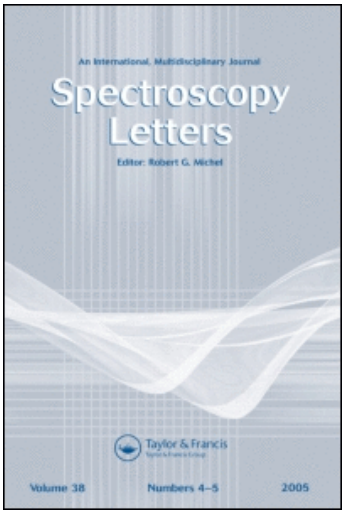

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New Identification Bands in the Infrared Spectra Of 1- and 2-Substituted Benzotriazoles

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NEW IDENTIFICTION BANDS IN THE INFRARED SPECTRA OF 1- AND 2-SUBSTITUTED BENZOTRIAZOLES

Key words: Infrared spectra, Benzotriazoles, Identification bands

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ABSTRACT

Some new identification bands characteristic of 1- and 2-substituted benzotriazole derivatives have been found in their infrared spectra. The skeletal in-plane rings vibration near 1490 cm^{-1} and some bands in the 795-760 cm^{-1} region have been typical for 1-substitiuted compounds whereas the vibrations at 875-820 cm^{-1} have been observed as characteristic of a quinoid system of 2-substituted benzotriazoles. New characteristic bands examination allows to identify better both isomers.

INTRODUCTION

The characteristic of 1-substituted benzotriazole derivatives bands at 1618 and 1588 cm^{-1} as well as of 2-substituted derivatives at 1570-1550 cm^{-1} and 1330-1325 cm^{-1} have been described in the infrared spectra of some dialkylaminoalkyl or hydroxyalkyl derivatives of benzotriazole[1]. The bands at 1625-1610 cm^{-1} have

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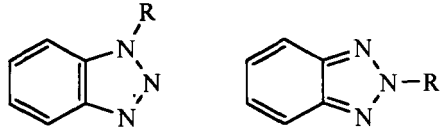
been attributed to the stretching vibrations of N=N bond whilst in the 1600-1595 cm^{-1} region absorption to the C=N stretching vibrations in the IR spectra of some 1-acyl- and 1-alkenylbenzotriazoles[2]. Alternatively, the bands at 1618 cm^{-1} have been described as arising from C=C bond streching vibrations, at 1601 cm^{-1} from C=N, and in the region of 1500 cm^{-1} corresponding to skeletal in-plane rings vibrations of benzotriazole molecule in the IR spectra of some 1-substituted or unsubstituted at nitrogen atoms benzotriazoles[3].

The problem to distinguish 1- and 2-substituted benzotriazole derivatives is important considering the formation of usually both isomers after alkylation:



1- 2-

The 1- and 2-substituted benzotriazoles can also be distinguished using other spectroscopic methods, as the ultraviolet absorption spectra in hexane (1-substituted compounds - two maxima at 254 and 284 nm, 2-substituted - one maximum at 275-276 nm)[4] or the electron impact mass spectra (typical for 1-substituted compounds was $M^{+\cdot}$- N_2 and *m/z* 104 ions; and for 2-substituted ones - the *m/z* 105 ion)[5].

In this paper the infrared spectra of some 1- and 2-substituted benzotriazoles were described and discussed. Some new identification bands characteristic of 1- and 2-substituted benzotriazole derivatives were found in the spectra.

EXPERIMENTAL

Materials

1-Methylbenzotriazole **2** and 2-methylbenzotriazole **3** were obtained from benzotriazole **1** according to the literature[5]. The mixture of isomers was separated by column chromatography on silica (Merck Kieselgel 60 mesh), mobile phase: hexane + ethyl acatate (1:1 *v/v*); **2**: R_f= 0.71; **3**: R_f= 0.54.

1- and 2-carboalkoxyalkylbenzotriazoles **4-23** were synthesised from benzotriazole 1 and appropriate C_1-C_4 alkyl chloroacetate, 1-chloropropionate or 2-chloropropionate in the presence of anhydrous potassium carbonate in dry acetonitrile. After vacuum distillation the products were purified by column chromatography in the described above conditions; thus, the following compounds were obtained: 1-

carbomethoxymethylbenzotriazole **4**, 2-carbomethoxymethylbenzotriazole **5**, 1-carboethoxymethylbenzotriazole **6**, 2-carboethoxymethylbenzotriazole **7**, 1-carbopropoxymethylbenzotriazole **8**, 2-carbopropoxymethylbenzotriazole **9**, 1-carbobutoxymethylbenzotriazole **10**, 2-carbobutoxymethylbenzotriazole **11**, 1-(2-carbomethoxy)ethylbenzotriazole **12**, 2-(2-carbomethoxy)ethylbenzotriazole **13**, 1-(2-carboethoxy)ethylbenzotriazole **14**, 2-(2-carboethoxy)ethylbenzotriazole **15**, 1-(2-carbopropoxy)ethylbenzotriazole **16**, 2-(2-carbopropoxy)ethylbenzotriazole **17**, 1-(1-carbomethoxy)ethylbenzotriazole **18**, 2-(1-carbomethoxy)ethylbenzotriazole **19**, 1-(1-carboethoxy)ethylbenzotriazole **20**, 2-(1-carboethoxy)ethylbenzotriazole **21**, 1-(1-carbobutoxy)ethylbenzotriazole **22** and 2-(1-carbobutoxy)ethylbenzotriazole **23**.

1- and 2-carboamidoalkylbenzotriazoles **24-29** and analogical hydrazides **30-31** were obtained in the reaction of the appropriate ester with ammonia or hydrazine following the crystallization or above chromatographic separation.

The structures of all compounds were entirely confirmed by other spectral methods as NMR and MS. The synthetic details will be published in a separate paper.

Apparatus

The infrared spectra were measured on a Zeiss Specord M 80 or Specord 75 IR spectrometers in KBr pellets (solids, 0.8 mg/270 mg KBr) or as a film between KBr plates (liquids) at 2 cm^{-1} resolution.

RESULTS

In obtained infrared spectra some bands typical for appropriate functional group were observed. Thus, in the spectra of compounds **4-31** (solids) the characteristic vibrational bands were present: the C=O stretching vibrations of -COOR group in the esters **4-23** at 1740-1730 cm^{-1}, the amide I band at 1680-1650 cm^{-1} and the II band at ca. 1630-1620 cm^{-1} in the amides **24-29** as well as some analogous bands characteristic of hydrazides at 1655 cm^{-1} and ca. 1610-1600 cm^{-1}.

In the spectra of compounds **1-31** the majority of known identification bands[1] were also found: for 1-substituted benzotriazole derivatives at 1604-1619 and 1581-1590 cm^{-1} whilst for 2-substituted derivatives at 1568-1541 and 1340-1322 cm^{-1} regions, depending on the substitution position. A few exceptions were IR spectra of some 1-substituted amides **24**, **26** i **28** and hydrazide **30**, where the

TABLE 1

Infrared band frequencies in *A*, *B*, and *C* regions of 1- and 2- substituted benzotriazole derivatives **1-3** and esters **4-31**.

No	Substituent	Position	Band frequencies, cm^{-1}		
			A	*B*	*C*
1	-H	1			790m, 780m
2	$-CH_3$	1	1490m		775m, 755m
3		2		870w, 840s	
4	$-CH_2COOCH_3$	1	1490m		790m, 775w, 770m
5		2		860m, 837 w	
6	$-CH_2COOC_2H_5$	1	1495m		780m, 770w, 765m
7		2		875w, 845w	
8	$-CH_2COOC_3H_7$	1	1495m		793m, 770w, 760m
9		2		855m, 837w	
10	$-CH_2COOC_4H_9$	1	1495m		785m, 770m, 760m
11		2		863m, 840w	
12	$-(CH_2)_2COOCH_3$	1	1487m		775m, 765m
13		2		847m, 821w	
14	$-(CH_2)_2COOC_2H_5$	1	1485m		780m, 765w, 760m
15		2		865m, 840w	
16	$-(CH_2)_2COOC_3H_7$	1	1490m		780m, 765m
17		2		857w, 821w	
18	$-CH(CH_3)COOCH_3$	1	1490m		780m, 765m
19		2		856m, 825m	
20	$-CH(CH_3)COOC_2H_5$	1	1485m		780m, 765m, 760m
21		2		857m, 826m	
22	$-CH(CH_3)COOC_4H_9$	1	1490m		780m, 767m
23		2		840w, 826m	

TABLE 2

Infrared band frequencies in *A*, *B*, and *C* regions of 1- and 2- substituted benzotriazole derivatives - amides and hydrazides **24-31**.

No	Substituent	Posi-tion	Band *A*	frequencies, *B*	cm^{-1} *C*
24	$-CH_2CONH_2$	1	1495m		773w, 762m
25		2		847w, 856w	
26	$-(CH_2)_2CONH_2$	1	1490m		775m, 760w, 750m
27		2		851m	
28	$-CH(CH_3)CONH_2$	1	1495w		783m, 755m
29		2		844w	
30	$-CH_2CONHNH_2$	1	1495m		791w, 764w
31		2		874w	

identifications bands in the region of 1620-1590 cm^{-1} were covered with the amide bands.

However, in the IR spectra of all benzotriazoles **1-31** some new band groups characteristic of 1- and 2-substituted compounds were observed. This bands may be found in three regions: *A* region at 1495-1485 cm^{-1}, *B* at 875-821 cm^{-1} and *C* at 793-760 cm^{-1}. The measured frequencies of these bands in the spectra of compounds **1-3** and esters **4-23** are presented in Table 1, and in the spectra of amides and hydrazides **25-31** are shown in Table 2.

DISCUSSION

In the *A* region at 1495-1485 cm^{-1} only one (usually medium) band was observed, but exclusively for 1-substituted benzotriazoles. It can be attributed to skeletal in-plane rings vibration of heterocyclic ring system in aromatic 1-substituted benzotriazoles[3], which is absent from the spectra of all 2-substituted compounds containing a quinoid ring system. However, this band seems to be non-specific and it may be expected in IR spectra of other non-chinoid benzotriazole derivatives; *e.g.* in the spectrum of 1-acetyl-5-methoxybenzotriazole[3] this vibration band can be observed at 1500 cm^{-1}.

TABLE 3
Infrared band frequencies in *A*, *B*, and *C* regions of some selected 1- and 2-substituted benzotriazole derivatives **32-40.**

No	Substituent	Position	Band *A*	frequencies, *B*	cm-1 *C*	Reference
32	$-(CH_2)_2OH$	1	1495m		790s, 773s, 768m	1
33		2		837s		1
34	$-(CH_2)_3N(CH_3)_2$	1	1495m		785s, 770m	1
35		2		865w, 835m		1
36	$-COCH_3$	1	1495m		794m, 782s	2
37	$-CH=CH_2$	1	1495m		790s, 770m	2
38	$-C(CH_3)=CH_2$	1	1495m		788s, 770m	2
39	$-CH_2COOH$	1	1495m		771m, 761w	6
40	$-CH_2CONHOH$	1	1495m		770m, 760m	6

In the *B* region at 875-820 cm^{-1} two or sometimes one band (medium to weak) was found only in the 2-substituted benzotriazole series whilst in the 795-760 cm^{-1} *C* region absorption, two to three bands (usually medium to strong) were observed as characteristic only for 1-substituted compounds. These groups of bands can arise from either out-of-plane rings vibrations or C-H deformations of benzotriazole aromatic or quinoid systems.

We have checked that all above bands may be easily observed in many previously publihed infrared spectra as well as in IR spectra of some new compounds. Some exemples are presented in Table 3.

CONCLUSION

New identification bands in IR spectra of 1- and 2-substituted benzotriazoles in the 1495-1485, 875-820 and 795-760 cm^{-1} regions allows to identify better both isomers. The confirmation of the presence of these bands is especially usefull when other identification bands at 1618-1588, 1570-1540 and 1330-1325 cm^{-1} are covered with the bands of another functional groups.

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