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## VIBRATIONAL SPECTRA AND CONFORMATIONAL EQUILIBRIUM

# OF 1,1-DICHLORO-1-NITROSOETHANE AND ITS DEUTERIUM ANALOG

S.	V.	Trepalin, A	. V.	Yarkov,	V. J	Β.	Sokol	Lov,	UDC	543.422.4:	543.	424:54	41.121:
A.	N.	Ivanov, N.	A. A	ksinenko,	and	d V	. I.	Fetisov		541.63:547.	231'	131:54	46.11.2

Conformational equilibrium has been detected in 1,1-dichloro-1-nitrosoethane, and the structures of the conformers have been determined. H/D isotope exchange has been used in assigning and calculating the normal vibrations.

As reported previously [1], we had investigated the vibrational spectra of 2-chloro-2nitrosopropane and had shown that the most stable conformation is that with an eclipsed Cl-C-N=O fragment. Such a conformation is usually realized either with internal rotation relative to the double bond or with the presence of conjugated multiple bonds in the molecule. There are no conjugated bonds in  $(CH_3)_2CC1NO$ , and isomerism is due to rotation around the C-N single bond. Therefore, a study of  $\alpha$ -halonitroso compounds is of theoretical interest. In the work reported here, we investigated the vibrational spectra of  $CH_3CCl_2NO(1)$ and CD<sub>3</sub>CC1<sub>2</sub>NO (II), and also performed the assignment and calculation of the normal vibrations.

### EXPERIMENTAL

1,1-Dichloro-1-nitrosoethane (I). Into a solution of 2.95 g (0.05 mole) of acetaldehyde oxime and 0.5 g (0.05 mole) of potassium acetate in 50 ml of water, 9.3 g (0.13 mole) of  $Cl_2$  was passed slowly at a temperature of -5°C to 0°C; the solution was then warmed to 20°C, and the organic layer was separated, washed three times with 150-ml portions of water, dried over CaCl<sub>2</sub>, and fractionated. Yield 5.13 g (80%), bp 24°C (90 mm),  $n_D^{20}$  1.4168. Deuterated 1,1-dichloro-l-nitrosoethane (II) was prepared analogously from acetaldehyde-d4 oxime, using  $D_2O$  as the solvent. Yield 17.7%, bp 27°C (90 mm),  $n_D^{20}$  1.4178.

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Fig. 1. IR spectra of  $CH_3CCl_2NO$  in crystalline phase (A) and in  $CCl_4$  solution (B), and Raman spectra of this compound (C).

The IR spectra of the gaseous samples were registered in 10-cm gas cuvettes for the 4000-400 cm<sup>-1</sup> interval and in 100-cm gas cuvettes for the 400-30 cm<sup>-1</sup> interval, with a resolution of 0.25 cm<sup>-1</sup>, in a Bruker IFS-113 V Fourier-transform spectrometer. The IR spectra of solutions in CH<sub>3</sub>CN, CD<sub>3</sub>CN, CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and CH<sub>3</sub>NO<sub>2</sub> were obtained with a resolution of 2 cm<sup>-1</sup>. Raman spectra of the liquid samples were registered in a Ramanor Hg2S instrument (Jobin Yvon) with a resolution of 4 cm<sup>-1</sup>. Since (I) has an intense absorption band in the 6000 Å region, we used as the excitation source the 4579 Å line of an Ar<sup>+</sup> laser (100 mW).

The force field was refined using programs given in [2]; the quantum-chemical calculations were performed by the MNDO method [3]. The numerical calculation of the vibrationalrotational contours of the absorption bands in the IR spectra of the gaseous compounds was performed in accordance with a program described in [4]; the maximum J = 100.

### RESULTS AND DISCUSSION

The IR and Raman spectra of (I) are shown in Fig. 1. Indications of the presence of both conformers can be found in these spectra. We studied the possibility of realizing the following equilibria:

$$\operatorname{cis-Cl} - \operatorname{cis-Me}$$
 (1)

trans-Me 
$$\leftarrow$$
 trans-Cl (3)

The Me-C-N=O dihedral angles for the cis-Cl, cis-Me, trans-Me, and trans-Cl conformers vary within the respective limits 90-150°, -30° to +30°, 150-210°, and 30-90°. Other equilibria

	0	CD <sub>3</sub> CCl <sub>2</sub> NO							
	IR	Paman	cal-	IR		cal-	Distribution of		
solution crystal		liquid	cula- tion	solu- tion	solu- cry- tion stal		%		
3167 m	3159 m			3162			$1597 \pm 1597$		
3140 <b>w</b> 3004 <b>sh</b>	3019 w		3007		2260	2246	1582+1582 100 vCH,		
2995 <b>m</b>	3007 m		3007			2245	100  vCH.		
2935 w 1597 vs 1582 m	2936 w 1592 vs	1593 W	2944 1593	1596 1581	2130 1593	2121 1593	-1 vCH/CH 98 vCH. 2 vCH/CH 92 vNO, 4 8CNO		
1443 <b>w</b>	1520 vw 1433 w	1456 <b>m</b>	1441	1044	1042	1038	822+701 89 6HCH, 10 6CCH		
1375W 1237VW	1378 w 1240 vw 1141 vw	1379 <b>vw</b>	1376	1141	1142 1199	1141	46 δHCH, 60 δCCH 620+620 620+527		
1132 W 1103 S	1109 s	1135 VW	1107	999	<b>99</b> 9	998	54 8CCH, 15 vCCl,		
1086 <b>m</b>	1085 w	1039 W	1096	921	917	913	$63  \delta CCH, 8  vCCI,$		
1066 w	1071 vw 1056 m	1064 W	1059	955	958	958	7 OUCN 701+376 52 vCC, 24 SCCH, 8 SCCC1		
819m 713m	953 vw 902 vw 872 vw 822 m 757 vw 701 w	818 ₩ 697 m	832 705	658	866 742 655	738 647	2 527+376 527+345 54 vCCl, 34 δCNO, 15 δCCH 527+236, 376+376 99 vCN, 15 vCCl, 15 δCNO		
694 m	692 <b>v</b> w				691		376+315		
622 m 521 w	620 m 525 w	623 m 530 vs 467 m	617 526	600 506 453	600 500	595 494	61 vCCl, 28 8CNO 32 vCCl, 25 vCC		
	376 vw		386	356	368	375	42 δNCC].		
	345 vw 315 vw	348 m 317 s	340 314	338 318 290	339 318 290	311 294	72 SCCCI 43 SCCN. 36 vCN, 26 SCCCI		
	301 vvw 274 vw		301 266	261	266	214 265	97 tCC 53 vCCl, 50 &ClCcL 25 vCN		
Ŧ	236 vw	239 m	224	232	234	223	78 8NCCl, 18 8CNO, 10 8CCN		
79 <b>v</b> w T	I ,	1	77	l .		77	99 tCN		

TABLE 1. Wave Numbers (cm<sup>-1</sup>), Assignments of Bands, and Results from Calculation of Vibrational Spectra of  $CH_3CCl_2NO$  and  $CD_3CCl_2NO$ 

\*Band assigned to less polar conformer. +Wave number in gas phase.

are possible only if the number of conformers is greater than 2, and this has not been observed experimentally.

It can be expected that the trans-Cl conformer, in which the unshared electron pair of the N atom eclipses the C-Cl bond, will be less stable than the cis-Me conformer [1, 5-7]. Consequently, realization of the equilibrium (3) is very improbable.

The absence of the trans-Me conformer was confirmed by analysis of  $\Delta vQQ$  for bands of the B type. If the trans-Me conformer were stable,  $\Delta vQQ$  would amount to less than 0.5 cm<sup>-1</sup>; upon realization of the cis-Cl conformer,  $\Delta vQQ$  is 2.4 cm<sup>-1</sup>. In the IR spectra of gaseous (II), three bands - 453, 340, and 236 cm<sup>-1</sup> - have two Q branches each with  $\Delta v = 2.2$  cm<sup>-1</sup>. An appropriate value of  $\Delta vQQ$  (2.6-1.9 cm<sup>-1</sup>) is realized with a change of the Me-C-N=O angle from 80° to 130°, and from -35° to +35°. Consequently, the equilibrium (1) is realized in (I).

Analysis of the vibrational-rotational contours of vNO was performed on the basis of procedures given in [1]. When the equilibrium (1) is taken into account, the R-factor is

TABLE 2. Force Constants Obtained by Solving Inverse Vibrational Problem for CH<sub>2</sub>CCl<sub>2</sub>NO\*

Coordi- nates	Value	Coordinates	Value	Coordi- nates	Value
CH CC CNO CCCI CC tors. CN/CNO CCI/NCCI CN/NCCI CCI/CICCI	$\left \begin{array}{c} 4.87(0.01)\\ 3.73(0.70)\\ 2.04(0.39)\\ 1.26(0.09)\\ 0.17(0.01)\\ 0.88(0.20)\\ 0.55(0.15)\\ 0.45(0.24)\\ 0.12(0.29)\end{array}\right $	NO CCI CICN HCN C-N tors. CC/CCH CCI/CN CC/NCCI CN/CCN	$\begin{array}{c} 10,46(0,15)\\ 3,15(0,49)\\ 1,10(0,11)\\ 0,52(0,01)\\ 0,051(0,01)\\ 0,66(0,07)\\ 0,89(0,25)\\ -0,51(0,32)\\ -0,17(0,19) \end{array}$	CN ClCCl CCN CCH CH/CH CH/CCH CN/CCH CCI/CCCl	$\begin{array}{c} 2.64(0.26)\\ 1.50(0.44)\\ 0.87(0.27)\\ 0.67(0.02)\\ 0.06(0.01)\\ -0.04(0.01)\\ -0.07(0.32)\\ 0.67(0.30) \end{array}$

\*Dimensions of force constants: bond stretching constant and bond/bond interaction constant in mdyn/Å; angle deformation and interaction constants in mdyn·Å; angle/bond interaction constant in mdyn.

21.8%, for equilibrium (2) it is 25.7%, and for equilibrium (3) it is 26.9%. Consequently, equilibrium (1) is preferred; this supports the conclusion drawn on the basis of analysis of  $\Delta vQQ$ .

We were not successful in measuring the degree of depolarization in Raman spectra of (I), since the absorption at 4579 Å is some 10 times stronger for (1) than for  $(CH_3)_2CC1NO$ . Correspondingly, there are substantial increases in the rates of photochemical processes.

A calculation by the MNDO method with complete optimization of geometry indicates realization of two conformers with C-C-N=O dihedral angles of 120° and 240° (cis-Cl) and 0° (cis-Me). However, the barrier for the reaction cis-Me  $\rightarrow$  cis-Cl amounts to less than 0.1 kcal/mole. The barrier between the two equivalent minima for the cis-Cl conformer is likewise very small (0.2 kcal/mole). The results of this calculation do not contradict the conclusion that the equilibrium (1) is realized.

The difference in energy between the cis-Cl and cis-Me conformers, according to the calculation, is 0.85 kcal/mole; the experimentally determined enthalpy is 835 ± 28 cm<sup>-1</sup> (2.39 kcal/mole) in  $C_6H_{14}$ . The cis-Cl conformer is more stable.

All 21 vibrations of (I) should be manifested in the IR and Raman spectra. All vibrations have been found (Table 1). Using results from [1] and also literature data on halonitrosomethanes [5-7] and 1,1,1-trihaloethanes [8, 9], we can make a rather reliable assignment of all vibrations of (I). Certain difficulties arise in assigning the vibrations in the 1100-1200 cm<sup>-1</sup> region. There are two weak bands in this region, one of which (1084 cm<sup>-1</sup>, Table 2) was assigned to  $\rho$ CH<sub>3</sub>. However, we have not eliminated the possibility of assigning this band to a composite (822 + 274 cm<sup>-1</sup>).

<u>Analysis of Normal Coordinates.</u> For the analysis of the normal coordinates, we used the geometric parameters of related molecules: halonitroalkanes [10],  $CF_3NO$  [5], and  $CF_2$ -CINO [7]. The bond lengths (Å) were as follows: CC 1.529, CN 1.51, NO 1.195, CCl 1.731, and CH 1.09. All bond angles were taken as tetrahedral, with the exception  $\angle CNO = 112.4^{\circ}$ . As the initial approximation for the force fields we used literature data on  $CF_3NO$  [5, 6],  $CH_3CHF_2$  [8], and  $CCl_3NO_2$  [10].

The initial force field gave a poor description of the vibrational spectra of the cis-Cl conformer of (I). Therefore, we carried out a refinement of the valence-force field. The calculated frequencies and the potential-energy distribution are given in Table 1, and the set of force constants that were obtained is given in Table 2. The final 26-parameter force field describes the vibrational frequencies of the topological isomers of (I) with a standard deviation of 5.5 cm<sup>-1</sup>, maximum deviation 13 cm<sup>-1</sup>.

Using the results of the present work and those reported in [1, 5-7], we can conclude that the conformational equilibrium of  $\alpha$ -chloronitrosoalkanes is determined by repulsion of the unshared electron pair of the N atom. This leads to stabilization of conformers with the cis position of the N=0 and C-Cl bonds [1, 5-7]. A consequence of the stronger repulsion of the unshared electron pair from bulky methyl groups is the absence of the conformer with the trans position of the C-C and N=O bonds.

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## ELECTRONIC STRUCTURE AND MODELS OF RECEPTOR OF MONOOXYGENASE

INDUCTORS FROM A NUMBER OF POLYCHLORINATED POLYCYCLIC COMPOUNDS.

2. CALCULATION OF SUBSTRATE-RECEPTOR PAIRS IN PERTURBATION-THEORY APPROXIMATION

A. V. Fokin, N. P. Vorob'eva,UDC 530.145:547.722.4:547.556.3'131:Yu. A. Borisov, and A. F. Kolomiets547.841.2

A theoretical quantum-chemical analysis of the interaction of xenobiotics of the dioxin type with a model of their receptor in the ground state supports the possibility of forming rather stable substrate-receptor pairs, with not only oxidized but also reduced cytochrome P-450. General features have been identified in the interaction of the most dangerous xenobiotics of the dioxin type with the model of their receptor.

Kinetic studies of the interaction of the receptor of 2,3,7,8-tetrachlorodibenzo-pdioxin (TCDD) with its substrates [1, 2] have left no doubt that this act is the initial stage in the induction of specific isozymes of cytochrome P-450 by xenobiotics (XBs) of the dioxin type. To a certain degree this enables us to consider further that, in the present case, substrate-receptor interactions are also responsible for mediation of toxic effects. However, this hypothesis requires supporting evidence to the effect that 2,3,7,8-TCDD and similar substances can interact with cytochrome P-450, not only in the oxidized state (the effectiveness of interaction of  $\pi$ -donors with heme has been generally known for some time), but also in the reduced state.

Here we are reporting on quantum-chemical studies of the interaction at the molecular level, of 2,3,7,8-TCDD, 2,3,7,8-tetrachlorodibenzofuran (TCDF), 2,3,6,7-tetrachlorobiphenylene (TCBP), 3,3',4,4'-tetrachloroazobenzene (TCAB), and 3,3',4,4',5,5'-hexachlorodiphenyl (HCDP) with a model of a reduced receptor — iron porphyrin (FePr) in its ground state. To this end, we calculated the ground state of FePr; constructed correlation diagrams of the intermolecular interaction of the XBs with FePr; and, by means of the many-electron perturbation theory of Salem and Klopman [3] with a specially developed program, calculated the energies of their interaction.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2540-2544, November, 1989. Original article submitted September 16, 1988.