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Determination of force fields for two conformers of nitromethane by CNDO/Force method

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Abstract. CNDO/Force method is used to evaluate the redundancy free internal valence force fields for two conformers of nitromethane. The initial force field is set up by taking the interaction and bending force constants from this method and transferring the stretching force constants from the force fields of chemically related molecules. The final force field is obtained by refining the initial force field using vibrational frequencies of isotopic species *viz* CH_3NO_2, CD_3NO_2, $CH_3{}^{15}NO_2$ and $CH_3N^{18}O_2$. The final force field thus obtained is reasonable on the basis of frequency fit and potential energy distribution. The barrier to internal rotation is found to be 0·048 kcal mol^{-1}.

Keywords. Force field; normal coordinate analysis; nitromethane; two conformers; CNDO/Force method.

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1. Introduction

The vibrational spectra of nitromethane and its isotopic species have been studied by a number of authors. Nitromethane is known to have a six fold rotational barrier with a C_s molecular symmetry. It exists in two conformers as given in figure 1. Popov and Shlyapochnikov (1963a) concluded from an analysis of the vibrational spectra that the rotation of methyl group is hindered and it exists in only one isomer, namely conformer II. McKean and Watt (1976) studied the IR spectra in gas and crystalline phases and concluded that it exists in conformer II in crystalline phase. Mezey *et al* (1976) carried out *ab initio* calculation on the two conformers and found that conformer I is more stable. However, the barrier to internal rotation was found to be rather small (0·026 kcal mol^{-1}) indicating that the movement is essentially free at normal temperature.

Various methods have been adopted to compute the force fields of nitromethane. Popov and Shylapochnikov (1963b) calculated the force constants of nitromethane for conformer II by using theoretical and experimental data of vibrational spectroscopy to solve the question of mutual influence of nitrogroups in nitroalkanes. By assuming a C_{2v} symmetry for nitromethane, Verderame *et al* (1972) carried out normal coordinate analysis (NCA) using matrix isolation data and found that the force constants evaluated agree well with those of the gas phase force constants. Trinquecoste *et al* (1974) calculated valence force constants of nitromethane for conformer II using C_s

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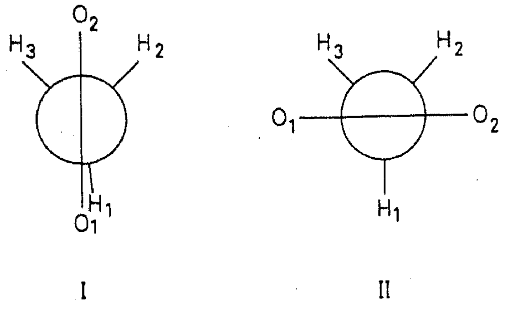

Figure 1. Two conformers of nitromethane.

symmetry. In another study NCA was carried out by Wilson (1943) assuming a C_{2v} symmetry of the molecule and tetrahedral symmetry for the methyl group.

In the determination of the harmonic force field, the least squares method is generally employed for the refinement of force constants using vibrational frequencies. In the above method, the initial force field is set up by transferring the force constants from structurally related molecules. While it is quite justified to transfer diagonal force constants from chemically related molecules, the transfer of off-diagonal force constants is not reasonable since the sign and magnitude of these force constants very much depend on the geometry of the molecules considered. Moreover, the final force fields depends largely on the set of force constants and their signs selected for the initial force field. Therefore, a reasonable initial set of interaction force constants is very important. Kanakavel *et al* (1976), Annamalai and Singh (1982a, b, 1983a, b) and Jothi *et al* (1982) have demonstrated in their studies that the sign and magnitude of bend-bend and stretch-bend interaction constants as well as bending force constants are well predicted by CNDO/Force method whereas stretching force constants and stretch-stretch interaction constants are overestimated by a factor of 2 to 2·5 times and $\sim$ 1·5 times respectively. It was pointed out by IUPAC (1977) that the force constants corresponding to the coordinates expressed by redundancy conditions are indeterminate and recommendations were made that the redundancy-free coordinates should be used to have meaningful force fields. The initial force field is set up by taking the bending and bend-bend interaction force constants from CNDO force field, scaling down the stretch-stretch interaction constants by a factor of 0·65 and transferring the stretching force constants from the force fields of chemically-related molecules. Redundancy-free internal valence force field (RFIVFF) is then calculated by refining the initial force field using vibrational frequency data of various isotopic species of nitromethane.

2. Computational details and results

The CNDO/Force calculations are carried out using a modified form (Kanakavel *et al* 1976) of Pople's computer program CNINDO (Pople and Beveridge 1970). The molecular geometry is optimised for both the conformers using the steepest descent method proposed by Pulay and Torok (1973). The optimised geometries of the two conformers are given in table 1. The forces are calculated by distorting the molecule from the

Table 1. Calculated and experimental geometries of two conformers of nitromethane (distances in Å and angles in deg.).

	Conformer I		Conformer II		
Description	CNDO	*ab initio* (Mezey *et al* 1976)	CNDO	*ab initio* (Mezey *et al* 1976)	Experimental (Tannenbaum *et al* 1956)
$R_{C\text{-}N}$	1·4173	1·531	1·4172	1·529	1·489
$R_{N\text{-}O}$	1·2242	1·278	1·2243	1·279	1·224
$R_{C\text{-}H_1}$	1·1165	1·090	1·1189	1·091	1·088
$R_{C\text{-}H_2}$	1·1174	1·091	1·1168	1·091	1·088
$\angle C\text{-}N\text{-}O_1$	118·77	117·67	119·09	117·58	—
$\angle C\text{-}N\text{-}O_2$	119·46	117·05	119·10	117·58	—
$\angle N\text{-}C\text{-}H_1$	110·47	107·59	109·61	108·06	107·2
$\angle N\text{-}C\text{-}H_2$	110·21	108·23	110·59	108·06	107·2

Barrier-to-internal rotation:
CNDO = 0·048 kcal mol^{-1}; *ab initio* = 0·026 kcal mol^{-1}; Microwave = 0·006 kcal mol^{-1}

optimised geometry in the positive and negative directions of redundancy-free internal coordinates. The distortions considered are 0·01 Å, 1° and 2° respectively for stretching, bending and torsional coordinates. The CNDO force constants are then derived from the forces using the relationships given earlier (Kanakavel *et al* 1976). The redundancy-free internal coordinates are given in table 2. The internal coordinates are illustrated in figure 2.

In table 1, the optimised geometries obtained from CNDO/Force calculations are compared with the *ab initio* values reported by Mezey *et al* (1976) and experimental geometries reported by Tannenbaum *et al* (1956). In general, the calculated geometries agree well with the *ab initio* and experimental values. From CNDO/Force energies, it is found that conformer I is more stable. The barrier to internal rotation is found to be rather low (0·048 kcal mol^{-1}) which is consistent with the experimentally observed barrier to rotation value (0·006 kcal mol^{-1}) reported by Tannenbaum *et al* (1956) and *ab initio* results (0·026 kcal mol^{-1}) reported by Mezey *et al* (1976).

The initial force field is constructed according to the procedure given above. The computer program FPERT developed by Schachtschneider (1964) is used to carry out the refinement after including the damped least-squares subroutine. All the calculations were performed on an IBM 370/155 computer. The vibrational frequencies of CH_3NO_2, CD_3NO_2, $CH_3{}^{15}NO_2$ and $CH_3N^{18}O_2$ reported by Trinquecoste *et al* (1974) and the vibrational frequencies of CHD_2NO_2 reported by McKean *et al* (1976) are employed in our calculations. The calculated vibrational frequencies of the two conformers were found to be not too different from each other (McKean *et al* 1976). We have therefore taken the same frequencies for both the conformers for refinement. Based on C_s geometry, the 15 fundamental modes of conformer I can be distributed as 10 A′ + 5 A″ vibrations and for conformer II they are distributed as 9 A′ + 6 A″ vibrations. In both cases, the number of independent force constants exceed the number of vibrational frequencies for all the isotopes considered. Therefore, some reasonable constraints on

Table 2. Redundancy-free internal coordinates of nitromethane.

Coordinate	Description
1. $\nu_{CH} = r_1$	CH stretch
2. $\nu_{CH} = r_2$	CH stretch
3. $\nu_{CH} = r_3$	CH stretch
4. $\nu_{CN} = R$	CN stretch
5. $\nu_{NO} = d_1$	NO stretch
6. $\nu_{NO} = d_2$	NO stretch
7. $^*\delta s_{CH_3} = [3(1+b^2)]^{-1/2}[b(\alpha_1+\alpha_2+\alpha_3)-(\beta_1+\beta_2+\beta_3)]$	CH_3 sym. deform
8. $\delta s'_{CH_3} = \frac{1}{\sqrt{6}}(2\alpha_1-\alpha_2-\alpha_3)$	CH_3 sym. deform
9. $\gamma_{\|}CH_3 = \frac{1}{\sqrt{6}}(2\beta_1-\beta_2-\beta_3)$	CH_3 rock
10. $\delta_{NO_2} = \frac{1}{\sqrt{6}}(2\theta-\eta_1-\eta_2)$	NO_2 deform
11. $\delta a_{CH_3} = \frac{1}{\sqrt{2}}(\alpha_2-\alpha_3)$	CH_3 asym. bend
12. $\gamma_{\perp}\,CH_3 = \frac{1}{\sqrt{2}}(\beta_2-\beta_3)$	CH_3 rock
13. $\gamma_{NO_2} = \frac{1}{\sqrt{2}}(\eta_1-\eta_2)$	NO_2 rock
14. $\omega_{NO_2} = \phi$	NO_2 wag
15. $\tau_{CH_3} = \frac{1}{\sqrt{6}}(\tau_1+\tau_2+\tau_3+\tau_4+\tau_5+\tau_6)$	CH_3 torsion

* $b = -3\sin\beta\cos\beta/\sin\alpha$

The corresponding redundant coordinate is

$$[3(1+b^2)]^{-1/2}[b(\alpha_1+\alpha_2+\alpha_3)+(\beta_1+\beta_2+\beta_3)].$$

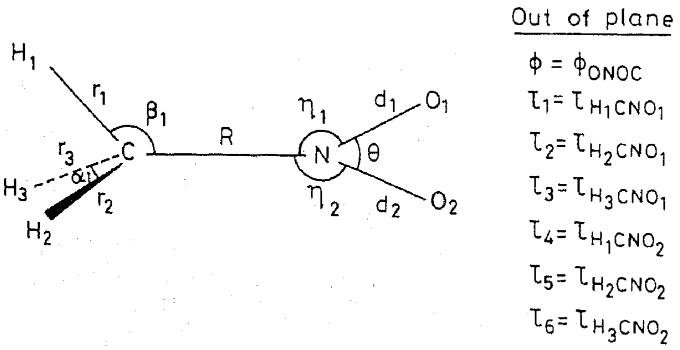

Figure 2. Internal co-ordinates of nitromethane.

the force fields are imposed. For conformer I, 43 force constants are taken into account and for conformer II, 47 force constants are considered for refinement.

Two types of force fields FF1 and FF2 are evaluated. In the case of FF1, the signs of interaction constants are kept unaltered during the iterations and in FF2, the signs of interaction constants are allowed to vary for a better frquency fit. The redundancy-free internal valence force fields thus obtained are given in tables 3 and 4. The vibrational frequencies are also calculated for the two conformers along with the potential energy distribution (PED) in terms of redundancy-free internal valence force fields FF1 and FF2. However, they are not included for the sake of brevity.

3. Discussion

The force fields reported for the two conformers are rather elaborate and include a large number of off-diagonal and diagonal terms. Most of the previous studies were confined to a limited number of force constants. Between the force fields FF1 and FF2 only a few force constants differ in sign and these force constants are found to have in general very small magnitude. The force constants obtained by this method in general agree with those of the valence force constants reported by Trinquecoste *et al* (1974). However, many interaction constants which were neglected in the previous studies are found to be quite significant. Since for FF1 the signs of interaction constants are retained as predicted by theoretical calculations, the discussion on force constants is limited in FF1 only. All the diagonal force constants are well predicted by these calculations. For example, the force constant for CH_3 symmetric deformation ($F_{7,7}$) for both the conformers (0·6277 mdyn Å rad^{-2} for conformer I and 0·6289 mdyn Å rad^{-2} for conformer II) are found to be in agreement with the value of 0·596 mdyn Å rad^{-2} reported by Trinquecoste *et al* (1974). The CNDO/Force calculations predict the NO_2 symmetric bending force constants to be 3·9528 mdyn Å rad^{-2} for conformer I and 3·3183 mdyn Å rad^{-2} for conformer II. The valence force field reported by Trinquecoste *et al* (1974) predicts this value as 1·318 mdyn Å rad^{-2}. The NO_2 wagging force constant is also found to be fairly large (0·4537 mdyn Å rad^{-2} for I and 0·6834 mdyn Å rad^{-2} for II) when compared to the reported value of 0·28 mdyn Å rad^{-2}. The ν_{CN}/δ_{NO_2} interaction constant (0·6319 mdyn rad^{-1} for I and 0·7170 mdyn rad^{-1} for II) also differs from the reported value ($-0·38$ mdyn rad^{-1}). A strong ν_{NO}/ν_{NO} interaction is fairly evident from both studies (1·7762 mdyn Å^{-1} for I and 1·0032 mdyn Å^{-1} for II) as against the reported value of 1·372 mdyn Å^{-1}.

Because of the different orientation of the $-NO_2$ group in the two conformers, the force constants associated with the $-NO_2$ group are found to be different. For example, the NO_2 stretching, bending, rocking and wagging force constants for conformer I are respectively 7·9713 mdyn Å^{-1}, 3·9529 mdyn Å rad^{-2}, 1·1419 mdyn Å rad^{-2} and 0·4537 mdyn Å rad^{-2} against 9·4531 mdyn Å^{-1}, 3·3183 mdyn Å rad^{-2}, 0·9376 mdyn Å rad^{-2} and 0·6834 mdyn Å rad^{-2} for conformer II. Some interaction constants change sign from one conformer to the other. For example, ν_{NO}/γ_{NO_2} interaction constant ($F_{5,13}$) for conformer I is $-0·2781$ mdyn rad^{-1} while for conformer II, the value is calculated to be 0·4689 mdyn rad^{-1}. Further, some force constants which were neglected in one conformer are found to have significant values in the other. For example, the force constants $F_{2,6}$ and $F_{4,8}$ which were neglected in conformer I have the values 0·0222 mdyn rad^{-1} and 0·0312 mdyn rad^{-1} respectively

Table 3. Redundancy-free internal valence force fields for conformer I[a].

Force constant	CNDO/Force	Refined	
		FF1	FF2
$F_{1,1}$	11·9458	5·0464	5·0473
$F_{1,2}$	0·0270	0·0125	0·0126
$F_{1,4}$	0.2791	0·1560	0·1592
$F_{1,5}$	0·0262	0·0209	0·0218
$F_{1,7}$	−0·0036	—	—
$F_{1,8}$	−0·1428	−0·1291	−0·1304
$F_{1,9}$	0·0973	0·0804	0·0843
$F_{1,10}$	0·0355	0·0354	0·0354
$F_{1,13}$	−0·0344	−0·0247	−0·0262
$F_{2,3}$	0·1052	0·0900	0·0892
$F_{2,5}$	−0·0087	—	—
$F_{2,8}$	0·0720	0·0564	0·0582
$F_{2,9}$	−0·0536	−0·0498	−0·0517
$F_{2,10}$	0·0186	0·0177	0·0178
$F_{2,11}$	−0·0364	−0·0141	−0·0172
$F_{2,13}$	−0·0243	−0·0256	−0·0256
$F_{4,4}$	18·1423	4·9785	4·9765
$F_{4,5}$	0·6897	0·4517	0·4519
$F_{4,6}$	0·8357	0·5572	0·5558
$F_{4,7}$	−0·5280	−0·5184	−0·5195
$F_{4,10}$	0·6291	0·6319	0·6352
$F_{5,5}$	32·4161	7·9713	7·9623
$F_{5,6}$	2·7682	1·7762	1·7841
$F_{5,7}$	−0·0806	−0·1133	−0·1092
$F_{5,8}$	−0·0429	−0·0526	−0·0514
$F_{5,9}$	−0·0166	−0·0380	−0·0144
$F_{5,10}$	−0·1623	−0·1664	−0·1661
$F_{5,13}$	−0·2612	−0·2781	−0·2756
$F_{7,7}$	0·6340	0·6277	0·6279
$F_{7,10}$	−0·0475	−0·0423	−0·0432
$F_{8,8}$	0·5317	0·5300	0·5508
$F_{8,9}$	0·0025	0·0025	−0·0389
$F_{8,13}$	−0·0195	−0·0036	0·0085
$F_{9,9}$	0·9536	0·9485	0·9249
$F_{9,10}$	0·0997	0·0973	−0·0964
$F_{9,13}$	−0·1527	−0·1603	−0·1629
$F_{10,10}$	3·9175	3·9528	3·9490
$F_{10,13}$	0·0190	0·0224	0·0225
$F_{11,11}$	0·5088	0·5321	0·5301
$F_{11,12}$	0·0267	0·0034	0·0056
$F_{11,14}$	0·0097	—	—
$F_{12,12}$	0·8393	0·8096	0·8130
$F_{12,14}$	0·0341	0·0410	0·0418
$F_{13,13}$	1·1282	1·1419	1·1390
$F_{14,14}$	0·4591	0·4537	0·4533
$F_{15,15}$	0·0100	0·0009	0·0015

[a] Units for force constants: stretch, stretch-stretch in mdyn A^{-1}; stretch-bend in mdyn rad^{-1} and bend-bend in mdyn Å rad^{-2}. $F_{1,1} = F_{2,2} = F_{3,3}$; $F_{1,2} = F_{1,3}$; $F_{1,4} = F_{2,4} = F_{3,4}$; $F_{1,5} = -F_{1,6}$; $F_{2,8} = F_{3,8}$; $F_{2,9} = F_{3,9}$; $F_{2,10} = F_{3,10}$; $F_{2,11} = -F_{3,11}$; $F_{2,13} = F_{3,13}$; $F_{5,5} = F_{6,6}$; $F_{5,7} = F_{6,7}$; $F_{5,8} = -F_{6,8}$; $F_{5,9} = F_{6,9}$; $F_{5,10} = F_{6,10}$; $F_{5,13} = F_{6,13}$.

Table 4. Redundancy-free internal valence force fields for conformer II[a].

Force constant	CNDO/Force	Refined FF1	 FF2
$F_{1,1}$	11·7588	5·0491	5·0445
$F_{1,2}$	0·0334	0·0245 (0·055)	0·0159
$F_{1,4}$	0·2900	0·1609	0·1631
$F_{1,5}$	−0·0158	−0·0099	−0·0099
$F_{1,7}$	0·0228	0·0010	−0·0327
$F_{1,8}$	−0·1093	−0·1061	−0·1062
$F_{1,9}$	0·1016	0·1001	0·0999
$F_{1,10}$	0·0247	0·0274	0·0273
$F_{2,3}$	0·0839	0·0692	0·0642
$F_{2,5}$	−0·0175	−0·0108	−0·0108
$F_{2,6}$	0·0335	0·0222	0·0222
$F_{2,8}$	0·0262	0·0555	0·0565
$F_{2,9}$	−0·0089	—	—
$F_{2,10}$	0·0282	0·0283	0·0283
$F_{2,11}$	−0·0514	−0·0103	−0·0108
$F_{2,13}$	−0·0021	—	—
$F_{2,14}$	−0·0123	−0·0178	−0·0170
$F_{4,4}$	18·2012	4·9300	4·9296
$F_{4,5}$	0·8208	0·5440	0·5437
$F_{4,7}$	−0·5391	−0·5513 (−0·40)	−0·5508
$F_{4,8}$	0·0441	0·0312	0·0314
$F_{4,10}$	0·7272	0·7170	0·7172
$F_{5,5}$	37·5486	9·4531	9·4530
$F_{5,6}$	1·5311	1·0032 (1·372)	1·0031
$F_{5,7}$	−0·0945	−0·1020	−0·0014
$F_{5,8}$	−0·0343	−0·0153	−0·0154
$F_{5,9}$	0·0071	—	—
$F_{5,10}$	−0·2055	−0·2160	−0·2158
$F_{5,11}$	0·0506	0·0620	0·0618
$F_{5,12}$	−0·0090	—	—
$F_{5,13}$	0·4573	0·4689	0·4688
$F_{5,14}$	−0·0311	−0·0261	0·0127
$F_{7,7}$	0·6279	0·6289 (0·596)	0·6308
$F_{7,8}$	0·0108	0·0126	0·0127
$F_{7,9}$	−0·0247	−0·0365	−0·0367
$F_{7,10}$	−0·0518	−0·0479	−0·0478
$F_{8,8}$	0·5690	0·5724 (0·54)	0·5725
$F_{8,9}$	−0·0685	−0·0712 (−0·074)	−0·0718
$F_{9,9}$	0·6375	0·6365 (0·672)	0·6362
$F_{9,10}$	0·1051	0·1195	0·1191
$F_{9,14}$	−0·0762	−0·0782	−0·0783
$F_{10,10}$	3·2838	3·3183 (1·318)	3·3176
$F_{10,14}$	0·1176	0·1127	0·1127

Table 4. (*Contd.*)

Force constant	CNDO/Force	Refined FF1	 FF2
$F_{11,11}$	0·5594	0·5566 (0·533)	0·5567
$F_{11,12}$	−0·0428	−0·0417 (−0·053)	−0·0419
$F_{12,13}$	0·0166	0·0024	−0·0055
$F_{12,12}$	0·7768	0·8376 (0·743)	0·8375
$F_{12,14}$	−0·0403	−0·0010	0·0013
$F_{13,13}$	0·9477	0·9376 (1·079)	0·9376
$F_{14,14}$	0·6990	0·6834 (0·280)	0·6835
$F_{15,15}$	0·0200	0·0200	0·0202

[a] Values given in parentheses are taken from Trinquecoste *et al* (1974). Units for force constants as in table 3.
$F_{1,1} = F_{2,2} = F_{3,3}$; $F_{1,2} = F_{1,3}$; $F_{1,4} = F_{2,4} = F_{3,4}$; $F_{1,5} = F_{1,6}$; $F_{1,7} = F_{2,7} = F_{3,7}$; $F_{2,5} = F_{3,6}$; $F_{2,6} = F_{3,5}$; $F_{2,8} = F_{3,8}$; $F_{2,10} = F_{3,10}$; $F_{2,11} = F_{3,11}$; $F_{2,14} = F_{3,14}$; $F_{4,5} = F_{4,6}$; $F_{5,5} = F_{6,6}$; $F_{5,7} = F_{6,7}$; $F_{5,8} = F_{6,8}$; $F_{5,10} = F_{6,10}$; $F_{5,11} = F_{6,11}$; $F_{5,13} = F_{6,13}$; $F_{5,14} = -F_{6,14}$.

in conformer II. Similarly, the neglected force constants in conformer II $F_{1,13}$ and $F_{9,13}$ are found to have values $-0{\cdot}0247$ mdyn rad^{-1} and $-0{\cdot}1603$ mdyn Å rad^{-2} respectively in conformer I.

From PED of conformer I, it is found that the assignment of $\nu_{S_{NO_2}}$ and $\delta_{S_{CH_3}}$ are interchanged with respect to those reported by Trinquecoste *et al* (1974). The assignment of these two bands was found to be difficult (Wells and Wilson 1941) since these modes give rise to the polarised doublet near 1400 cm^{-1} in the Raman spectrum and it was concluded that separate motion may not be differentiated since they are probably mixed in the normal modes. In conformer I, the CN stretching mode and CH_3 symmetric bending mode contribute significantly to the NO_2 stretching vibrations for CH_3NO_2. Similarly, in CHD_2NO_2 the CH_3 symmetric bending and $\gamma_{11}CH_3$ rock modes are found to have significant contribution for the bands observed at 1057 cm^{-1} and 988 cm^{-1}. For conformer II, the bands at 655 cm^{-1} and 607 cm^{-1} were assigned to NO_2 bending and NO_2 wagging modes by Trinquecoste *et al* (1974) whereas according to our studies the band at 655 cm^{-1} is found to have a larger contribution from NO_2 wagging and that at 607 cm^{-1} from NO_2 bending mode. To conclude, the vibrational frequencies are found to be well reproduced by FF1 and FF2. The assignments are rather reliable as the initial force field considered is more justified.

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