

About the Nature of Carbon-Nitrogen Triple Bond in Complexes of Nitriles with Strong Lewis Acids

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Complexes of nitriles **1** – **7** with antimony(V) fluoride in cryogenic matrices were studied by FT-IR spectroscopy. A large increase in C≡N stretching frequency induced by complexing with SbF₅ is observed in all investigated nitriles. From the vibrational changes of the nitrile molecule skeleton, it was found that the polarity of the nitrile group is increased in the complex. The inductive effect caused by complexing with SbF₅ was studied by observing the changes of C-CN stretching and CH₃ or CH₂ deformation vibrations. The qualitative similarity between vibrational changes induced either by complexing or by ionization of nitriles is discussed. Current interpretations of the *nitrile effect* by rehybridization of nitrogen or by partially antibonding character of the σ orbital of CN bond are discussed on the basis of both the IR spectra and high level *ab initio* calculations.

INTRODUCTION

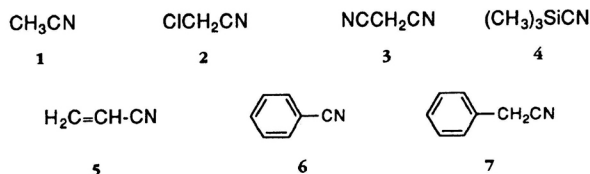
It is important to study the reactions of nitriles with strong Lewis acids because these reactions could *inter alia* be applied to the preparation of nitrenium ions under the stable ion conditions.¹ IR and Raman spectroscopic investigations of such reactions demonstrated that the *in situ* formed complexes of nitriles with metallic cations induce interesting spectral properties. Namely, the C≡N stretching frequencies are higher in the complexes than in the starting nitriles.² For this effect, we use the *terminus technicus*: *nitrile effect*. Similar spectral changes were observed also in cryogenic argon matrices³ if nitriles were protonated with HX (X = F, Cl, Br). *Ab initio* calculations have also shown that protonation of nitriles leads to a shortening of CN bonds accompanied by an increase in the CN stretching vibration.⁴ This vibrational effect is opposite to that observed in the complexes of ketones and aldehydes with Lewis acids which induce a »normal« low frequency shift of the C=O stretching.⁵ In the past, the *nitrile effect* was explained either as nitrogen rehybrid-

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zation effect⁶ or as a consequence of electron withdrawal from partially antibonding CN σ orbital.⁷ Frequency decrease in ketone-Lewis acid complexes is explained as a consequence of an additional polarization of the C=O π bond. Analogously, it could be expected that the polarity of the C \equiv N bond should also be increased in complexes. However, the *nitrile effect* is the dominant effect that prevents direct observation of the C \equiv N bond polarization by measuring its stretching frequency. For this reason, the C \equiv N polarization should be examined indirectly from the changes of vibrational frequencies and NMR chemical shifts *in the rest of the nitrile molecule*. Olah and co-workers⁸ have already observed a down-field shift of CH and CH₂ protons in ¹H-NMR spectrum of acrylonitrile-Lewis acid complex.

In the majority of spectral studies of nitrile complexes,^{2,8,9} a detailed analysis of IR spectra was carried out mainly for the CN stretching region. Detailed assignment of the complete spectrum (400 – 4000 cm⁻¹) was provided by Shriver and coworkers¹⁰ for the acetonitrile-SbF₅ complex. It follows from this analysis that not only the CN but also the C-C stretching frequency increases in the complex. The observed stretching frequency shifts were +61 cm⁻¹ for the CN bond and +30 cm⁻¹ for the C-C bond. This result supports the already mentioned hypothesis⁷ on the withdrawal of electrons from the partially antibonding σ orbital and also demonstrates the through- σ -bond interaction of the CN group with the rest of the molecule. Such an effect is a consequence of the *end-on coordination* of nitriles in which the nitrogen n electrons interact with the empty orbital of the Lewis acid molecule. However, in complexes with *side-on coordinated* nitriles,² electrons are drawn from CN π orbitals. Consequently, the C \equiv N stretching frequency of *side-on coordinated* nitrile complexes is lower than in the corresponding free nitriles.

This article is designed as an attempt to explain the relationship between the changes of the CN stretching frequencies and the nature of the C \equiv N bond. The *nitrile effect* is studied mainly on the basis of vibrational changes in the rest of the nitrile molecule obtained from the spectra of several nitrile-SbF₅ complexes. Nitriles **1** – **7**, used here as model compounds, have different structures of the hydrocarbon skeleton. As the simplest nitrile, acetonitrile **1** can serve as the referent structure for comparison with previously published spectra.^{9b,c,f,i,10} Chloroacetonitrile **2**, malononitrile^{9e} **3** and trimethylsilylnitrile **4** are good models for the study of the inductive effect on the *nitrile effect*. The conjugative effect, which should give information on the polarization of C \equiv N bonds, is investigated by complexing acrylonitrile^{9g} **5**, benzonitrile^{9h,i} **6** and phenylacetonitrile **7**. Additionally, the vibrational changes of the nitrile group of HCN, obtained by its complexing with Lewis acids, are also compared with the vibrational changes obtained by photoionization of the HCN molecule.¹¹ We wish to discuss the similarity between the structures of radical cations and the corresponding *carbocation-like* nitrile complexes. This analogy will provide a deeper insight into the problem of the *nitrile effect*. The change of the nature of the CN triple bond induced by protonation is investigated in more detail by means of high level *ab initio* calculations for acetonitrile (**1**), HCN, CN⁻, N₂ and their protonated forms.



RESULTS

Nitrile-SbF₅ complexes were prepared using the matrix isolation method previously developed for the isolation and IR spectroscopy of carbocations in SbF₅. In a typical experiment¹², nitrile and SbF₅ were codeposited on a CsI window cooled to 77 K. Conversion of nitriles to complexes was attained by warming up the matrix to 180 – 250 K. The appearance of complexes was followed by recording IR spectra at different temperatures.

TABLE I
Vibrational frequencies (ν/cm^{-1}) of nitriles 1 – 4 and their complexes with SbF₅

	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}-\text{C})$	$\delta(\text{CH}_3 \text{ and } \text{CH}_2)$
1	2248	920	1375
1-SbF ₅	2302	960	1357
$\Delta\nu$	+54	+40	-18
2	2255	927	1410
2-SbF ₅	2305	937	1393
$\Delta\nu$	+50	+10	-17
3	2274	892 A ₁	1394
		982 B ₂	
3-SbF ₅	2337	885 A ₁	1386
		1028 B ₂	
$\Delta\nu$	+63	-7 A ₁	-8
		+46 B ₂	
4	2192	—	—
4-SbF ₅	2256	—	—
$\Delta\nu$	+64	—	—

Acetonitrile (1). The observed spectral changes (Table I) are very similar to those previously reported.¹⁰ While the C≡N stretching frequency shift (+54 cm⁻¹) is somewhat smaller (Table I), the change of the C-C stretching frequency (+40 cm⁻¹) is larger than in Shriver's paper.¹⁰ An increase in frequency is also observed in the C-H stretching region where a new peak (a shoulder) appeared at 3002 cm⁻¹.

Chloroacetonitrile (2). Although the new C≡N stretching band at 2305 cm⁻¹ appeared already in the spectrum recorded at 77 K, the entire conversion to the complex was completed above 240 K. The change in the C≡N stretching frequency is +50 cm⁻¹ ($\nu_{\text{C}\equiv\text{N}}$ of the starting nitrile is 2255 cm⁻¹, Table I). This value is very close to the shift observed in acetonitrile. However, the increase in the C-C stretching frequency (+10 cm⁻¹) is smaller than in acetonitrile (+40 cm⁻¹). The frequency of the CH₂ bending is shifted to lower values.

Malononitrile (3). In the spectrum of 3, recorded at 77 K in the SbF₅ matrix, two C≡N stretching bands were observed. The band at 2274 cm⁻¹ belongs to the un-

reacted **3** and the band at 2337 cm^{-1} is assigned to the complex with SbF_5 . This 63 cm^{-1} increase in frequency is similar to that of **1-SbF₅** (Table I). In the C-C stretching region of the IR spectrum of the starting **3**, two vibrations are active: A_1 at 892 cm^{-1} and B_2 at 982 cm^{-1} . By complexing with SbF_5 , the A_1 band is shifted to 885 cm^{-1} and B_2 to 1028 cm^{-1} .

Although the effect of the second CN group cannot be unequivocally explained by the presented IR spectral data, it could not be excluded that both the CN groups are coordinated with SbF_5 . However, the intensity ratio of both signals assigned to the free and complexed CN groups, respectively, remained the same at all temperatures. This could be an indication that only one CN group is coordinated.

Trimethylsilylnitrile (4). After the reaction with SbF_5 , the $\text{C}\equiv\text{N}$ stretching frequency was shifted from 2192 to 2256 cm^{-1} ($\Delta\nu = +64\text{ cm}^{-1}$). In the spectrum recorded at 150 K , a new signal appeared at 2099 cm^{-1} , which is assigned to the $\text{C}\equiv\text{N}$ stretching of HCN. Appearance of HCN is a consequence of partial hydrolysis of **4**. Further warming of the matrix to 260 K revealed a new spectrum, which could be assigned to $(\text{CH}_3)_3\text{SiF}$, but the spectrum was not analyzed in detail.

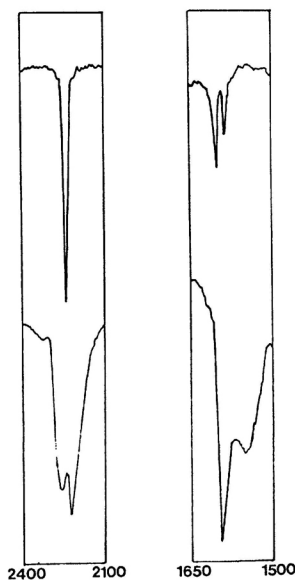


Figure 1. IR spectra of benzonitrile (upper spectrum) and benzonitrile-antimony pentafluoride complex (bottom spectrum) in cryogenic SbF_5 matrix.

Acrylonitrile (5). Two $\text{C}\equiv\text{N}$ stretching bands, at 2225 and 2275 cm^{-1} , appeared in the spectrum of **5** in the SbF_5 matrix at 77 K (Table II). The band at 2275 cm^{-1} belongs to the **5-SbF₅** adduct. The spectrum of precursor **5** disappeared above 220 K . The observed $\text{C}\equiv\text{N}$ stretching frequency shift ($+50\text{ cm}^{-1}$) is the same as in the case of **5-BF₃** adduct.^{9g} The most interesting spectral change is the decrease of the $\text{C}=\text{C}$ stretching frequency from 1605 cm^{-1} to 1592 cm^{-1} .

TABLE II
Vibrational frequencies (ν/cm^{-1}) of nitriles **5** – **7** and their complexes with SbF_5

	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$	$\delta(\text{CH}_2)$
5	2225	1605	1380
5-SbF₅	2275	1592	1380
$\Delta\nu$	+50	-13	0
6	2222	1600	–
		1536	
6-SbF₅	2260	1587	–
		1545	
$\Delta\nu$	+38	-13	–
		-41	
7	2260	1605	1419
		1590	
7-SbF₅	2298	1600	1385
		1586	
$\Delta\nu$	+38	-5	-34
		-4	

Benzonitrile (6). Vibrational changes observed by coordinating **6** with SbF_5 are more complicated. Positions of the $\text{C}\equiv\text{N}$ stretching bands changed at different temperatures. At 77 K, two bands, at 2222 and 2260 cm^{-1} appeared in the spectrum (Table II). Both bands vanished above 200 K with the appearance of a new signal at 2248 cm^{-1} . Like in the complex **5-SbF₅**, the spectral positions of bands assigned to $\text{C}=\text{C}$ stretching of the aromatic ring were changed (Figure 1).

Phenylacetonitrile (7). While the value of the $\text{C}\equiv\text{N}$ stretching frequency shift resembles the values observed in previous adducts (from 2260 cm^{-1} to 2298 cm^{-1}), the $\text{C}=\text{C}$ stretching frequencies remained unchanged upon complexing (Table II). However, a significant change was observed for the CH_2 bending. Its frequency was shifted from 1419 cm^{-1} in **7** to 1385 cm^{-1} in the **7-SbF₅** adduct. A similar frequency decrease was also observed in **1-SbF₅** and **2-SbF₅**.

The CN⁻ Ion. This anion was prepared from nitrile **4** using the Tesla coil discharge technique.¹³ Passing through the discharge tube, the precursor molecules split into fragments, which were immediately deposited into a CsI window cooled to 10 K. The signal at 2085 cm^{-1} was assigned to the CN stretching vibration of the CN^- ion. This value is almost identical to the frequency observed for the CN^- anion in water solution.^{7a} Protonation of CN^- leads to HCN, for which we found higher frequency (2099 cm^{-1}) in the spectrum recorded under similar experimental conditions.

DISCUSSION

Conjugative and Inductive Effects

Reorganization of electrons which takes place in a nitrile molecule during the formation of a nitrile-Lewis acid complex can be considered as a redistribution of π

and σ electrons. Delocalization of π electrons from CN group to the rest of the nitrile molecule is investigated in experiments with adducts **5**-SbF₅, **6**-SbF₅ and **7**-SbF₅. While complexing of **5** and **6** with SbF₅ induced a substantial decrease in the C=C stretching frequencies, the C=C stretching spectral region remained unchanged on the complexing of **7** with SbF₅. Namely, the conjugation of π electrons in this complex is hindered by the additional CH₂ group. The frequency decrease of C=C stretching vibrations supports an earlier Olah's suggestion⁸ about increased π conjugation in protonated **5**.

The inductive effect of the R group in R-CN molecules **1** – **4** on the $\Delta\nu_{\text{CN}}$ value was not observed because $\Delta\nu_{\text{CN}}$ does not correlate with the electron-donating (or electron-withdrawing) ability of different R groups. However, the through-bond σ effect induced by coordinated Lewis acids can be followed by measuring the vibrational changes of C-C and C-H bonds in the rest of the nitrile molecule. Such changes were observed in the acetonitrile complex. The C-C stretching frequency is increased by 40 cm⁻¹ and the CH₃ deformation frequency is decreased by 18 cm⁻¹. This latter decrease can be compared with a similar vibrational change measured in the fine structure of the photoelectron spectrum of acetonitrile.¹⁴ Ejection of an n electron from the acetonitrile molecule (2nd I.P. at 13.14 eV) reduces the CH₃ deformation frequency from 1376 to 1370 cm⁻¹. This through-bond effect was previously explained as a consequence of relatively large 4a₁ orbital coefficients situated at C-C and C-H bonds.¹⁴

A frequency decrease of the CH₂ deformation is also observed in the spectra of chloro- and phenylacetonitrile complexes ($\Delta\nu = -17$ and -34 cm⁻¹). The inductive withdrawal of electrons by the chlorine atom in the adduct **2**-SbF₅ reduces the increase in frequency of the C-C stretching vibration to only +10 cm⁻¹ (Table I). However, the inductive effect of the second nitrile group in the **3**-SbF₅ complex cannot be recognized from the changes in the C-C stretching region. The frequency increase of the B₂ vibration (asymmetric stretching of carbon-carbon bonds) is +46 cm⁻¹ in this complex, even larger than in **1**-SbF₅.

Comparison with the Vibrational Changes Induced by Photoionization

Frequency shifts observed upon the complexing of electron rich functional groups with strong Lewis acids can be qualitatively compared with the changes in vibrational frequencies measured from the fine structure of photoelectron spectra. In both cases, it is possible to identify the particular orbital from which an electron is ejected by photoionization or withdrawn by complexing. Ionization of carbonyl compounds by removal of an electron from the oxygen n orbital¹⁵ decreases the C=O stretching frequency by 180 cm⁻¹. Similarly, complexing of ketones with strong Lewis acids¹⁶ induces a decrease of this frequency by 120 – 220 cm⁻¹ (Table III). The analogy can be found in comparison of the CN stretching frequency shift in a side-on coordinated adduct of nitrile ($\Delta\nu = -220$ cm⁻¹) with the large reduction of this frequency in the first systems of photoelectron spectra of nitriles ($\Delta\nu = 257$ cm⁻¹). Even a very simple molecule like N₂ decreases the stretching frequency by 153 cm⁻¹ in the ionic N₂⁺ state¹⁷ and by -82 or -42 cm⁻¹ in the protonated form N₂H⁺, as calculated by HF/6-31G* and MP2/6-31G*, respectively.

Increase of C≡N stretching frequency ($\Delta\nu = +100$ cm⁻¹) obtained by end-on coordination of HCN with BBr₃^{9a} is not followed by the corresponding frequency increase induced by the photoionization of electrons from the n orbital of HCN. In-

TABLE III

Changes of the stretching frequencies of the carbon-heteroatom multiple bonds obtained by photoionization (PES) and by complexing with strong Lewis acids.

orbital	$\Delta\nu/\text{cm}^{-1}$		
	PES	complexing	coordination
$>\text{C}=\text{O}$ n	-184 ^a	-120b	end-on
$\text{C}\equiv\text{N}$ π	-257 ^c	-220 ^d	side-on
$\text{C}\equiv\text{N}$ n	-47 ^c	+100 ^e	end-on

a) measured for CH_3CHO (Ref. 15);

b) measured for acetone (Ref. 16);

c) in the photoelectron spectrum of HCN (Ref. 11);

d) from Ref. 2;

e) from HCN-HBr complex (Ref. 9a).

stead, a negligible decrease of ν_{CN} by $40 \pm 30 \text{ cm}^{-1}$ was observed. However, this decrease is substantially smaller than PES $\Delta\nu$ values of other precursors (Table III). Explanation of these observations requires more theoretical and experimental work, which is in progress in our laboratory.

Discussion of the Results of Calculations

Stretching frequencies and the internuclear distances of the CN group were calculated for the simple CN^- , HCN and HCNH^+ structures (Table IV) as well as for acetonitrile **1** (Table V). In general, a better agreement with experimental data was achieved with the values calculated by the MP2 method. Although the CN distance (r_{CN}) is oversized on the MP2 level, Δr_{CN} , calculated on this level of theory, is very close to the experimental value (Table V).

TABLE IV

The CN bond lengths (r_{CN}/pm) and stretching frequencies ($\nu_{\text{CN}}/\text{cm}^{-1}$) for CN^- , HCN and HCNH^+ , calculated by the *ab initio* methods. The changes of parameters ($x\text{HCN} - x\text{CN}^-$ or $x\text{HCNH}^+ - x\text{HCN}$) are labelled with Δ .

	method	CN^-	HCN	Δ	HCNH^+	Δ
r_{CN}	HF/6-31G*	116.07	113.25	-2.82	111.73	-1.52
	HF/6-31+G*	116.16	112.60 ^a	-3.56	111.28a	-1.32
	MP2/6-31G*	120.14	117.98	-2.16	115.32	-2.66
	MP2/6-31+G*	120.18	117.09 ^b	-3.09	114.79 ^b	-2.30
ν_{CN}	HF/6-31G*	2360	2438	+78	2447	+9
	HF/6-311++G*		2407		2419 ^a	+12

a) HF/6-311++G**;

b) MP2/6-311++G**

TABLE V

The CN bond lengths (r_{CN}/pm) and stretching frequencies ($\nu_{\text{C=N}}/\text{cm}^{-1}$) for CH_3CN and CH_3CNH^+ , calculated by the *ab initio* methods. The changes of parameters ($\alpha\text{CH}_3\text{CNH}^+ - \alpha\text{CH}_3\text{CN}$) are labelled with Δ .

	method	CH_3CN	CH_3CNH^+	Δ
r_{CN}	HF/6-31G*	113.47	112.37	-1.10
	MP2/6-31G*	117.96	115.88	-2.08
ν_{CN}	HF/6-31G*	2623	2600	-23
	MP2/6-31G*	2230	2324	+94

The calculated frequency changes of the CN stretching vibration can be estimated by HF/6-31G* with satisfactory accuracy only for very simple structures. Namely, while $\Delta\nu_{\text{CN}}$ values calculated for the protonation of CN^- or HCN are positive (+9) and +12 cm^{-1} , respectively) on both levels of calculation, $\Delta\nu_{\text{CN}}$ for the protonation of acetonitrile was calculated to be positive (+94 cm^{-1}) only if MP2 was used (Table V). The CN frequency change for the protonation of acetonitrile calculated by HF/6-31G* is negative (-23 cm^{-1}), quite contrary to the experimental observation.

In order to examine the role of rehybridization in the phenomenon of *nitrile effect*, we have also calculated (MP2/6-31G*) changes of s and p characters induced by the protonation of **1**. The total hybridization of the nitrogen atom is changed on protonation from $s^{1.59}p^{3.76}$ to $s^{1.31}p^{4.19}$. From the data presented in Table VI, it follows that the protonation of **1** decreases also the s character and increases the p character on the n orbital on nitrogen (which becomes σ N-H in the protonated form). However, an increase of s character was found for N-atom in the CN σ orbital. It increases from 47% in **1** to 52.3% in 1-H^+ . This trend is in accord with the previously calculated changes of hybrids induced by the protonation of methylimine.¹⁸

TABLE VI

The changes of s and p characters on N and C atoms, calculated by MP2/6-31G*.

atom	n_{N}		$\sigma_{\text{N-H}}$	
	s	p	s	p
N	53.0%	46.9%	47.5%	52.4%
	σ_{CN}		$\sigma_{\text{CN(H)}^+}$	
N	47.0%	52.6%	52.3%	47.5%
C	46.9%	52.9%	43.7%	56.2%

The best way to discuss the bonding-antibonding character of CN σ and n bonds is to visualize the corresponding molecular orbitals (Figures 2, 3 and 4). Strengthening of the CN bond can be explained by the increased π electron density of 1E orbitals on going from **1** (Figure 2) to 1-H^+ (Figure 3). The n orbital of **1** ($7A_1$ in Figure 2) is by protonation shifted below the $\text{CH}_3\text{-C}$ π orbitals (Figures 3 and 4). This change could also cause strengthening of the $\text{CH}_3\text{-C}$ single bond, which was observed as an increase in frequency from 920 to 960 cm^{-1} (Table I).

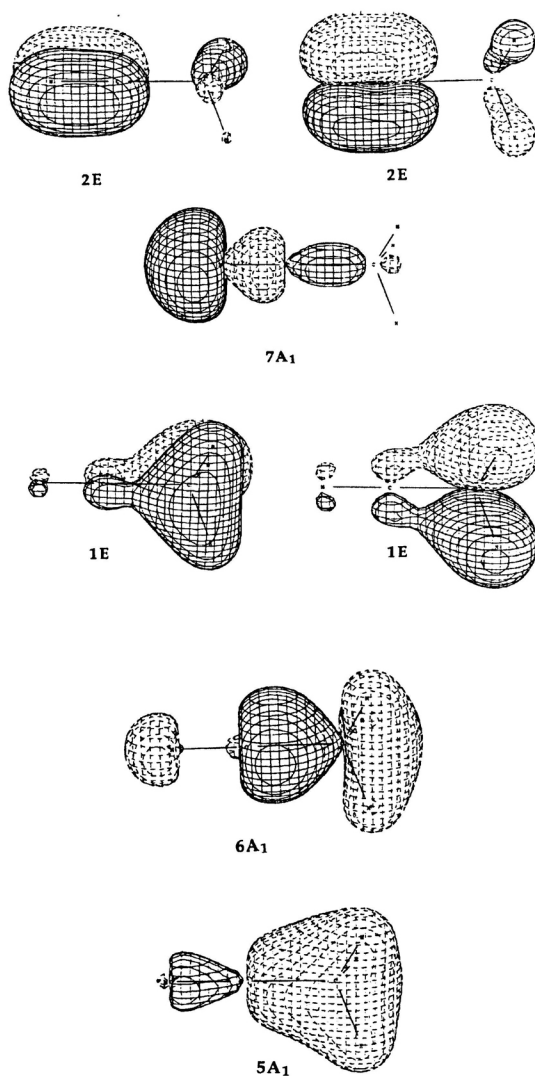


Figure 2. Molecular orbitals of acetonitrile (1) calculated by HF/6-31G*.

On the basis of the orbital coefficients on $5A_1$ and $6A_1$ in both forms of 1, it is not possible to decide in which form of acetonitrile a more antibonding character of σ orbital in CN group exists. In the nonprotonated form, $6A_1$ is antibonding and $5A_1$ bonding, but in the protonated form this is quite opposite. $6A_1$ is bonding and $5A_1$ is antibonding (Figures 2 and 3). Thus, it seems that the changes of these bonding/antibonding characters play no important role in the observed strengthening of the CN bond.

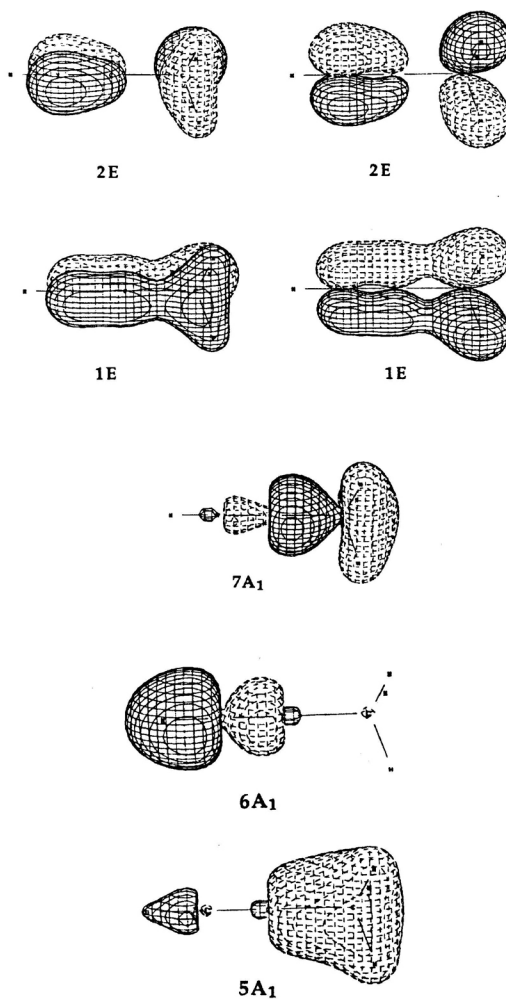


Figure 3. Molecular orbitals of the protonated acetonitrile (1-H^+) calculated by HF/6-31G*.

CONCLUSIONS

Formation of the complexes of nitriles with SbF_5 in the solid cryogenic matrix can be followed by FT-IR spectroscopy. In the majority of cases, the reaction occurs already during the deposition. Increases of the frequencies of the CN stretching vibrations, observed by the reactions of nitriles with SbF_5 , are only slightly dependent on the structure of the rest of the nitrile molecule. Contributions of the σ and π network to the total *nitrile effect* can be estimated by observing the vibrational changes in the rest of the nitrile molecule. Vibrational changes in the cation-like molecules (complexes with Lewis acids) are qualitatively similar to those observed in the cor-

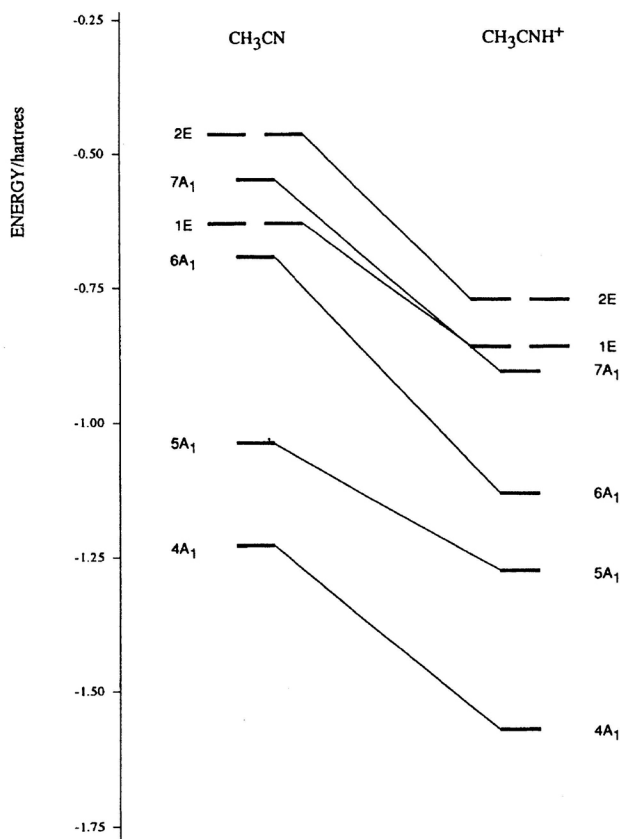


Figure 4. Energy levels of the molecular orbitals of CH_3CN and CH_3CNH^+ calculated by HF/6-31G*.

responding radical cations obtained by photoionization. Consequently, both vibrational effects can be explained on the basis of the same molecular orbital picture. From the pictorial representation of orbitals in **1** and **1-H⁺**, it follows that the strengthening of the CN bond is caused by a drastic increase of the π electron density. It is difficult to discuss the role of the antibonding character of CN σ orbitals, but it can be unambiguously concluded that protonation of CN group increases the s character on the nitrogen atom. This effect, which was also found in the protonation studies of imines, can give a satisfactory explanation of the *nitrile effect*.

EXPERIMENTAL SECTION

Compounds **1** – **7** are commercially available. SbF_5 was provided by Aldrich and distilled before use.

All the »matrix« samples in experiments with **1** – **3** and **5** – **7** were prepared in a liquid nitrogen-cooled cryostat. A liquid nitrogen-cooled cryostat was specially constructed for the SbF_5 matrix work. During the deposition, the temperature was held at 77 K. Typically, approx.

15 – 25 mg of the substrate was used. Deposition times were 5 – 35 min, depending on the substrate. For the deposition of **4**, a closed cycle helium cryostat Leybold-Heraeus ROK 10 – 300 was used. The deposition temperature was 10 K, the deposition time was 35 min and the matrix to sample ratio nearly 500 : 1. In the electron discharge experiment, the sample was passed through a 10 cm long chamber covered with aluminium foil which was connected with a Tesla transformer (20 000 V). This chamber was mounted directly to a vacuum shroud. IR spectra were recorded on the Perkin-Elmer 1725x FT-IR and Perkin-Elmer 167 spectrometers with 2 cm⁻¹ resolution.

Methods of calculations

Quantum mechanical *ab initio* calculations were performed by GAMMES (Jan. 1993 version)^{19a} and Gaussian 92 packages^{129b} at HF or MP2 level using the 6-31G*, 6-31+G* and 6-311++G** basis sets.

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SAŽETAK

O prirodi trostruke veze ugljik-dušik u kompleksima nitrila s jakim Lewisovim kiselinama

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Kompleksi nitrila **1 – 7** s antimonovim(V) fluoridom proučavani su FT-IR spektroskopijom u kriogenim matricama. Opažen je značajan porast $C\equiv N$ rastezne frekvencije do kojega dolazi kompleksiranjem sa SbF_5 . Povećana polarnost veze $C\equiv N$ kao i induktivni efekt ostatka molekule u kompleksima, ustanovljeni su na temelju promjena skeletnih vibracija u molekulama nitrila. Raspravljena je kvalitativna sličnost među vibracijskim promjenama potaknutima kompleksiranjem sa SbF_5 , s onima opaženim u fotoelektronskim spektrima nitrila. Dosadašnja tumačenja ovog efekta rehibridizacijom dušikova atoma, odnosno nastajanjem protuvezne σ -veze C-N, ponovno su razmatrana na temelju IR spektara i rezultata proračuna *ab initio*.