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Conformational Analysis and Electronic Structure of Monothiodiacetamide: Normal Coordinate Analysis and Molecular Orbital Study

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The infrared spectra of monothiodiacetamide (*MTDA*, $CH_3CONHCSCH_3$) and its N-deuterated compound in solution, solid state and at low temperature are measured. Normal coordinate analysis for the planar vibrations of *MTDA*-d_0 and -d_1 have been performed for the two most probable *cis-trans*-CONHCS- or -CSNHCO-conformers using a simple *Urey-Bradley* force function. The conformation of *MTDA* derived from the vibrational spectra is supported by the all valence CNDO/2 molecular orbital method. The vibrational assignments and the electronic structure of *MTDA* are also given.

(Keywords: CNDO/2; Conformation; Electronic structure; Normal vibrations)

Konformationsanalyse und elektronische Struktur von Monothiodiacetamid. Normalkoordinatenanalyse und MO-Studie

Das Infrarotspektrum von Monothiodiacetamid (*MTDA*, $CH_3CONHCSCH_3$) und der entsprechenden N-deuterierten Derivate wurde in Lösung, im Festzustand und bei tiefer Temperatur gemessen. Die Normalkoordinatenanalyse der möglichen planaren Konformeren wurde mittels einer einfachen *Urey-Bradley*-Funktion durchgeführt. Die dabei abgeleitete Konformation von *MTDA* steht im Einklang mit einer semiempirischen quantenchemischen Rechnung (CNDO/2). Die Zuordnung der Schwingungen und die Elektronendichteverteilung in *MTDA* werden angegeben.

Introduction

Vibrational spectra of compounds containing the group O=C—*X*—C=O (*X* = O, S, NH) have been reported in the literature with the aim of studying the vibrational coupling between the double bonded stretchings as well as the conformation of these groups in acyclic compounds[1–8]. In this context, the results of an investigation

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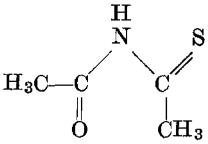
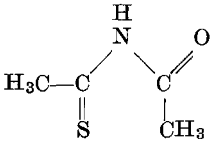
on the vibrational spectra of monothiodiacetamide (*MTDA*, $H_3CCONHCSCH_3$) are presented here. This molecule is structurally related to the biochemically important diacetamide[9] but contains —CONHCS-grouping instead. Such acyclic imides containing both —CONH- and —CSNH-groups are apparently not investigated.

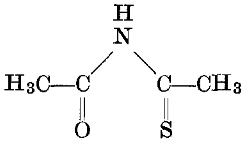
An interesting problem of *MTDA* concerns the identification of minimum energy conformations. From analogy with other related molecules[5,6,10–12], the two most probable conformations of *MTDA*, **I** and **II** in the solid state are indicated below. The structure **III** is expected to be unstable.



I



II



III

The infrared spectra of *MTDA* is of interest for determining its stable conformation as well as to know the nature of the constituent amide and thioamide vibrations. A normal coordinate treatment of the planar vibrations of *MTDA*-d_0 and -d_1 has been carried out. An all valence electron molecular orbital study by the CNDO/2 method has been made to determine its conformation and electronic structure.

Experimental

MTDA was synthesized[13] starting from thioacetamide and acetic anhydride and recrystallised from benzene-petrolether-ether (1:1) mixture. It was further purified by sublimation at 50 °C (1 mm). M. P. 62 °C. The *MTDA*-d_1 was prepared using N-deuterated thioacetamide-d_2 in the above method. The deuteration was however about 50%.

Infrared spectra of the samples were recorded from 4,000 to 400 cm^{-1} by means of a Carl-Zeiss UR 10 spectrophotometer in Nujol mull, KBr pellet and in CCl_4. The spectra between 600 to 200 cm^{-1} were recorded on a Beckman IR 12 instrument in KBr and Nujol mull. The infrared spectrum of *MTDA* was also measured at liquid nitrogen temperature (cell construction[14]: Physics Department, Indian Institute of Science, Bangalore).

Methods of Calculation

All computations were made on an IBM 360/44 computer.

Normal Coordinate Treatment: It was carried out by *Wilson*'s FG matrix method[15] for the two conformations of *MTDA*, **I**, **II**, both having the molecular symmetry C_s. There are 36 normal vibrations ($23\,a' + 13\,a''$) for *MTDA* and the coordinate treatment was carried only for the in-plane (a') modes. The internal and symmetry coordinates same as those used for *trans-cis* diacetamide[6] (*DAM*) were employed. The molecular parameters transferred from *DAM*[6] and thioacetamide[16] are, C—O 1.24, C—S 1.713, C—N 1.402, C—C 1.527, N—H 1.02, C—H 1.08 Å; NCS, CCS, C′CN 120°, OCC 126.5°, OCN 120°, NCC 113.5°, CNC 130.8°, HNC 114.6° and CCH, HCH 109.47°.

A simple *Urey-Bradley* force field was employed and the initial values of the force constants were transferred mainly from *N*-methyl-acetamide[17] (*NMA*) and *N*-methyl-thioacetamide[18, 19] (*NMTA*). These force constants were refined by an iterative procedure[12] to obtain the desired agreement between the calculated and observed frequencies. The values of the final force constants listed in Tab. 1 appear reasonable and compare well with the initial set thus demonstrating the transferability of the *Urey-Bradley* force constants.

Molecular Orbital Treatment: The all valence CNDO/2 molecular orbital calculation was carried out using standard parameters[20, 21]. The program listed in *Pople* and *Beveridge*[21] was employed. Sulfur d orbitals were included into the calculation. The two conformations **I** and **II** keeping the geometry of the rest of the molecule the same were considered.

Table 1. *Force constants* of MTDA*

Stretching (*K*)		Bending (*H*)		Repulsion (*F*)		Internal tension (*k*)	
CN	3.80	CCN	0.24	CCN	0.55	CH_3	—0.051
C′N	3.45	CCO	0.44	CCO	0.50	$C'H_3$	—0.051
CC	3.15	NCO	0.40	NCO	1.15		
C′C	3.30	C′CN	0.27	C′CN	0.50		
CO	9.45	C′CS	0.35	C′CS	0.40		
CS	3.55	NCS	0.26	NCS	0.75		
CH	4.35	CNC	0.24	CNC	0.22		
C′N	4.35	CNH	0.22	CNH	0.55		
NH	5.35	C′NH	0.30	C′NH	0.50		
		HCC	0.27	HCC	0.48		
		HC′C	0.29	HC′C	0.50		
		HCH	0.40	HCH	0.06		
		HC′H	0.39	HC′H	0.04		

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* *K*, *H*, *F* are in mdyn Å^{-1} and *k* in mdyn Å; C′ indicates the carbon atom adjacent to the C=S group.

Results and Discussion

Conformation

Operation of four factors (steric, hydrogen bonding, dipole-dipole interaction between C=S and C=O groups and crystal packing) determine the conformation of *MTDA*. Because of the close similarity between amide and imide molecules, *MTDA* may be expected to have a planar skeleton. Acyclic molecules with —CXNHCX— ($X = \mathrm{O, S}$) group are known to be stable in their *cis-trans* structure[5, 9–12]. Two *cis-trans* structures **I**, **II** are possible for *MTDA*. In CCl_4 and $CHCl_3$ solutions, the NH stretching band is found as a single sharp band around 3,400 cm^{-1}. At liquid nitrogen temperature, the intensification of some of the bands occurs but no new bands or changes in band positions occur. Thus only one stable conformation appears to be likely.

The normal coordinate treatment may be useful in an attempt to distinguish between possible structural models[22–25]. The method involves the transfer of a set of reliable force constants from structurally related molecules and the calculation of a set of frequencies for each possible model. Selection of the correct model depends on the fit between the observed and calculated frequencies.

The infrared wave numbers of *MTDA* are collected in Tab. 2. First, a zero order normal coordinate calculation for both the conformations **I** and **II** was made with the force constants transferred from *NMA* and *NMTA*. The *Urey-Bradley* force field which has proved successful for amides and thioamides was employed[16–19]. The calculated zero order inplane frequencies of structure **I** and **II** of *MTDA* (Tab. 2) notably show one major change. For **II**, the 940 cm^{-1} band of *MTDA* does not appear in the calculated frequencies and hence it must be assigned to an out of plane (a'') NH bending. Whereas the calculation for **I** indicates the band at 830 cm^{-1} to be an a'' mode, that is due to NH out of plane bending. The assignment of the 830 cm^{-1} band to NH out of plane bending compares well with that of *trans-cis DAM*[6] at 815 cm^{-1} and also is in agreement with the shift of this band to 555 cm^{-1} in the spectrum of *MTDA*-d_1. The other calculated frequencies of **I** and **II** are relatively closer to each other. The lower frequency modes which should be more sensitive to the conformations appear to show better agreement with **I** rather than **II**. Thus the zero order frequencies seem to support conformer **I**. Similar observations have been made in succinonitrile[22], dichloroethane[23] and various acyl halides[24, 25] where zero order calculations have been employed in a similar fashion for conformational study; it was noted that only one or two vibrational frequencies are sensitive to the azimuthal angle change from 0 to 180°.

In order to supplement the above inference from the vibrational analysis, a theoretical study by the widely employed CNDO/2 method was made. The total energy for conformation **I** was found to be 74.6809 a.u. and for **II**, 74.6323 a.u. Thus the conformation **I** is more stable than **II** in agreement with the results of the normal coordinate treatment. The difference of about 30 kcal mol^{-1} in favour of **I** might be overestimated, since geometry optimization was not performed completely.

The steric factors same as those in *DAM* are expected and may be expected to favour a *cis-trans* structure[5, 6] and the same is true for the dipole—dipole interactions due to the large negative charges on carbonyl oxygen and the thiocarbonyl sulfur (Fig. 1). Because of the

Table 2. *Observed and calculated fundamentals and assignments of MTDA*

Zero Order*		Obs.	Final	P. d[a]	Assignment[b] (*PED*, %)[c]
Str. **I**	Str. **II**		Calc.		
		3280	3264	0.4	νNH (100)
		3220			
		2995	—	—	νCH$_3$ (a″)
		2945	2936	0.3	ν_aCH$_3$ (100)
		2945	2936	0.3	ν_aC′H$_3$ (100)
		2870	2866	0.1	ν_sCH$_3$ (100)
		2870	2856	0.5	ν_sC′H$_3$ (100)
1672	1699	1720	1715	0.3	νCO (70)
1572	1509	1535	1536	0.1	δNH (71), νCN (12)
1471	1449	1430	1431	0.1	δ_aCH$_3$ (78), rCH$_3$ (15)
		1430	—	—	δCH$_3$ (a″)
1418	1438	1430	1426	0.3	δ_aC′H$_3$ (66), rC′H$_3$ (27)
1382	1375	1400			
		1382	1390	0.1	δ_sC′H$_3$ (91)
1376	1361	1382	1380	0.1	δ_sCH$_3$ (91)
1365	1337	1316	1325	0.7	νCN (25), νC′N (23), νC′C (13), νCC (13)
1255	1288	1250	1236	1.1	νC′C (30), νCC (15), νC′N (13), νCN (10)
1201	1160	1195	1210	1.3	νCS (24), νC′H$_3$ (17), δ_aC′H$_3$ (15)
		1085	—	—	rCH$_3$ (a″)
1029	1020	1025	1024	0.1	rCH$_3$ (50), rC′H$_3$ (16), δ_aCH$_3$ (10)
1007	1005	1015	993	2.2	νCC (24), rC′H$_3$ (21), rCH$_3$ (17)
945	832	932	911	2.3	νCN (21), νCS (19), C′N (11), rC′H$_3$ (11)
		830	—	—	πNH (a″)
805	750	780	786	0.8	νCS (23), νC′C (23), δCNC (12)
605	621	613	612	0.2	δCO (56), νCC (15), νCS (12)
		595	—	—	πCO (a″)
		508	—	—	πCC (a″)
444	512	458			
		450	455	0.2	δCS (44), δCCN (27)
370	347	370	362	2.2	δC′CN (52), δCCN (21)
309	336	305	303	0.7	δCS (37), δCCN (23), νCN (12)
		232	—	—	πCS (a″)
107	111	ni[d]	136	—	δCNC (65), δC′CN (16), δCCN (10)

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* Frequencies below 1,800 cm^{-1} only are shown and matched with the observed ones.

[a] Percent deviation = $(|\nu_{obs.} - \nu_{calc.}| \times 100)/\nu_{obs.}$

[b] a = antisymmetric, s = symmetric, ν = stretching, δ = bending, r = rocking, w = wagging, π = out of plane bending; C and C′ have same meaning as in Tab. 1.

[c] Those less than 10% are omitted.

[d] ni = not investigated.

more polarizable nature of the sulfur atom, structure **I** may from stronger intermolecular hydrogen bond and hence it may be stabilized through hydrogen bonding. This may be expected since it is known from bond length and force constant considerations that thiourea forms hydrogen bonding to a greater degree than urea in the crystalline state[26]. It is therefore likely that *MTDA*, at least in the solid phase, has a *trans-cis* —CONHCS— structure.

Band Assignments

The calculated frequencies were refined for structure **I**, which has been shown to be the most stable form, to obtain a better fit between the observed and calculated frequencies. The resulting frequencies and the potential energy distributions are presented in the fourth and sixth columns of Tab. 2. Some of the out-of-plane vibrations are assigned empirically. The deuterium shifts for *MTDA*-d_1 agree with the assignments given. The band assignments of *MTDA* are compatible with the general spectral features of *DAM*[6–8], *NMA*[17] and *NMTA*[18, 19]; therefore a discussion of the assignments seems not to be necessary.

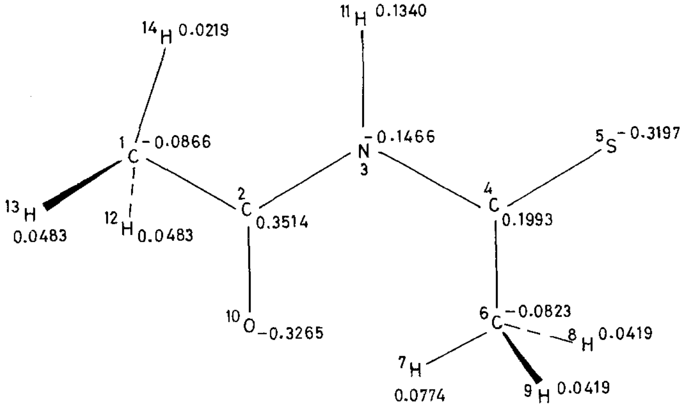

Fig. 1. Charge distribution (CNDO/2)

Electronic Structure

The charge density distribution for conformation **I** is shown in Fig. 1. The lone pair on the nitrogen atoms is delocalized as evident from the π-bond orders of CN (C_2N_3 and C_4N, 0.380 and 0.471 respectively). As is to be expected, the C=S group has less double bond character than the C=O bond; $\pi CS = 0.741$ and $\pi CO = 0.862$. The greater positive charge on the methyl proton nearest to the carbonyl oxygen compared to that of the other two protons on the methyl groups attached to the carbonyl carbon may indicate the presence of an intramolecular hydrogen bonding in the molecule. The calculated dipole moment of structure **I** including the contributions from hybridization was found to be 3.805 D.

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