On the Conformational Analysis of N,N-Dimethyloxamide

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The results of an energy optimization, using CNDO/2, with respect to two internal dihedral angles in N,N-dimethyloxamide are reported. The lowest minimum is found for a planar dimethylamide function, twisted around the C – C bond over an angle of 80.5 degrees with respect to the other amide function. Some calculated properties are compared with experimental data.

Introduction

A number of years ago, Persson et al.[1] concluded from their study of the ultraviolet spectra of N,N-dimethyldithiooxamide that this compound, due to sterical hindrance, can not be planar, but appears to be twisted around the C – C bond connecting the two amide functions. Recently this was confirmed by the X-ray analysis of this compound [2], were both functions were found to be twisted over an angle of 86.9 degrees, starting from the trans configuration, with each of the amide functions planar. From an investigation of the vibrational spectra of N,N-dimethyloxamide and its dithio-derivative, it became clear that the oxamide itself also probably is not planar [3]. As no structure determination for this compound appears to have been published, we have performed a theoretical study of this compound. As for the dithio-derivative the deformation of the molecule occurs by twisting around the C – C bond, it was natural to investigate the energy as a function of the dihedral angle governing this twist. While it is sufficiently known that in thioamides the conjugation within the thioamide function is stronger than for the corresponding amide, leading to stronger C – N bonds in the thio-derivative, it could not be excluded a priori that for N,N-dimethyloxamide the sterical hindrance is lowered through twisting around the $C-N(CH_3)_2$ bond. Therefore, the energy of the molecule as a function of this parameter was also studied. Inspired by the order of the problem (40 base-functions in the all-valence electron, minimal Slater-type basis), and the large number of conformations to be studied, the sophistication of the method was restricted to the CNDO/2 level of approximation [4].

Experimental

A model of the molecule is shown in Fig. 1, which also indicates the numbering of the atoms used further in this study. For the calculations, both amide functions were treated to be planar, i. e. the atoms 1 through 5 define one plane, while the other plane is defined by the atoms 6, 7 and 8. The geometrical data used to set up the cartesian coordinates of the model are gathered in Table I: for the N – C, C = O and C – C bond lengths and for the angles in both amide functions the values given by Scott [5] were used. For the N – Me, N – H and C – H bonds, "standard bondlengths" [4] were used. The H – N – H and H – N – C angles were set to 120°, the H – C – H and H – C – N angles were treated as tetrahedral. The energy was calculated with an 18-degree interval for Φ_1, governing the rotation around the N – C bond, from 0 to 90°, and with the same interval for Φ_2, which describes the rotation around the C – C bond, from 0 to 360°. The positive sense of Φ_1 is obtained by turning around the

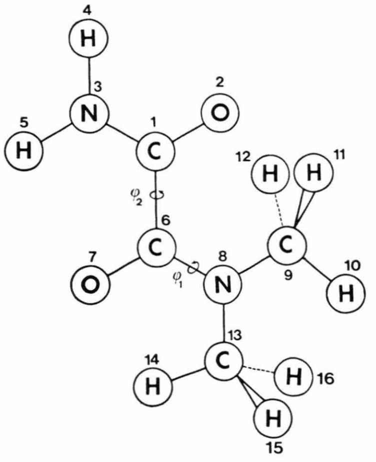

Fig. 1. Model, and numbering of the atoms in N,N-dimethyloxamide.

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Table I. Structural Parameters.

Bond	Length (pm)
C(1) – C(6)	154.2
C(1) – O(2)	124.3
C(6) – O(7)	124.3
C(1) – N(3)	131.5
C(6) – N(8)	131.5
N(8) – C(9)	147.0
C(9) – H(10)	109.0
Angle	(degree)
N(3) – C(1) – O(2)	125.7
N(3) – C(1) – C(6)	114.8

C – N bond so as to bring C_9 above, and C_{13} below the plane of the plane defined by the atoms 1, 6 and 7. The positive sense for Φ_2 is defined by the rotation around the C – C bond that brings the oxygen atom 2 above the plane of the dimethylamide function.

The calculations were performed on an IBM 370/135 system using a standard CNDO/2 program, QCPE n° 141. Where possible, use was made of symmetry to reduce the number of calculations. Smooth curves describing the energy as a function of a single parameter were traced through the calculated points with the aid of cubic splines[6]. The contour lines in the conformation map were constructed using the algorithm described by Robinson et al[7]. Extrema in the conformation map were determined numerically.

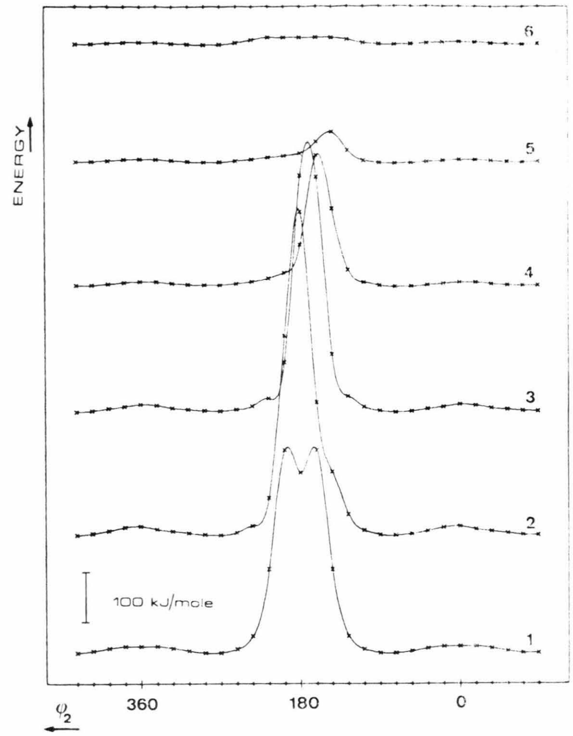


Fig. 2. Conformation Surface Intersections for Constant values of Φ_1.
1. $\Phi_1=0°$, 2. $\Phi_1=18°$, 3. $\Phi_1=36°$,
4. $\Phi_1=54°$, 5. $\Phi_1=72°$, 6. $\Phi_1=90°$.

Table II

Φ_2	ΔE_0 *
18	11.756
36	26.031
54	41.313
72	56.893
90	63.235

* All energy differences are given in kJ/mol.

Discussion

In Fig. 2 we present the curves which describe the energy as a function of Φ_2, for values of Φ_1 ranging from 0 to 90 degrees. The calculated points are indicated as crosses. The curves for values: $\Phi_1 = 90 + \alpha$ can be obtained as the mirror image, reflected through $\Phi_2 = 180°$, of the curves: $\Phi_1 = 90 - \alpha$. All the curves in Fig. II are plotted with the same scale, as indicated, but are shifted with respect to one another to augment the visibility. In Table II are given the energy differences ΔE_0 between the point $\Phi_2 = 0$ of each curve and the corresponding point in the curve $\Phi_1 = 0$. These numbers allow the correct positioning of the different curves. For N,N-dimethyloxamide, two conformations in which both amide functions are coplanar are possible: one with the two oxygen atoms cis, the other with these atoms trans with respect to the central C – C bond. When coplanar, the sterical hindrance between the two amide moieties is at maximum. For the trans-conformation, one of these hindrance is stabilized by hydrogen bonding, i. e. from atom 7 to 5. In all cases, as is clear from Fig. 2, the cis-conformations represent a region of higher energy compared to the corresponding trans-conformation. Comparing curve 1 with curve 6 then shows that the large barrier is caused by the interaction of the N – H bond, atoms 3 and 5 in Fig. 1, with one of the methyl groups on the opposite side of the molecule. The local minimum at $\Phi_2 = 180°$ in curves 1 and 6 also can be understood in terms of this hindrances, although of course contributions to these from conjugational stabilisation, which is at maximum for the coplanar conformations, cannot be excluded. The relative shallowness of the local minimum in 6 however indicates that the more pronounced minimum in curve 1 is mainly due to steric factors.

The simultaneous dependance of the energy on Φ_1 and Φ_2 is shown in the conformation map, Figure 3. This map allows the localisation of the minima, which correspond to stable conformers. The absolute minimum is found at $\Phi_1 = 0^\circ$ and $\Phi_2 = \pm 80.5^\circ$. This means that the most stable conformer has a planar dimethylamide function. The high value for Φ_2 is nevertheless lower than the angle found for the dithio derivative[2], which of course is in agreement with the smaller Van der Waals radius of oxygen compared to sulphur. Also two other minima are indicated in Figure 3. The contour lines surrounding these have been drawn with dotted lines to indicate that they were not computed, but inferred from the curves presented in Figure 2. The relative heights of these minima, together with the barriers separating them from the lowest minimum have been gathered in Table III. In what follows, the numbering used in this table will serve to identify the minima. Minimum 3, occurring for the cis-coplanar conformation corresponds to the local minimum at $\Phi_2 = 180^\circ$ in curve 1 of Fig. 2, discussed above. Minimum 2 corresponds to the trans-coplanar conformation, and can scarcely by detected at $\Phi_2 = 0$ in curve 1 of Figure 2. From the data in Table III follows that conformation 3 is of no practical importance. The energy difference between 1 and 2, and the height of the barrier between them, is of such a magnitude that, at least in solutions at room temperature, both conformers will interchange extremily rapid, making conformer 2 hard to detect. In the part of the conformation space represented by Fig. 3, two identical, as to their energy, absolute minima occur. By using the plane defined by the atoms 1, 2 and 3 as a mirror plane, these two conformers are found to be nonsuperimposable mirror images of each other, and thus optical activity should be possible. However, because of the very low barrier separating the two conformers, this barrier is essentially the one from conformer 1 to 2, optical activity will not be detectable in a solution at any reasonable temperature.

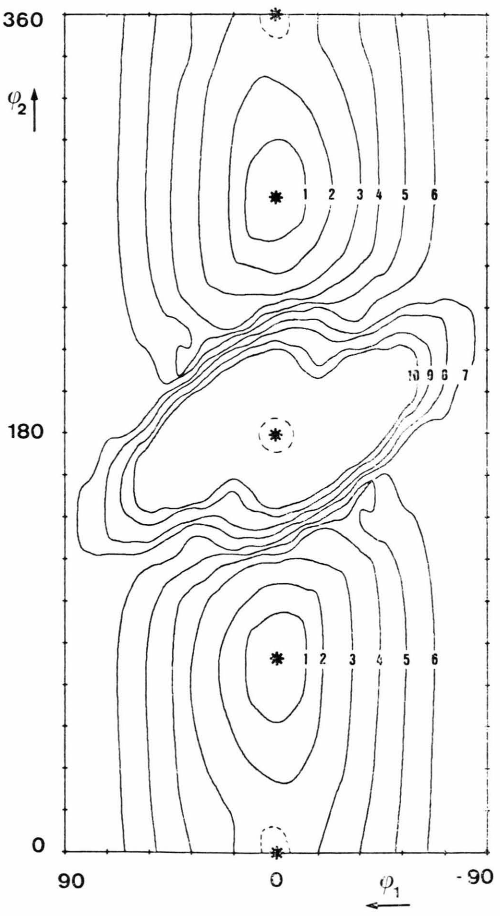


Fig. 3. Conformation Map. Heigths above absolute minimum, in kJ/mol are as follows:
1. 4.2, 2. 12.1, 3. 25.3, 4. 38.4, 5. 51.5,
6. 64.6, 7. 90.9, 8. 117.2, 9. 169,7, 10. 222.2.

Table III. Energy differences and rotational barriers [a].

	Φ_1	Φ_2	ΔE
1	0.0	80.51	0.0
2	0.0	0.0	13.555
3	0.0	180	363.933
ΔE (1 → 2) [b]		13.894	
ΔE (2 → 1)		0.339	
ΔE (1 → 3)		410.073	
ΔE (3 → 1)		46.140	

[a] All energy differences are given in kJ/mol.

[b] $\Delta E\ (i \rightarrow j)$ is the rotational barrier when passing from conformer *i* to *j*.

In Table IV we have gathered the net atomic charges and total overlap populations, calculated as described by Mulliken[8]. For the central C – C bond, the overlap population of 0.7092 indicates that some conjugation is present between the two amide functions. This value however is much closer to

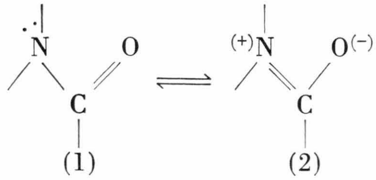
Table IV. Molecular properties.

Atom	Charge	Bond	Top *
1	3.6926	1 − 2	0.8663
2	6.3533	1 − 3	0.8481
3	5.2248	3 − 4	0.6244
4	0.8662	3 − 5	0.6295
5	0.8732	1 − 6	0.7092
6	3.7059	6 − 7	0.8680
7	6.3469	6 − 8	0.8370
8	5.1341	8 − 9	0.6470
9	3.9104	9 − 10	0.6789
10	1.0002	9 − 11	0.6781
11	0.9962	9 − 12	0.6783
12	0.9917	8 − 13	0.6499
13	3.9206	13 − 14	0.6785
14	0.9931	13 − 15	0.6781
15	0.9860	13 − 16	0.6770
16	1.0047		
μ: 5.125 Debye			

* Total overlap population.

single bond values, compare for instance to the bonds 8 − 9 or 8 − 13, than to double bonds, for which no examples are present in this molecule, but which have higher overlap populations than the bonds 1 − 2 or 6 − 7. This explains the low value of the C − C stretching frequency found in the vibrational spectra of this compound: this mode is assigned to a band at 876 cm^{-1}. This is in the region for single C − C bonds, and much lower than the values found for compounds in which conjugated C − C bonds appear, as for instance in dithio-, monomethyldithio- of N,N′-dimethyldithio-oxamide, where ν(C − C) is found at respectively 949, 1016 and 1064 cm^{-1} (see [9]).

The chemical bonding in amide functions can be described in terms of the two mesomeric forms:



(1) (2)

The very similar magnitudes of the total overlap populations in C = O and the C − N bonds, see Table IV, indicate that both forms are almost equally important, with only a slight preference for mesomeric form 1. From Table IV also can be seen that O(7) is charged less negative than O(2). This indicates that for the amide function in this compound, the form 2 is more important than for the dimethylamide function. Such a conclusion leads to a higher overlap population in C(6) − O(7) compared to C(1) − O(2), and a lower one in C(6) − N(8) than in C(1) − N(3). It is clear from Table IV that this is indeed the case. Another consequence of the above conclusion might be that N(3) is more positive than N(8). Yet this is contradicted by Table IV. This discrepancy probably is due to the differences in the substituents on both N-atoms. It seems not easy to give a simple explanation for the different bonding in both functions in terms of for instance electronegativity, as it is well known that also hyperconjugational contributions may be present [1]. That some opposing factors are important, in each case can be inferred from the smallness of the effect.

By treating the rest of the molecule as rigid, a barrier hindering the rotation around C − N(Me)$_2$ of 71.750 kJ/mol is calculated. Due to non-relaxation of Φ_2 and the rest of the structure when calculating this barrier, this value may be a little overestimated; inspection however of the conformation map in the neighbourhood of the path followed to obtain the above number shows that, as far as the nonrelaxation of Φ_2 is concerned, the error is very small. The barrier obtained here is in good agreement with experimental data on other tertiary amides, where barriers ranging from 75 to 100 kJ/mol can be found [10]. The magnitude is of course in accord with the double bond character of the C − N bond obtained from the total overlap populations. The value is much higher than the barriers, near $\Phi_2 = 0$, for rotation around the C − C bond, so that it is logical that the molecule will only distort along the C − C bond to minimize its energy.

For the absolute minimum, a dipole moment of 5.125 Debye is calculated. As the solubility of N,N-dimethyloxamide in apolar solvents like benzene is very low, the dipole moment cannot be determined very accurately. For solutions in 1,4-dioxane, a value of 4.70 D has been determined, although the experimental data indicate that for these solutions some solute-solvent interactions occur [9]. As the group moments for amide and tertiary amide functions are very much alike, from the high experimental value a severelly twisted molecule can be expected (the cis conformation being ruled out by sterical considerations), which is indeed confirmed by the present calculations.

Conclusion

By optimizing two dihedral angles, N,N-dimethyloxamide appears twisted around the central C – C bond over an angle of 80.5 degrees, and with a planar dimethylamide function. The coplanar cis and trans conformations represent secondary minima, which, in view of their characteristics, are of limited practical importance. The CNDO/2 method has been found to underestimate the conjugational effects in a number of compounds[11], but the generalization of this statement has been refuted by calculations on a number of amides[12]. The result obtained in this study appears to lend support to the latter: in accord with sterical considerations, the dihedral angle calculated here is smaller than for the dithio-equivalent, for which the corresponding angle is known from experiment[2].

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