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C—H STRETCHING VIBRATIONS AND STRUCTURE OF NITROMETHANE DERIVATIVES $M(CH_2NO_2)$, M = Li, Na, K, Et_2In, Et_2Tl

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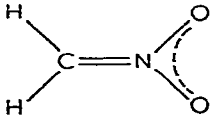
Summary

IR and Raman spectra of nitromethane derivatives $M(CH_2NO_2)$, (M = Li, Na, K, Et_2In, Et_2Tl) in the CH stretching region have been studied. ν(CH) frequencies at 3040 and 3170 cm^{-1} correspond to the aci-form of CH_2NO_2 with a sp^2 hybridized carbon atom. The nature of the metal has little influence on the CH stretching frequencies but strongly affects their intensity.

Introduction

While studying the IR spectra of diethylindium and diethylthallium derivatives of nitromethane we noticed the very high values of the CH stretching frequencies in the nitromethyl group; ~3040 and ~3170 cm^{-1} (see Table 1 and Fig. 1). As a rule, the CH frequencies of sp^2 hybridized carbon are found in this region of spectra, therefore these data confirm the aci-form of the compounds and a planar structure for fragment I, proposed for the sodium salt of nitromethane in [1] and confirmed in [2,3]. However, Jonathan and Brookes [2] found only weak bands at 2847 and 2920 cm^{-1} in the IR spectrum of the sodium salt of nitromethane, which they assigned to ν(CH) of the CH_2 group but were unable to explain the abnormally low frequencies of these bands. Yarwood and Orville-Thomas [4] rejected planar structure I and reinterpreted the IR data in terms of a model with an approximately sp^3 hybridized carbon atom with a



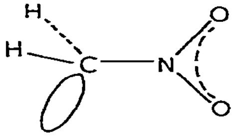
(I)

TABLE 1

THE CH STRETCHING FREQUENCIES IN THE SPECTRA OF NITROMETHANE DERIVATIVES $M(CH_2NO_2)$

M	$\nu(1)$ (cm^{-1})	Intensity R	Intensity IR	$\nu(2)$ (cm^{-1})	Intensity R	Intensity IR
Li	3030—3040	w(br)	m	3162	w	m
Na	3042	m	—	3172	w	—
K	3028	w	—	3159	m	—
Et_2In	3047	—	m	3174	—	s
Et_2Tl	3042	—	mw	3172	—	m

lone pair of electrons:



(II)

The nitromethyl and other nitroalkyl derivatives of boron [5], silicon [6], tin, lead [7] and monovalent thallium [8] are described in the literature. They were all shown to exist in the aci-form, however the region of CH stretching vibration of the CH_2NO_2 group has not been investigated. Thus, a contradiction arises between the values of ν(CH) for the sodium salt of nitromethane and structure I whereas the values of ν(CH) for nitromethane derivatives of diethylindium and diethylthallium are in agreement with structure I. It is unlikely that the replacement of the sodium cation by Et_2In or Et_2Tl groups would shift ν(CH) by ~200 cm^{-1}. In view of these facts we have undertaken further investigation of this spectral region for different metal nitromethane derivatives. We have obtained IR and Raman spectra of $M(CH_2NO_2)$, where

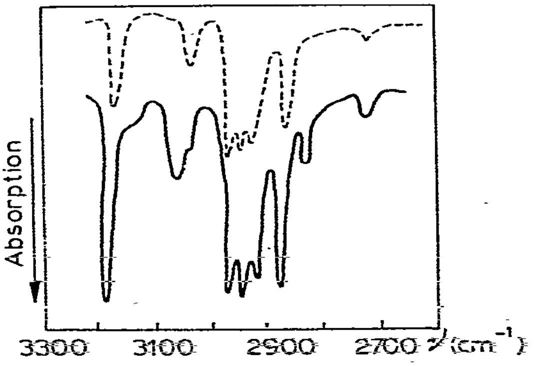


Fig. 1. ------ IR spectrum of $Et_2Tl(CH_2NO_2)$; ——— IR spectrum of $Et_2In(CH_2NO_2)$. The bands below 3000 cm^{-1} belong to CH stretching vibrations of the Et_2M group.

M = Li, Na, K, Et_2In and Et_2Tl. In this communication we report only the CH stretching frequencies of the nitromethyl group, the complete spectra will be discussed later [9].

Results and discussion

First of all we were unable to detect in the CH stretching region of the IR spectrum of the sodium salt either the bands, reported in [1,2], or any other bands. However, in the Raman spectrum the lines at 3042 and 3172 cm^{-1} are distinct (Fig. 2). Apparently, the authors of [2] had not observed these lines because they had used a Cary-81 spectrometer with a helium-neon laser; this instrument does not allow spectra to be run at frequencies greater than 2850 cm^{-1}.

The spectrum of the potassium salt is the same as for the sodium salt with only a certain redistribution of the intensities of the two Raman lines (Fig. 2). We only once succeeded in obtaining the Raman spectrum of the lithium salt, all other attempts ended in explosion of samples in the laser beam, even at low power. Consequently the Raman data for the lithium salt given in Table 1 should be considered as preliminary. However, in the IR spectrum of this salt the 3040 and 3162 cm^{-1} bands are sufficiently intense (Fig. 2).

The picture, observed for diethylindium and diethylthallium derivatives, is the reverse of that observed for the sodium and potassium salts: no Raman lines, corresponding to the intense IR ~3040 and ~3170 cm^{-1} bands, were found. The aci-form of $Et_2MCH_2NO_2$ (M = In, Tl) is indicated not only by the ν(CH) frequencies, but also by other frequencies of the vibrational spectra: ν(C=N) 1580 cm^{-1}, $\nu_{as}(NO_2)$ 1255 cm^{-1}, $\nu_{sym}(NO_2)$ 950 cm^{-1} and others, which will be reported in detail in [9]. Thus the structure, $M-CH_2-NO_2$ with a covalent M—C bond, proposed for these compounds in [10] and used by some of us in [11,12] seems to be erroneous. The data obtained do not allow us to

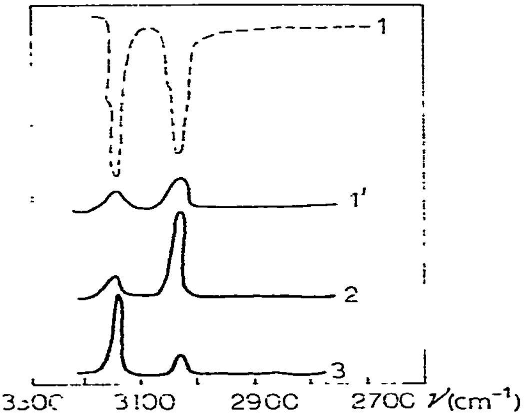


Fig. 2. 1 ------ IR spectrum of $Li(CH_2NO_2)$; 1^{1} ——— Raman spectrum of $Li(CH_2NO_2)$; 2 ——— Raman spectrum of $Na(CH_2NO_2)$; 3 ——— Raman spectrum of $K(CH_2NO_2)$.

conclude whether these compounds are ionic or whether the M—O bond is to a certain extent covalent. The latter structure was discussed in [7] for similar compounds of tin and lead and in [8] for monovalent thallium.

Our results allow to conclude that all nitromethane derivatives studied have structure I with a *sp*^{2} hybridized carbon atom and that the nature of the metal has little influence on the CH stretching frequencies but strongly affects their intensity. For sodium and potassium salts these vibrations are observed only in Raman spectra, for Et_2In and Et_2Tl derivatives only in IR spectra, whereas for the lithium salt these vibrations are observed in both spectra. The nature of this phenomenon is still unclear.

Experimental

The Li, Na and K salts of nitromethane were prepared as described in the literature [13], by mixing a solution of alkaline metal methoxide in absolute methanol with nitromethane and filtering the precipitate obtained. Diethylindium and diethylthallium derivatives of nitromethane were made by the methods described in [10,12]. All the compounds studied were fine-dispersed white powders, more or less unstable in air. They explode when heated and form yellow methazonates [14] when left in air.

The spectroscopic samples were prepared immediately after the synthesis in an atmosphere of purified dry argon. The Raman spectra were obtained using Coderg-PHO spectrometer equipped with a helium-neon laser of 5—50 mW, the samples were sealed in ampoules. Infrared spectra were obtained as Nujol mulls and in hexachlorobutadiene using UR-20 and Perkin—Elmer 457 spectrophotometers.

Acknowledgements

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References

1 N. Jonathan, J. Mol. Spectros., 7 (1961) 105.
2 M.J. Brookes and N. Jonathan, J. Chem. Soc. A, (1968) 1529.
3 M.J. Brookes and N. Jonathan, Spectrochim. Acta, 25A (1969) 187.
4 J. Yarwood and W.J. Orville-Thomas, J. Chem. Soc., (1963) 5991.
5 O.P. Shitov, L.M. Leontjeva and S.L. Ioffe, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2782.
6 M.V. Kashutina, S.L. Ioffe and V.A. Tartakovski, Dokl. Akad. Nauk SSSR, 218 (1974) 109.
7 J. Lorbert, J. Pebler and G. Lange, J. Organometal. Chem., 54 (1973) 165, 177.
8 A.G. Lee, Spectrochim. Acta, 28A (1972) 133.
9 L.A. Leites, A.P. Kurbakova, L.M. Golubinskaya and V.I. Bregadze, in press.
10 M.V. Kashutina and O.Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 1650.
11 V.I. Bregadze, T.I. Ivanova, L.A. Leites, L.V. Okhlobystina and O.Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 1505.
12 L.M. Golubinskaya, V.I. Bregadze, E.V. Bryuchova et. al., J. Organometal. Chem., 40 (1972) 275.
13 H. Feuer, C. Savides and C.N.R. Rao, Spectrochim. Acta, 19 (1963) 431.
14 C.M. Drew, J.R. Mc Nesby and A.S. Gordon, J. Amer. Chem. Soc., 77 (1955) 2622.