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Potential energy calculations for the double internal rotation in acetone and dimethylamine

Yves G. Smeyers and Antonio Huertas-Cabrera

Instituto de Estructura de la Materia, C.S.I.C., c/Serrano, 119, Madrid-6, Spain

Sandor Suhai

Lehrstuhl für Theoretische Chemie, Friedrich-Alexander Universität, Erlangen-Nürnberg,
Egerlandstr. 3, 8520 Erlangen, Federal Republic of Germany

In the present work, the problem of the determination of the potential energy surface of double rotor molecules is examined in the case of acetone and dimethylamine. From the symmetry adapted functional form for the potential of acetone that of dimethylamine is deduced and the minimum number of conformations to be calculated is derived in order to have a reliable surface (minimal expansion).

The potential energy functions for acetone and dimethylamine are then determined using different standard procedures. Special emphasis is put on the electronic correlation effects in the calculation. It is found that these effects significantly improve the potential energy function.

Key words: Potential energy calculations—Acetone—Dimethylamine.

1. Introduction

In a previous work, we studied the internal dynamics corresponding to the rotation of the methyl groups in acetone [1]. For that purpose we determined the potential energy function for the rotation applying different methods: the CNDO/2, the STO-3G and the 4-31G procedures. Surprisingly, the CNDO/2 procedure yielded the most satisfactory results, in reproducing the experimental barrier height as well as in giving the energy value for the solely known torsional band. Assuming that the CNDO/2 results were accidental, we tested also *ab initio* methods, in a second work, by performing calculations with increasing basis sets [2]. Special efforts were made in order to introduce the polarization effects. A significant improvement was found with a large and balanced set. Finally, the influence of the electronic correlation effects in the barrier height was tested.

In the present work, 6-31G calculations are reported for acetone and dimethylamine. Using these results as reference functions, Moller–Plesset PT calculations, limited to the valence shells, are carried out up to the second order. A significant improvement for the barrier heights is found, in acetone as well as in dimethylamine, when compared with the experimental data.

2. Determination of the potential energy function of acetone and dimethylamine

2.1. *The Altmann groups*

As it is well known, the potential energy surface for a double rotor molecule may be represented by a two-fold Fourier series expansion, which possesses the full symmetry of the Hamilton operator [3]. In this respect, the group theory for non-rigid molecules will give the correct symmetry of the Hamiltonian, and hence the exact functional form for the potential. The number of conformations to be calculated will be determined by the number of terms retained in the Fourier expansion [4, 5].

As it is also well known, the Altmann group for acetone is [1]:

$$I = (\mathscr{C}_3^I \times \mathscr{C}_3'^I) \wedge (W^I \times V^I) \sim G_{36} \tag{1}$$

where $\wedge$ means semi-direct product. In this expression, $\mathscr{C}_3^I$ is the intrinsic subgroup of the rotations of $2\pi/3$ of one of the methyl groups:

$$\mathscr{C}_3^I = [\hat{\varepsilon} + \hat{\mathscr{C}}_3 + \hat{\mathscr{C}}_3^2] \tag{2}$$

and $\mathscr{C}_3'^I$ the intrinsic subgroup of the rotation of the other methyl group.

W^I is the exchange restriction subgroup defined by the operations:

$$W^I = (\hat{\varepsilon} + \hat{W})$$

where $\hat{W}$ is the angle exchange operation which exchanges the rotation angles of both methyl groups:

$$\hat{W} f(\theta_1, \theta_2) = f(\theta_2, \theta_1) \tag{3}$$

V^I is the double switch restriction subgroup defined by the operations:

$$V^I = (\hat{\varepsilon} + \hat{V})$$

where $\hat{V}$ represents the simultaneous sign change of the rotation angles of both methyl groups:

$$\hat{V}f(\theta_1, \theta_2) = f(-\theta_1, -\theta_2). \tag{4}$$

Now, let us deduce from (1) the Altmann group for dimethylamine. For this purpose, let us underline that the frame of dimethylamine, in its pyramidal structure, loses the molecular sigma symmetry plane, as well as the C_2 rotation axis, because of the existence of an out-of-plane hydrogen atom. The dimethylamine frame conserves, however, a symmetry plane passing through the nitrogen and the out-of-plane hydrogen atoms. This symmetry plane allows the double switch exchange operation between the rotation angles of both rotors:

$$(\hat{W}\hat{V})f(\theta_1, \theta_2) = f(-\theta_2, -\theta_1). \tag{5}$$

As a result the Altmann group of dimethylamine is:

$$I = (\mathscr{C}_3^I \times \mathscr{C}_3'^I) \wedge (WV)^I \sim G_{18} \tag{6}$$

where $(WV)^I$ is the restricted subgroup of exchange-double-switch:

$$(WV)^I = [\hat{\varepsilon} + \hat{W}\hat{V}].$$

2.2. *The functional forms*

The functional form for the potential energy of acetone is given in [1–2]:

$$V(\theta_1, \theta_2) = \sum_{K \geq L = 0}^{N}\sum^{N} A_{KL}^{CC}[\cos 3K\theta_1 \cos 3L\theta_2 + \cos 3L\theta_1 \cos 3K\theta_2]$$
$$+ \sum_{K \geq L = 1}^{N-1}\sum^{N-1} A_{KL}^{SS}[\sin 3K\theta_1 \sin 3L\theta_2 + \sin 3L\theta_2 \sin 3K\theta_2]. \tag{7}$$

It is easy to verify that this form is invariant under the operations of the Altmann group (1).

The summation on K and L should run, in principle, up to infinity. In fact, few terms are only necessary to reproduce the major features of the potential energy as a function of the rotation angles. As it is well known, the cosine terms of this expansion describe the global repulsion between the frame and the rotors and between the rotors themselves, whereas the sine terms, which depend on the sign of the rotation angles, describe in some way the "cog-wheel" effects [6]. Furthermore, because the sine functions take the zero value at the limits, where $K\theta$ or $L\theta = 0$ (or π), the sine expansion needs two terms less than the cosine one.

The functional form of the potential energy for dimethylamine is not any more invariant under the $\hat{W}$ and $\hat{V}$ operations separately. Thus it may contain terms of mixed products of sine and cosine functions, but these terms must be invariant under the exchange operations. The way to obtain such terms is to combine each pair of mixed products of given K and L, with identical coefficients of opposite sign.

Thus the functional form for dimethylamine is:

$$\begin{aligned}V(\theta_1,\theta_2)=&\sum_{K\geq L=0}^{N}\sum^{N} A_{KL}^{CC}[\cos 3K\theta_1\cos 3L\theta_2+\cos 3L\theta_1\cos 3K\theta_2]\\&+\sum_{K=0}^{N}\sum_{L=1}^{N-1} A_{KL}^{CS}[\cos 3K\theta_1\sin 3L\theta_2-\sin 3L\theta_1\cos 3K\theta_2]\\&+\sum_{K\geq L=1}^{N-1}\sum^{N-1} A_{KL}^{SS}[\sin 3K\theta_1\sin 3L\theta_2+\sin 3L\theta_1\sin 3K\theta_2].\qquad(8)\end{aligned}$$

It is easy to verify that this expansion is invariant under the operations of the Altmann group (6).

2.3. *Minimal expansion*

The minimal expansion is defined as the expansion which contains at least one "pure" sine term in order to introduce the "cog-wheel" interactions between the rotors [2]. Consequently, the summation for the cosine terms will run from 0 to 2.

As a result, the minimal expansion for acetone will contain from (7), seven terms, namely six cosine and one sine terms:

$$\begin{aligned}V(\theta_1,\theta_2)=&A_{00}^{CC}+A_{10}^{CC}[\cos 3\theta_1+\cos 3\theta_2]+A_{11}^{CC}\cos 3\theta_1\cos 3\theta_2\\&+A_{20}^{CC}[\cos 6\theta_1+\cos 6\theta_2]+A_{21}^{CC}[\cos 6\theta_1\cos 3\theta_2+\cos 3\theta_1\cos 6\theta_2]\\&+A_{22}^{CC}\cos 6\theta_1\cos 6\theta_2+A_{11}^{SS}\sin 3\theta_1\sin 3\theta_2.\qquad(9)\end{aligned}$$

In the same way, the minimal expansion for dimethylamine will contain from (8), ten terms, six cosine, three mixed, and one sine terms:

$$\begin{aligned}V(\theta_1,\theta_2)=&A_{00}^{CC}+A_{10}^{CC}[\cos 3\theta_1+\cos 3\theta_2]+A_{11}^{CC}\cos 3\theta_1\cos 3\theta_2\\&+A_{20}^{CC}[\cos 6\theta_1+\cos 6\theta_2]+A_{21}^{CC}[\cos 6\theta_1\cos 3\theta_2+\cos 3\theta_1\cos 6\theta_2]\\&+A_{22}^{CC}\cos 6\theta_1\cos 6\theta_2+A_{01}^{CS}[\sin 3\theta_2-\sin 3\theta_1]\\&+A_{11}^{CS}[\cos 3\theta_1\sin 3\theta_2-\sin 3\theta_1\cos 3\theta_2]\\&+A_{21}^{CS}[\cos 6\theta_1\sin 3\theta_2-\sin 3\theta_1\cos 6\theta_2]\\&+A_{11}^{SS}\sin 3\theta_1\sin 3\theta_2.\qquad(10)\end{aligned}$$

It may be underlined that the first mixed term, which apparently does not contain cosine function, is actually a mixed term because $1=\cos 0$.

3. The calculations

3.1. *Acetone*

The potential energy map for acetone was already calculated by the CNDO/2 procedure [1], and the *ab initio* STO-3G, 4-31G, 6-31G and 6-31G plus bond functions in order to introduce the polarization effects [1–2]. In the present work, this map is determined again using a Moller–Plesset PT procedure, limited to the valence shells and to the second order. In this calculation, HF results obtained with the 6-31G basis set were used as reference functions, since polarization functions in the basis set gave rise to a too large number of configurations.

The geometry of acetone employed in this last step was the same as in papers [1, 2], i.e., the standard one. No relaxation effect during the rotations was taken into account. Although the potential energy function for acetone (7) is invariant under the sense of rotations, this was counterclockwise, when viewed from the center of the molecule, in accordance with the definition (3) and (4). The origin of the rotations was the doubly staggered conformations in which the coplanar methyl hydrogens are pointing outwards.

In the conformational map calculation only seven conformations were considered in order to determine the seven coefficients of the minimal expansion (9). These seven conformations were: 0°, 0°; 0°, 30°; 0°, 60°; 30°, 30°; 30°, 60°; and 60°, 60° for determining the cosine coefficients, and 30°, −30° for the sine one.

3.2. Dimethylamine

In the present work, the potential energy map for dimethylamine was calculated by the CNDO/2, the *ab initio* 6-31G, and the Moller–Plesset PT procedures, in the same way as for acetone.

The geometry of dimethylamine employed now was the following:

$CN = 1.47$ Å $\quad HNC = 107°$

$CH = 1.091$ Å $\quad CNC = 108°$

$NH = 1.016$ Å $\quad HCH = 109.5°$

according to the experimental data [7]. No relaxation of the structure during the rotation was considered, except for the out-of-plane hydrogen atom. The potential energy function for dimethylamine (8) is not invariant under the sense of rotations because of the presence of the mixed terms. This was also counterclockwise. The origin of the rotations was the doubly staggered conformation in which the two hydrogen atoms lying in the CNC plane point outwards.

In these map calculations ten conformations were considered in order to determine the ten coefficients of the minimal expansion (10). These ten conformations were those considered for acetone, for determining the cosine and sine coefficients, plus three: 0°, −30°; −30°, 30°; and −30°, 60°, for the mixed configurations.

Finally, a conformational calculation for the planar dimethylamine is in addition calculated in order to analyze a possible interaction between the inversion of the out-of-plane hydrogen atom and the rotations. In this calculation, the CNDO/2 and the *ab initio* 6-31G procedures were only used. The internal coordinates were the same as in dimethylamine (except for the CNH angle), as well as the sense and origin of rotations.

The planar dimethylamine has the same symmetry as acetone, so only seven conformations must be taken into account. These were the same as for acetone.

4. Results and discussion

In all the calculations on acetone, dimethylamine and planar dimethylamine, the doubly staggered conformation (0°, 0°) is found to be the preferred conformation, whereas the doubly eclipsed one, in which the hydrogen atoms are pointing inwards (60°, 60°) turned out to be the less stable one.

The representation of the potential energy surface for acetone is symmetric with respect to the two diagonals [1–2], whereas that of dimethylamine is found to be symmetric with respect to only one diagonal, as it can be seen in Fig. 1. These representations agree with the symmetry properties for acetone and pyramidal dimethylamine, expressed by (3) and (4), and (5), respectively.

In Table 1, the expansion coefficients for the potential energy function of acetone are given. These coefficients were obtained from the energy values of only seven conformations (except those of CNDO/2 where 25 conformations were considered), determined in the CNDO/2, 6-31G, and 6-31G+MP approximations. The results obtained in these three approaches show the same trends.

It may be underlined, that the electronic correlation effects somewhat smooth the potential energy surface, as expected, because of the repulsive nature of the interactions between the rotors. Therefore, in column 4 of the same table, we give as an insert also the coefficients of the potential energy function of acetone, which were evaluated from the RHF energy values calculated with polarization

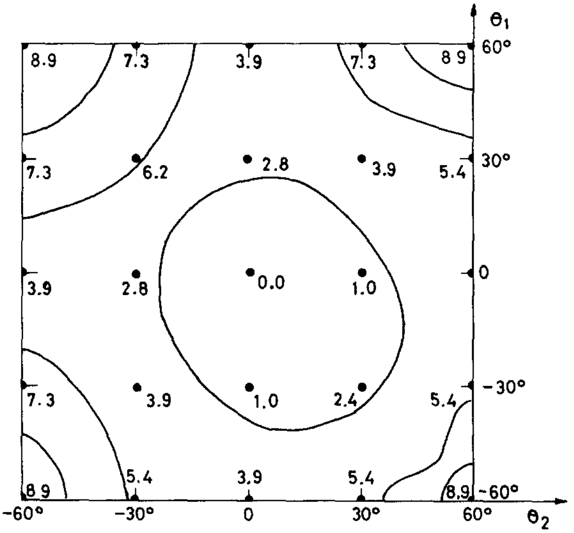

Fig. 1. Potential energy surface for the double rotation in dimethylamine in kcal/mol as a function of the rotation angles θ_1 and θ_2, determined in the 6-31G+MPPT approximation

Table 1. Expansion coefficients in kcal/mol for the potential energy function (9) of acetone calculated in different approaches

	KL	CNDO/2	6-31G	6-31G+MPPT	6-31G**+MPPT
A_{KL}^{CC}	00	0.54248	0.83540	0.78014	0.77488
	10	−0.32478	−0.49297	−0.46950	−0.45344
	11	0.11820	0.16070	0.18250	0.20920
	20	−0.00401	−0.00255	−0.00511	−0.00438
	21	−0.00177	−0.00275	−0.00685	−0.06139
	22	0.00038	0.00030	0.00029	0.05433
A_{KL}^{SS}	11	−0.11869	−0.16850	−0.19485	−0.22513

orbitals, plus the correlation energy found in the previous MP calculations without polarization. In this way, a still smoother potential energy surface is encountered.

As it has been pointed out in [2], the mean barrier height to internal double rotation is approximately given by twice the absolute value of the second term of the potential expansion: $V_{10} = 2|A_{10}|$. In Table 2, we give the mean barrier height for acetone evaluated in such a way, together with earlier results (STO 3G), and the experimental data [8–9]. In this table, it is seen that the CNDO/2 value seems to be too low, whereas the *ab initio* values are too high. However, these latter ones show a clear improvement when the quality of the approximation increases. In any case, some doubts subsist in the actual experimental value, because of the way used for determining this datum.

In Table 3, the expansion coefficients for the potential energy function of pyramidal dimethylamine are given. These were obtained from the energy values of ten conformations determined in the CNDO/2, 6-31G and 6-31G+MP approximations. As in the case of acetone, the results encountered in these three approaches show the same trend.

The electronic correlation effects smooth also somewhat the potential energy surface of dimethylamine. The correlation effects are now maximum in the −30°, 30° conformation in which the interactions with the out-of-plane hydrogen atom

Table 2. Mean barrier height to internal double rotation in acetone and dimethylamine in kcal/mol

Procedure	Acetone	Dimethylamine
CNDO/2	650	3075
STO 3G	1233	—
6-31G	986	4560
6-31G+MPPT	939	4460
6-31G**+MPPT	907	—
experimental IR	830 [9]	3280 [9]
MW	778 [8]	

Table 3. Expansion coefficients in kcal/mol for the potential energy function of pyramidal and planar dimethylamine calculated in different approaches

		Pyramidal dimethylamine			Planar
	KL	CNDO/2	6-31G	6-31G+MPPT	6-31G
A^{CC}_{KL}	00	2.57738	4.19059	4.14791	3.81397
	10	−1.53754	−2.28027	−2.23011	−2.11468
	11	0.50914	0.36048	0.27652	0.38777
	20	0.01205	0.01858	0.02975	0.02366
	21	−0.02047	−0.01439	−0.00367	−0.01122
	22	0.00557	0.00162	0.00133	0.00294
A^{CS}_{KL}	01	−0.18698	−0.75628	−0.94173	—
	11	0.00137	0.00846	0.01487	—
	21	0.00029	−0.00031	−0.00135	—
A^{SS}_{KL}	11	−0.44191	−0.32007	−0.22244	−0.31196

are minimum, and they are minimum in the +30°, −30° conformation, in which these interactions are maximum. Therefore the mixed term coefficients are larger in the 6-31G + MP approximation. This reverse behavior of the correlation effects may be probably explained taking into account the existence of the nitrogen lone pair.

In table 2, we also give the mean barrier height for dimethylamine evaluated as in the acetone case, together with the experimental value [9]. It is seen, that the CNDO/2 value seems to be too low, although closer than the *ab initio* results, which are too high. The correlation effects, however, introduce some improvements.

In order to study the possible interaction of the rotations with the inversion of the out-of-plane hydrogen atom, we calculated the potential energy function for the planar dimethylamine. This surface is situated at 16.5 and 2.76 kcal/mol above the surfaces corresponding to the pyramidal structure, in the CNDO/2 and 6-31G approximations, respectively. In Table 3, the expansion coefficients determined in the 6-31G approach for the potential energy function of the planar form are given. These coefficients are very similar to those of the pyramidal structure, except for the mixed terms. Thus, from this point of view, a very small interaction may be expected. The energy separation, however, found in the 6-31G approximation suggests that this interaction should be not so small. Further calculations seem to be necessary to clear up this aspect of the internal dynamic of dimethylamine.

In the present work, the possible relaxation of the structure of acetone and dimethylamine during the rotation was not taken into account, since we are mainly interested in an effective potential energy surface for studying the coupled rotations of the methyl groups. We expect that the interactions between the rotation and the other vibrational modes should be small, except for hydrogen in dimethylamine. It might be pointed out, however, that the C-X-C bending mode could be relevant [10]. So, the consideration of a variable C-X-C angle should be also taken into account.

5. Conclusions

The results described in this paper show that the group theory for non-rigid molecules is a powerful tool in order to simplify the calculation of potential energy surface of many rotor molecules. This theory permits us to establish the functional form for the potential energy function of a molecule of a given symmetry and foresee the number of conformations to be calculated for a given expansion length of the potential.

In this paper, we propose the use of minimal expansions of seven and ten terms for acetone-like and dimethylamine like molecules, respectively. Calculations are performed on acetone and dimethylamine, using different approaches for determining the energy of the configurations considered. It is found that the expansions converge satisfactorily and that the minimal expansion describes the major features of the potential energy surfaces corresponding to the double rotation.

On the other hand, it is seen that the *ab initio* approximations give a too sharp potential energy surface, but the electronic correlation effects, taken into account in the calculation (50% of the total) somewhat smooth the surface, together with polarization effects in the atomic basis set.

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