
	1.4327	5.7440	0.4260	1.2365	6.2822	0.6318
				1.2331	6.3794	0.6330
	1.4563	5.1902	0.3433	1.2168	6.8739	0.6800
				1.2296	6.4814	0.6361
BOLPEX	1.4720	4.8608	0.0326	1.2385	6.2260	0.6910
				1.2032	7.3264	0.7187
	1.4711	4.8789	0.1559	1.2289	6.5021	0.6922
				1.2114	7.0489	0.6992
CELBAW	1.4320	5.7565	0.3267	1.2351	6.3220	0.6293
				1.2262	6.5827	0.6876
CEPSIZ	1.4113	6.3163	0.3883	1.2285	6.5140	0.6536
				1.2291	6.4962	0.6313
YUFGUV	1.4140	6.2400	0.3943	1.2192	6.7979	0.6224
				1.2320	6.4112	0.6155
YUFGOV	1.4456	5.4321	0.3656	1.2445	6.0613	0.6502
				1.2075	7.1791	0.6486
DACZIQ	1.4299	5.8148	0.3852	1.2156	6.9123	0.6443
				1.2333	6.3736	0.6388
DAVXAZ	1.4745	4.8109	0.1414	1.2186	6.8168	0.6998
				1.2173	6.8580	0.6949
DAVXED	1.4652	4.9999	0.095	1.2083	7.1522	0.7019
				1.2026	7.3473	0.7015
DAVXIH	1.4759	4.7813	0.1147	1.2175	6.8516	0.6940
				1.2079	7.1656	0.7063
DAVXON	1.4856	4.5957	0.1273	1.1930	7.6921	0.7023
				1.2107	7.0721	0.6961
DAVXUT	1.5001	4.3374	0.0992	1.2254	6.6068	0.6944
				1.2116	7.0424	0.7083
DIMYON10	1.4416	5.5263	0.3217	1.2296	6.4814	0.6525
				1.2110	7.0622	0.6770
	1.4309	5.7894	0.3549	1.2115	7.0457	0.6727
				1.2385	6.2260	0.6314

[a] The subscript "exp" means either "observed" or deduced from experimental bond length.

[b] Compound not used for that bond

Table 2b. Selected molecules for the determination of the stretching parameters.

Refcode	C - N bond [a]			N - O bonds [a]		
	l_{exp} (Å)	k_{exp} (mdyn/Å)	P_{exp}	l_{exp} (Å)	k_{exp} (mdyn/Å)	P_{exp}
FABHUL		[b]		1.2276	0.6673	6.5408
				1.1905	0.7168	7.7855
				1.2274	0.6591	6.5467
				1.1909	0.6902	7.7705
				1.1898	0.7071	7.8119
				1.2159	0.7010	6.9018
				1.2077	0.6819	7.1724
				1.2162	0.6605	6.8931
FUJTUZ	1.4563	5.1902	0.2669	1.2019	7.3717	0.6897
	1.4443	5.4624	0.2961	1.2170	6.8675	0.6653
				1.2013	7.3927	0.6784
				1.2152	6.9252	0.6597
HNFMNO	1.4156	6.1954	0.3783	1.2231	6.6769	0.6410
				1.2319	6.4141	0.6482
HNIM0Z	1.4000	6.6494	0.4096	1.2250	6.6190	0.6514
				1.2362	6.2907	0.6182
JIZJIL	1.4100	6.3534	0.3837	1.2250	6.6129	0.6530
				1.2190	6.8042	0.6353
MNFURP	1.4207	6.0560	0.3713	1.2228	6.6861	0.6437
				1.2321	6.4083	0.6500
MNIMET	1.4138	6.2400	0.3820	1.2258	6.5948	0.6542
				1.2221	6.7077	0.6351
SEGFAL	1.4608	5.0928	0.2571	1.2022	7.3612	0.6856
				1.2114	7.0490	0.6732
	1.4499	5.3331	0.2616	1.2227	6.6892	0.6984
				1.2134	6.9835	0.6545
VETWAS	1.4259	5.9180	0.3052	1.2266	6.8803	0.6889
				1.2266	6.5707	0.6443
	1.4491	5.3513	0.2415	1.2140	6.9640	0.6826
				1.2125	7.0128	0.6815
	1.4259	5.9180	0.3052	1.2266	6.8803	0.6889
				1.2266	6.5707	0.6443
	1.4491	5.3513	0.2415	1.2140	6.9640	0.6826
				1.2125	7.0128	0.6815
YAPMEH	1.4166	6.1677	0.4157	1.2282	6.5229	0.6388
				1.2363	6.2879	0.6187
NITROSO COMPOUNDS						
AMHPYR		[b]		1.3671	3.6726	0.1542
CEYSUU	1.3513	8.3869	0.5845	1.3161	4.4784	0.3922
	1.3576	8.1304	0.5827			
HAHCIC	1.4073	6.4316	0.4390	1.2805	5.1857	0.4985
	1.3782	7.3612	0.5808	1.2268	6.5647	0.5199
HPZTDX	1.3474	8.5511	0.6729	1.3012	4.7578	0.4283
	1.3927	6.8771	0.4358			
	1.3467	8.5810	0.6722	1.2968	4.8447	0.4312
	1.3918	6.9059	0.4362			
JKJAO	1.4046	6.5110	0.4263	1.2903	4.9771	0.4358
	1.3605	8.0158	0.6668			
	1.3388	8.9287	0.6720	1.2920	4.9420	0.4403
	1.4014	6.6068	0.4273			
JKJAO	1.3916	6.9123	0.4292	1.2895	4.9937	0.4363
2d conformation	1.3549	8.2390	0.6714			
in the unit cell	1.3285	9.4108	0.6812	1.2981	4.8188	0.4349
	1.4062	6.4638	0.4206			

[a] The subscript "exp" means either "observed" or deduced from experimental bond length.

[b] Compound not used for that bond

Table 3a. Comparison of the values of the calculated bond lengths (after complete optimization of the geometry) with the experimental (X-ray) ones for 32 reference molecules.

Refcode	C - N Bond			N - O bonds		
	$l_{\text{exp}} (\text{\AA})$	$l_{\text{cal}} (\text{\AA})$	$l_{\text{cal}} - l_{\text{exp}} (\text{\AA})$	$l_{\text{exp}} (\text{\AA})$	$l_{\text{cal}} (\text{\AA})$	$l_{\text{cal}} - l_{\text{exp}} (\text{\AA})$
AMNIFL	1.4574	1.4321	-0.0253	1.2314	1.2278	-0.0036
				1.2277	1.2278	-0.0001
AMNPHA	1.4609	1.4315	-0.0294	1.2277	1.2284	0.0007
				1.2211	1.2282	0.0071
BAKLII	1.4087	1.4356	0.0269	1.2763	1.2234	-0.0529
				1.2398	1.2326	-0.0072
	1.4231	1.4251	-0.002	1.2474	1.2293	-0.0181
				1.2475	1.2332	-0.0143
	1.4623	1.4522	-0.0101	1.2367	1.2190	-0.0177
				1.2087	1.2116	0.0029
BENCLNO2	1.4698	1.4576	-0.0122	1.2247	1.2149	-0.0098
				1.2228	1.2143	-0.0085
	1.4658	1.4382	-0.0276	1.2249	1.2218	-0.0031
				1.2240	1.2233	-0.0007
BEWYOR	1.4636	1.4394	-0.0242	1.2290	1.2168	-0.0122
				1.2305	1.2325	0.0020
	1.4327	1.4414	0.0087	1.2365	1.2193	-0.0172
				1.2331	1.2170	-0.0161
	1.4563	1.4418	-0.0145	1.2168	1.2156	-0.0012
				1.2296	1.2230	-0.0066
BOLPEX	1.4720	1.4918	0.0198	1.2385	1.2304	-0.0081
				1.2032	1.2070	0.0038
	1.4711	1.4771	0.006	1.2289	1.2093	-0.0196
				1.2114	1.2187	0.0073
CELBAW	1.4322	1.4350	0.0028	1.2351	1.2348	-0.0003
				1.2262	1.2115	-0.0147
CEPSIZ	1.4113	1.4195	0.0082	1.2285	1.2247	-0.0038
				1.2291	1.2307	0.0016
YUFGUV	1.4140	1.4211	0.0071	1.2192	1.2225	0.0033
				1.2320	1.2349	0.0029
YUFGOV	1.4456	1.4345	-0.0111	1.2445	1.2210	-0.0235
				1.2075	1.2297	0.0222
DACZIQ	1.4299	1.4234	-0.0065	1.2156	1.2319	0.0163
				1.2333	1.2300	-0.0033
DAVXAZ	1.4745	1.4885	0.014	1.2186	1.2070	-0.0116
				1.2173	1.2100	-0.0073
DAVXED	1.4652	1.4958	0.0306	1.2083	1.2068	-0.0015
				1.2026	1.2088	0.0062
DAVXIH	1.4759	1.4879	0.012	1.2175	1.2098	-0.0077
				1.2079	1.2065	-0.0014
DAVXON	1.4856	1.4863	-0.0007	1.1930	1.2104	0.0167
				1.2107	1.2073	-0.0034
DAVXUT	1.5001	1.4912	-0.0089	1.2254	1.2094	-0.0160
				1.2116	1.2064	-0.0052
DIMYON10	1.4416	1.4342	0.033	1.2296	1.2230	-0.0066
				1.2110	1.2188	0.0078
	1.4309	1.4346	-0.007	1.2115	1.2216	0.0101
				1.2385	1.2304	-0.0081
FUJTUZ	1.4563	1.4438	-0.0125	1.2019	1.2150	0.0131
				1.2170	1.2205	0.0035
	1.4443	1.4376	-0.0067	1.2013	1.2190	0.0177
				1.2152	1.2221	0.0069

Table 3b. Comparison of the values of the calculated bond lengths (after complete optimization of the geometry) with the experimental (X-ray) ones for 32 reference molecules.

Refcode	C - N Bond			N - O bonds					
	l_{exp} (Å)	l_{cal} (Å)	$l_{\text{cal}}-l_{\text{exp}}$ (Å)	l_{exp} (Å)	l_{cal} (Å)	$l_{\text{cal}}-l_{\text{exp}}$ (Å)			
HNFMNO	1.4156	1.4232	0.0076	1.2231	1.2300	0.0069			
				1.2319	1.2261	-0.0058			
HNIMTZ	1.4000	1.4102	0.0102	1.2250	1.2253	0.0003			
				1.2362	1.2361	-0.0001			
JIZJIL	1.4100	1.4189	0.0680	1.2250	1.2253	0.0003			
				1.2190	1.2321	0.0131			
MNFURP	1.4207	1.4246	0.0039	1.2228	1.2290	0.0062			
				1.2321	1.2259	-0.0062			
MNIMET	1.4138	1.4212	0.0074	1.2258	1.2244	-0.0014			
				1.2221	1.2307	0.0086			
SEGFAL	1.4608	1.4504	-0.0104	1.2022	1.2158	0.0136			
				1.2114	1.2187	0.0073			
				1.4499	1.4539	0.0040	1.2227	1.2075	-0.0152
VETWAS	1.4259	1.4352	0.0093	1.2134	1.2266	0.0132			
				1.2166	1.2112	-0.0054			
				1.2266	1.2273	0.0007			
				1.4491	1.4524	0.0033	1.2140	1.2139	-0.0001
				1.2125	1.2147	0.0022			
				1.4259	1.4352	0.0093	1.2166	1.2112	-0.0054
YAPMEH	1.4166	1.4169	0.0003	1.2266	1.2273	0.0007			
				1.2140	1.2139	-0.0001			
				1.2125	1.2147	0.0022			
				1.2166	1.2112	-0.0054			
				1.2266	1.2273	0.0007			
				1.4491	1.4524	0.0033	1.2140	1.2139	-0.0001
				1.2125	1.2147	0.0022			
				1.2282	1.2319	0.0037			
				1.2363	1.2374	0.0011			
NITROSO COMPOUNDS									
AMHPYR				1.3671	1.4030	0.0359			
CEYSUU	1.3513	1.3541	0.0028	1.3161	1.3152	-0.0009			
				1.3576	1.3534	-0.0042			
HAHCIC	1.4073	1.3934	-0.0139	1.2805	1.2663	-0.0142			
				1.3782	1.3538	-0.0244			
HPZTDX	1.3474	1.3418	-0.0056	1.2268	1.2813	0.0545			
				1.3012	1.3039	0.0027			
				1.3927	1.3856	-0.0071			
				1.3467	1.3410	-0.0057			
JIKJAO	1.3919	1.3840	-0.0079	1.2968	1.3045	0.0077			
				1.4046	1.3965	-0.0081			
				1.3605	1.3449	-0.0156			
				1.3388	1.3398	0.0010			
				1.4014	1.3778	-0.0236			
JIKJAO	1.3916	1.3942	0.0026	1.2895	1.3041	0.0146			
2d conformer in the unit cell	1.3549	1.3422	-0.0127						
	1.3285	1.3394	0.0109	1.2981	1.3008	0.0027			
	1.4062	1.3788	-0.0274						





Table 4. Parameters for the conjugated nitro group in the MM2 force field. The N atom (type 46) is involved in the PPP-SCF calculations.

Van der Waals parameters							
Atom types			ϵ_0	r_0	Origin		
46			0.055	1.820	[9]		
σ -bond dipole moments							
Atom types			μ	Origin			
2	46		0.625	This work			
7	46		-1.119	This work			
Stretching parameters							
Atom types			k2	l2	sslope	tslope	Origin
2	46		10.443	1.278	6.927	0.218	This work
7	46		9.220	1.106	7.388	0.342	This work
Bending parameters							
Atom types			k	Θ_0	Origin		
37	2	46	1.000	120.0	This work		
2	46	7	0.800	115.0	[9]		
40	2	46	2.000	120.0	This work		
7	46	7	0.800	124.6	This work		
Out of plane bending parameters							
Atom types			k_{op}	Origin			
0	46	2	0.80	This work			
0	46	7	0.80	This work			
0	2	46	0.80	This work			
Torsional Parameters							
Atom types			V1	V2	V3	Origin	
2	2	46	7	0.0	4.0	0.0	This work
40	2	46	7	0.0	4.0	0.0	This work
37	2	46	7	0.0	4.0	0.0	This work

Table 5. Calculated and Experimental (X-ray) bond lengths involving the NO₂ group (22) of the 17 reference molecules (for formulas see Figure 2).

Molecules Refcode	C - N (Å)			N - O (Å)		
	exp.	calc.	diff.	exp.	calc.	diff.
AMNIFL	1.4574	1.4216	-0.0358	1.2314	1.2293	-0.0021
				1.2277	1.2292	0.0015
BENCLNO2	1.4698	1.4525	-0.0173	1.2247	1.2157	-0.0019
				1.2228	1.2153	0.0008
				1.2249	1.2230	0.0009
				1.2240	1.2248	-0.0132
CELBAW	1.4322	1.4293	-0.0029	1.2351	1.2360	0.0009
CEPSIZ	1.4113	1.4152	0.0039	1.2262	1.2130	-0.0132
				1.2285	1.2258	-0.0027
CLNIB01	1.4815	1.4274	-0.0541	1.2291	1.2320	0.0029
				1.2218	1.2261	0.0043
DNBENZ01	1.4833	1.4330	-0.0503	1.2250	1.2263	0.0013
				1.2440	1.2252	-0.0188
				1.1969	1.2220	0.0251
				1.2138	1.2222	0.0084
DNITPY	1.4679	1.4303	-0.0376	1.2265	1.2249	-0.0016
				1.2198	1.2254	0.0056
				1.2119	1.2228	0.0109
				1.2073	1.2229	0.0156
FUXNAN	1.4349	1.4179	-0.0170	1.2145	1.2254	0.0109
				1.2262	1.2306	0.0044
				1.2406	1.2309	-0.0097
JIZJIL	1.4101	1.4145	0.0044	1.2252	1.2255	0.0003
MNIANL10	1.4082	1.4105	0.0023	1.2190	1.2333	0.0143
				1.2423	1.2269	-0.0154
MNIMET	1.4138	1.4155	0.0017	1.2102	1.2258	0.0156
				1.2258	1.2257	-0.0001
NANILI	1.4539	1.4178	-0.0361	1.2221	1.2323	0.0102
				1.2274	1.2310	0.0036
ONITAN	1.4285	1.4137	-0.0148	1.2289	1.2310	0.0021
				1.2478	1.2387	-0.0091
VETWAS	1.4259	1.4327	0.0068	1.2228	1.2282	0.0054
				1.2140	1.2156	0.0016
				1.2125	1.2139	0.0014
				1.2166	1.2105	-0.0061
YUFGOV a	1.4140	1.4172	0.0032	1.2266	1.2293	0.0027
				1.2192	1.2245	0.0053
				1.2320	1.2349	0.0029
				1.2122	1.2246	0.0124
YUFGUB a	1.4239	1.4170	-0.0069	1.2307	1.2351	0.0047
				1.2266	1.2238	-0.0008
				1.2061	1.2334	0.0273
				1.2445	1.2237	-0.0208
b	1.4457	1.4199	-0.0258	1.2074	1.2333	0.0259
				1.2014	1.2330	0.0316
c	1.4167	1.4203	0.0036	1.2264	1.2236	-0.0028
				1.1748	1.2259	0.0511
d	1.4145	1.4300	0.0155	1.1895	1.2226	0.0331
				1.2222	1.2150	-0.0072
				1.2223	1.2152	-0.0078
				1.2226	1.2150	-0.0074
ZZZFYW01	1.4723	1.4516	-0.0207	1.2212	1.2150	-0.0062
	1.4697	1.4515	-0.0182			
Unsigned mean value			0.0198	0.0095		
Maximum observed difference			0.0541	0.0511		

Table 6. Calculated and Experimental (X-ray) dihedral angles involving the NO_2 group (22) for the 17 reference molecules (for formulas see Figure 2)

Molecules		$\Omega_{\text{calc}} - \Omega_{\text{exp}}$ Dihedral Type				Unsigned Mean value [a]
Refcode						
	(°)	(°)	(°)	(°)		(°)
AMNIFL	6.32	6.46	4.84	4.78		5.59
BENCLN02	-1.44	0.84	1.27	0.67		1.06
	8.28	10.23	13.5	11.56		10.65
CELBAW	0.73	-0.17	0.47	-0.03		0.35
CEPSIZ	3.24	4.06	6.17	5.35		4.70
CLNIB01	-2.58	-2.85	-3.35	-3.09		2.92
DNBENZ01	-13.29	-10.85	-8.01	-10.45		10.65
	16.46	9.13	21.20	13.86		15.16
DNITPY	-7.51	-7.15	-6.62	-6.98		7.07
	1.59	1.54	0.58	0.631		1.09
FUXNAN	-2.45	-3.03	-1.39	-0.804		1.92
JIZJIL	0.31	0.35	0.45	0.34		0.36
MNIANL10	1.96	6.29	-2.04	-1.93		3.06
MNIMET	3.24	5.07	6.11	6.23		4.70
NANILI	1.98	1.23	-1.39	2.59		1.91
ONITAN	-4.18	-4.03	-1.79	-1.94		2.99
VETWAS	-0.06	1.01	-1.22	-2.29		1.15
	-1.27	-2.14	-0.30	1.17		1.22
YUFGOV	a	0.00	2.80	0.58	2.23	1.40
	b	1.41	1.68	1.65	1.43	1.54
unsigned mean value for the two conformers						1.47
YUFGUB	a	10.07	10.01	8.61	8.68	9.34
	b	-4.93	-1.10	-5.92	9.75	5.42
	c	15.63	19.85	12.01	13.81	13.83
	d	2.72	1.43	2.50	3.80	2.61
unsigned mean value for the four conformers						7.8
ZZZFYW01		2.82	0.270	-0.45	2.09	1.11
		3.30	-0.46	-0.53	3.23	1.88
Unsigned mean value [b]						4.05

[a] unsigned mean value of the differences for each distinct NO_2 group.

[b] unsigned mean value of the differences for the 22 distinct NO_2 groups.

Table 7. Comparison of the calculated and experimental (X-ray) angles around the N atom of the nitro groups of the reference molecules (for formulas see Figure 2).

Molecules Refcode	$\theta_{\text{calc}} - \theta_{\text{exp}} (^{\circ})$			Pyramidalisation ($^{\circ}$) [a]
	O-N-O	O-N-C	O-N-C	
AMNIFL	1.07	-0.43	-0.66	0.01
BENCLN02	-0.43	0.33	0.08	0.02
	-0.75	1.02	-0.24	-0.09
CELBAW	0.34	0.00	-0.33	0.01
CEPSIZ	1.18	-0.89	-0.29	0.00
CLNIBZ01	-0.48	0.49	-0.01	0.00
DNBENZ01	-1.14	-0.21	1.41	0.06
	-2.73	1.92	1.27	0.43
DNITPY	-0.74	0.92	-0.17	0.01
	-0.54	0.17	0.49	-0.22
FUXNAN	-0.07	-1.99	0.09	-1.97
JIZJIL	1.59	-0.60	-0.98	-0.01
MNIANL10	3.37	-1.40	-1.84	0.13
MNIMET	1.01	-0.29	-0.72	0.00
NANILI	0.46	0.42	-0.86	0.02
ONITAN	2.39	0.78	-3.13	0.04
VETWAS	0.41	-0.34	-0.10	0.37
	0.49	0.23	-0.75	-0.04
YUFGOV a	1.23	1.71	1.3	0.01
b	1.20	-0.38	-0.82	0.01
YUFGUB a	-1.26	1.22	0.04	0.00
b	-0.09	0.98	-0.78	0.11
c	-0.32	3.36	3.02	0.02
d	-0.38	-0.88	-0.73	0.01
ZZZFYW01	-0.46	0.41	0.06	0.01
	0.07	-0.46	0.42	0.03

[a] Difference from 360° of the sum of the angles around N.

Table 8. Comparison of the calculated differences in bond lengths (this work / MM2(91)).

$ l_{\text{calc}} - l_{\text{exp}} \cdot 10^4 (\text{\AA})$				
Molecules	This work	MM2 91	This work	MM2 91
Refcode	CN	CN	NO [a]	NO [a]
AMNIFL	358	194	18	84
BENCLNO2	173	73	18	25
	358	135	83	31
CELBAW	29	472	71	91
CEPSIZ	39	644	28	81
CLNIB01	541	39	28	20
DNBENZ01	503	41	220	235
	529	69	50	63
DNITPY	376	110	83	55
	376	111	133	104
FUXNAN	170	416	71	119
JIZJIL	44	655	73	28
MNIANL10	23	375	155	161
MNIMET	17	625	52	33
NANILI	361	229	29	67
ONITAN	148	486	73	141
VETWAS	68	506	15	77
	5	311	44	41
YUFGOV	a 32	666	41	59
	b 69	568	86	87
Mean value	51	617	64	73
YUFGUB	a 102	720	151	107
	b 258	439	234	179
	c 36	648	172	130
	d 155	661	421	395
Mean value	151	617	245	203
ZZZFYW01	207	54	75	4
	182	80	68	10
Mean values				
(5 membered rings)	51	556	74	78
(6 membered rings)	307	172	79	80
Global Mean value	216	312	77	79
Max Value	541	655	245	235

[a] As there are 2 N - O bonds for one C - N bond only the mean values of the 2 N - O bond lengths are reported.

Table 9. Comparison of the calculated differences in bond angles (this work / MM2(91)).

$ \theta_{\text{calc}} - \theta_{\text{exp}} (^{\circ})$				
Molecules Refcode	This work ONO	MM2 91 ONO	This work CNO [a]	MM2 91 CNO [a]
AMNIFL	1.07	3.82	0.55	1.91
BENCLNO2	0.43	2.27	0.21	1.12
	0.75	2.79	0.63	1.63
CELBAW	0.34	2.92	0.17	1.46
CEPSIZ	1.18	4.09	0.59	2.60
CLNIB01	0.48	2.32	0.25	1.16
DNBENZ01	1.14	1.82	0.81	0.89
	2.73	0.23	1.60	0.42
DNITPY	0.74	2.47	0.55	1.24
	0.54	2.28	0.33	1.14
FUXNAN	0.07	4.74	1.04	2.37
JIZJIL	1.59	4.35	0.79	2.18
MNIANL10	3.37	6.17	1.62	3.03
MNIMET	1.01	3.78	0.51	1.91
NANILI	0.46	3.28	0.64	1.64
ONITAN	2.39	6.11	1.96	3.07
VETWAS	0.41	3.70	0.22	2.42
	0.49	3.72	0.49	2.34
YUFGOV a	1.23	4.64	1.51	2.34
b	1.20	4.03	0.60	2.03
Mean value	1.22	4.34	1.06	2.19
YUFGUB a	1.26	2.35	0.63	1.20
b	0.09	3.00	0.88	1.64
c	0.32	3.28	3.19	3.13
d	0.38	5.03	0.81	2.78
Mean value	0.51	3.42	1.38	2.19
ZZZFYW01	0.46	2.50	0.23	1.71
	0.07	3.03	0.44	1.97
Mean value	0.97	3.37	0.73	1.85
Max value	3.37	6.17	3.19	3.13

[a] As there are 2 C - N - O angles for one O - N - O, only the mean values of the 2 C - N - O bond angles are reported.

Table 10. Comparison of the calculated differences in dihedral angles (this work / MM2(91)) implying the NO₂ group.

Molecules	$ \Omega_{\text{calc}} - \Omega_{\text{exp}} $ (°) [a]	
Refcode	This work	MM2-91
AMNIFL	5.59	5.58
BENCLNO2	1.06	7.05
	10.90	12.57
CELBAW	0.35	0.60
CEPSIZ	4.70	10.43
CLNIB01	2.92	2.97
DNBENZ01	10.65	10.82
	15.16	15.26
DNITPY	7.07	7.09
	1.09	1.03
FUXNAN	1.92	1.88
JIZJIL	0.36	1.43
MNIANL10	3.06	3.15
MNIMET	4.70	8.92
NANILI	1.91	1.92
ONITAN	2.99	22.35
VETWAS	1.15	4.43
	1.22	7.95
YUFGOV a	1.40	22.86
b	1.54	21.43
mean value (2 conf.)	1.47	22.14
YUFGUB a	9.34	12.85
b	5.42	29.29
c	13.83	8.21
d	2.61	34.17
mean value (4conf.)	7.80	21.13
ZZZFYW01	1.11	4.01
	1.88	3.70
Mean value	4.05	8.02
Max value	15.16	22.35

[a] Values reported are in fact the mean values for the 4 dihedral angles whose hinge is the C - N bond.