Reports of the Academy of Sciences of the USSR

O. A. Raevskii, R. R. Shagidullin, Yu. P. Kitaev

1964

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Vol. 159, No. 4

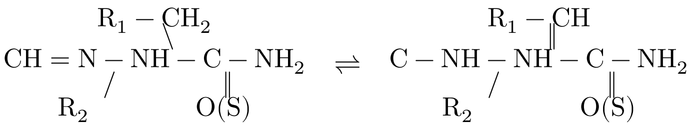
PHYSICAL CHEMISTRY

O. A. Raevskii, R. R. Shagidullin, Yu. P. Kitaev

VIBRATIONAL SPECTRA AND STRUCTURE OF THIOSEMICARBAZONES OF ESTERS OF CERTAIN KETO ACIDS

(Presented by Academician B. A. Arbuzov on 13 VI 1964)

Earlier (1), on the basis of a study of infrared absorption spectra, it was shown that the semi- and thiosemicarbazones (SC and TSC) of a number of aldehydes and ketones, of the two tautomeric forms assumed (2),



$$\underset{R_2}{\overset{R_1-CH_2}{CH}}=N-NH-\underset{O(S)}{\underset{\|}{C}}-NH_2 \rightleftharpoons \underset{R_2}{\overset{R_1-CH}{\overset{\|}{C}}}-NH-NH-\underset{O(S)}{\underset{\|}{C}}-NH_2$$

(I) (II)

exist in the free state in form I. It was natural to continue these investigations under conditions favoring a shift of the tautomeric equilibrium, and also on compounds for which a greater probability of existence in form II could have been expected.

Fig. 1

As such compounds we chose the TSC of esters of α-, β-, and γ-ketocarboxylic acids: (1) the TSC of the ethyl ester of pyruvic acid, (2) the TSC of acetoacetic ester, and (3) the TSC of ethyl levulinate. It may be assumed that conjugation should stabilize the enthiosemicarbazide form II in (2). For comparison, (3) was taken as a compound in which conjugation with the carboxyl group is excluded for both tautomeric forms.

We have found no information on the spectral study of these compounds. It is known, however, that on the basis of refractometric data Auwers (3) came to the conclusion that the phenylhydrazone of acetoacetic ester is already in the hydrazine form in the free state. In addition, a recently published work (4) gives the IR spectra of hydrazones of pyruvic acid without discussion of questions of tautomerism.

The IR absorption spectra of the compounds studied were recorded on double-beam infrared spectrophotometers IKS-14 and UR-10 using

using NaCl and LiF prisms. The spectral slit width was, for 700 cm^{-1}, 4.0 cm^{-1}; 1000–4.0; 1500–6.0; 2000–6.5; 3000–15.0. In the solid phase the substances were recorded as pressed tablets with KBr. The Raman spectra (R.s.) were obtained on a DFS-12 spectrometer.

Figures 1 and 2 show the obtained spectrograms of the IR absorption spectra and Raman spectra. The most distinct differences may be expected for forms I and II of compound (2). For tautomer I an unconjugated carbonyl should be observed; for II, a conjugated one. As model compounds, compound (3) may serve for judging the position of the unconjugated carbonyl, and compound (1) for that of the conjugated carbonyl. Table 1 gives the frequencies of the double bonds in the crystalline state and in solutions.

Table 1

	$\nu_{C=O}$ 1	$\nu_{C=O}$ 2	$\nu_{C=O}$ 3	$\nu_{C=N}$ 1	$\nu_{C=N}$ 2	$\nu_{C=N}$ 3
IR spectrum of crystal	1708	1719	1719	1628 (assigned to NH and NH_2)	superimposed on δNH_2	superimposed on δNH_2
Raman spectrum of crystal	1706	1726	1727	1627	1645	1660
Raman spectrum of solution in nitromethane	1719	not detected	not detected	1614	1643	1654

	$\nu_{C=O}$ 1	$\nu_{C=O}$ 2	$\nu_{C=O}$ 3	$\nu_{C=N}$ 1	$\nu_{C=N}$ 2	$\nu_{C=N}$ 3
Raman spectrum of solution in acetone	1719	»	»	1612	1642	–
Raman spectrum of solution in triethylamine	1720	»	»	1606	–	–
Raman spectrum of solution in methanol	1720	»	»	1605	1643	1655

The spectra of the substances isolated from solutions by evaporation coincided with the spectra of the initial substances, which makes it possible to exclude from consideration chemical interaction with the solvent.

As can be seen from these data, in (1) both $\nu_{C=O}$ and $\nu_{C=N}$ have values lowered in comparison with (3), in agreement with the assumption of the possibility of conjugation. $\nu_{C=O}$ of (2) has the same value as $\nu_{C=O}$ of (3). The relative intensities of $\nu_{C=O}$ in the Raman spectra of (1) are also appreciably higher than in (2) and (3). All this indicates the absence of conjugation of the carboxyl group in compound (2) with any other multiple bond and, consequently, as already mentioned, argues in favor of its existence in tautomeric form I. The frequency of the double bond in (2) is somewhat lower than in (3), but is sufficiently close to the range of its usual occurrence in the thiosemicarbazones of the aliphatic series (1640–1660) (1). A certain lowering of the frequency for (2) in comparison with $\nu_{C=N}$ of (3) apparently can be explained by interaction of the π-clouds of the double bonds through the methylene group. It is also seen from the table that the frequency $\nu_{C=N}$ of (2) and (3) does not undergo substantial changes upon dissolution. These frequencies retain their values also when the concentrations of the solutions are changed. From all this it may be concluded that compounds (2) and (3) do not undergo tautomeric transformations. The absence in the spectrum of (3).

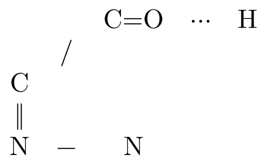
Fig. 2

in the 700–1000 region, any additional bands in comparison with (2) (out-of-plane CH in C=C vibrations), and the appreciable increase in the absorption intensity at ~ 2900 cm^{-1} (ν_{CH_2}) also indicate its existence in form (I). Spectrum (2) has characteristic features: the $\nu_{C=O}$, δ_{NH_2}, and ν_{NH_2} bands are split. We explain this by interaction of the indicated vibrations in the crystal lattice. The lower value of $\nu_{C=O}$ for (2) and (3), compared with that usual for a complex-ester grouping, may be explained by the presence of hydrogen bonds. For (1) this is confirmed by the increase of $\nu_{C=O}$ in solution. To resolve the question of the structure of compound (1), UV spectra and NMR spectra in acetone and pyridine were also obtained.* In the NMR spectrum of a concentrated solution of the compound in acetone, the protons of the $-CH_2$ group (for form II) are not observed. These protons are also not observed in the case of a pyridine solution; moreover, the integral intensities of the signals of the acid methyls ($\tau = 7.80$ ppm) and of the ester group ($\tau = 8.56$–9.20 ppm) proved to be equal, which indicates the absence of appreciable amounts of form II.

The following three variants are possible: a) in the crystalline state and in concentrated solution, compound (1) exists in form I, and in dilute solution, in form II; b) in the crystalline state, in II, and in concentrated and dilute solutions, in I; c) in the crystalline state and in solutions, in form I.

The fact that in the spectra of solutions of different polarity no appearance of two bands of the stretching vibrations of double bonds (apart from the carbonyl one) was observed, and also the absence of changes upon variation of concentration, casts doubt on the first variant. For case (b), it could have been expected that some band of appreciable intensity in the 700–1000 cm^{-1} interval (out-of-plane deformation vibrations of CH in C=C) should be absent in the spectra of solutions, which, however, was not observed. A complete transition into one of the forms immediately upon dissolution also seems unlikely.

Thus it appears possible to state also for compound (1) the absence of tautomeric transformation under the conditions studied and its existence in form I. This conclusion is also supported by the absence of substantial differences between the UV spectra of (1) in the solid state and in solutions. The structure of compound (1) permits the formation of a chelate ring with an intramolecular hydrogen bond—



However, the increase of $\nu_{C=O}$ in solution to 1719 cm^{-1}, a value normal for a conjugated complex-ester carbonyl, indicates that C=O participates only in the

(V) and (IV)

Figure 2: (V) and (IV)

(VII) and (VIII)

Figure 3: (VII) and (VIII)

formation of an intermolecular hydrogen bond. Therefore we consider it possible to propose the following arrangement of bonds for this part of the molecule (III).

$$C_2H_5O{-}C(=O){-}C(CH_3){=}N{-}N{-}C{=}N{-}N{=}C(SCH_3)NH_2$$

(III) (IV)

* The NMR spectra were obtained on a YaMR-KGU-1 spectrometer by Yu. Yu. Samitov and A. A. Musina, to whom the authors express their sincere gratitude.

Previously it was shown[5] that methylation of TSC under mild conditions readily proceeds at sulfur with formation of structure (IV). Therefore it may be assumed that the $C = S$ and $N^2 - H$ bonds are close to one another (V), and that in the molecules of the starting TSC, apparently, there is a displacement of the electron clouds toward the limiting structure (VI).

Thus, taking the trans-configuration as the most probable, one may, using example (1), propose the following arrangement of bonds in the TSC molecule:

In this case conjugation is strengthened at the expense of structure VIII. The latter may explain the fact that all the compounds spectrally investigated so far have proved to be carbazone tautomers. This form must be stabilized owing to conjugation. The very high intensity of $\nu_{C=N}$ in the Raman spectra of the TSC, both those discussed in the present work and a number of other compounds studied by us, also agrees with the assumption of the presence of strong conjugation and, consequently, corresponds to the statements made concerning the features of their structure. The lowering of the frequency $\nu_{C=N}$ (1) in the polar solutions investigated apparently should be explained by the formation of associates with solvent molecules at the $C = N$ bond, which may be due to the presence in molecule I of a longer and, consequently, more readily polarizable conjugated chain.

Chemical Institute named after A. E. Arbuzov
Academy of Sciences of the USSR

Received
10 VI 1964

REFERENCES CITED

1. R. R. Shagidullin, F. K. Sattarova et al., *Izv. AN SSSR, ser. khim.*, 1964, 967.

2. Yu. P. Kitaev, G. K. Budnikov, A. E. Arbuzov, *DAN*, **127**, 818 (1959).

3. K. Auwers, H. Wunderling, *Ber.*, **63**, 1072 (1930).

4. M. K. Hargreaves, E. A. Stevinson, *Spectrochim. acta*, **20**, 317 (1964).

5. R. R. Shagidullin, F. K. Sattarova et al., *Izv. AN SSSR, ser. fiz.*, **25**, 1301 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.