

## $^1\text{H}$ NMR and FTIR Studies of Proton Transfer Reactions from C-acids to Proton Sponges

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Protonation of 1,2-bis(dimethylaminomethyl)benzene (DMAMB) and 1,8-bis(dimethylamino)naphthalene (DMAN) by various C-acids (1–5) in  $[\text{}^2\text{H}_3]$ acetonitrile has been studied by  $^1\text{H}$  NMR and FTIR spectroscopy. The mixtures of DMAMB or DMAN with C-acids in  $[\text{}^2\text{H}_3]$ acetonitrile form protonated bases, complicated species, and homoconjugated nitro-*aci*-nitro ( $-\text{NOO}\cdots\text{H}\cdots\text{OON}-$ )<sup>-</sup> hydrogen bonds. In the case of mixtures of DMAN with C-acids, a relatively slow chemical exchange in the  $^1\text{H}$  NMR spectrum is observed, whereas for the corresponding mixtures with DMAMB the chemical exchange is much faster and only sharp signals of ring and methyl group protons are observed. The complex equilibria occurring in the mixtures of DMAMB or DMAN with C-acids are discussed on the basis of NMR and FTIR results.

We have recently discussed the protonation of some proton sponges in acetonitrile by a wide variety of proton donors: inorganic acids, carboxylic acids, phenols, N–H acids and thiophenols. It has been shown that the protonation of the sponges depends on the  $\text{p}K_a$  and on the nature of proton donor used. In almost all cases we have observed, in acetonitrile solutions, the formation of the homoconjugated  $\text{OHO}^-$ ,  $\text{NHN}^-$  or  $\text{XHX}^-$  ( $\text{X} = \text{NO}_3^-$ ,  $\text{NCS}^-$ ,  $\text{Cl}^-$ ) hydrogen bonds.<sup>1–6</sup> In the case of thiophenols no corresponding  $\text{SHS}^-$  bonds were observed.<sup>7</sup>

We have also recently studied the kinetics of the deprotonation of some C-acids using very strong bases like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), tetramethylguanidine (TMG), amidine and DMAN. The kinetics of the proton transfer reaction from C-acid to strong bases seemed to be very complex, especially in the case of DMAN.<sup>8–12</sup>

Our C-acids are aromatic compounds containing nitro groups *ortho* or *para* to the C–H group in the benzene ring. It is well known that in the solutions of such compounds nitro  $\rightleftharpoons$  *aci*-nitro tautomeric equilibria exist.<sup>13</sup> When the  $\text{NO}_2$  group is in the *ortho* or *para* position to the C–H substituent intra- and inter-molecular proton transfer reactions were observed, respectively.<sup>14,15</sup>

The purpose of this work was to determine the protonation degrees of two proton sponges (DMAN,  $\text{p}K_a = 17.28$ , and DMAMB  $\text{p}K_a = 18.75$ )<sup>16</sup> by various C-acids in acetonitrile based on the intensity of Bohlmann bands. It was shown that the intensity of those bands can be used directly as a quantitative measure of the degree of protonation.<sup>1</sup> We also describe the deprotonation reaction equilibria of the C-acids in  $[\text{}^2\text{H}_3]$ acetonitrile.

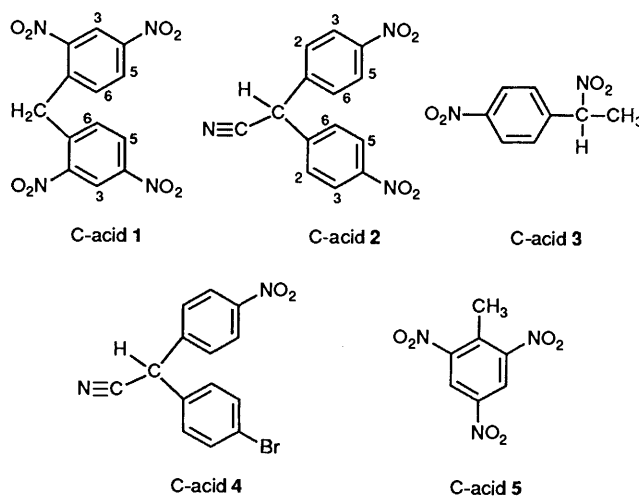
### Experimental

1,2-Bis(dimethylaminomethyl)benzene (DMAMB) was synthesized following the procedure given in ref. 17. 1,8-Bis(dimethylamino)naphthalene (DMAN) purchased from Aldrich was used after double recrystallization from absolute ethanol.

C-acids: bis(2,4-dinitrophenyl)methane (C-acid 1), bis(4-nitrophenyl)cyanomethane (C-acid 2), 1-(4-nitrophenyl)-1-nitroethane (C-acid 3), (4-bromophenyl)(4-nitrophenyl)cyanomethane (C-acid 4), and 2,4,6-trinitrotoluene (C-acid 5) were synthesized as described in refs. 9, 10, 18–20, respectively.

Spectroscopic grade  $[\text{}^2\text{H}_3]$ acetonitrile was dried over 3A molecular sieves.

The 1:1 and 1:2 mixtures of DMAN and DMAMB with C-



acids were obtained from 0.4 mol  $\text{dm}^{-3}$   $[\text{}^2\text{H}_3]$ acetonitrile solutions of the bases and 0.4 mol  $\text{dm}^{-3}$   $[\text{}^2\text{H}_3]$ acetonitrile solutions of the C-acids in the stoichiometry desired.

The IR spectra were recorded in  $[\text{}^2\text{H}_3]$ acetonitrile (0.1 mol  $\text{dm}^{-3}$ ). A cell with Si windows and a wedge-shaped layer to avoid interferences was used (mean layer thickness 0.26 mm). The spectra were taken with a Bruker IFS 113v FTIR spectrophotometer.

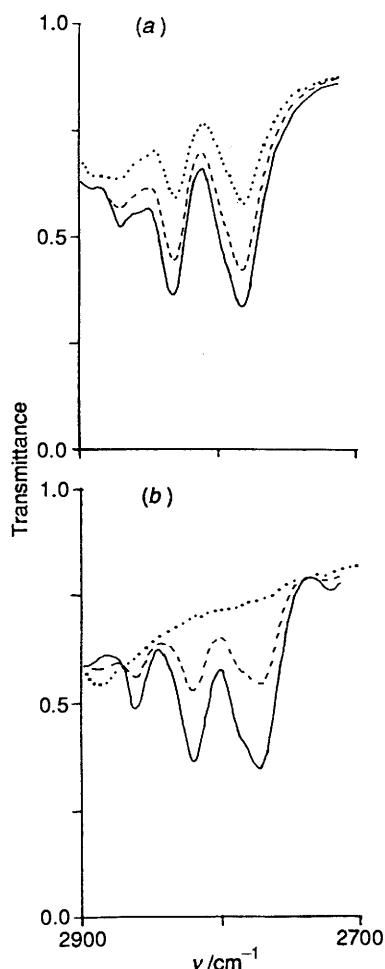
The  $^1\text{H}$  NMR spectra were recorded in  $[\text{}^2\text{H}_3]$ acetonitrile (0.1 mol  $\text{dm}^{-3}$ ) at 20 °C with a Varian Gemini VT-300 spectrometer at 300 MHz, using  $\text{Me}_4\text{Si}$  as internal standard. The spectral width was 30 000 Hz, the number of transients, 128, the acquisition time, 1.998 s and the pulse width, 8.0  $\mu\text{s}$ .  $[\text{}^2\text{H}_3]$ Acetonitrile was used as solvent and internal lock.

The degree of protonation of DMAN and DMAMB was determined from the intensity of so-called Bohlmann bands, which are characteristic for  $\text{CH}_3$  groups in the *trans* position, with respect to the lone electron pairs at the nitrogen atoms. The bands were integrated using Bruker spectrophotometer standard software.

### Results and Discussion

We studied 1:1 and 1:2 mixtures of DMAN and DMAMB with five C-acids 1–5 by FTIR and  $^1\text{H}$  NMR spectroscopy.

Fig. 1 shows one selected example of the IR spectra in the region of Bohlmann bands of the mixtures of C-acid 1, *i.e.*, with



**Fig. 1** IR spectra in the region of Bohlmann bands of bases (—) and their 1:1 (---) and 1:2 (····) mixtures with C-acid 1: (a) DMAN; (b) DMAMB

**Table 1** Degree of protonation (%) of DMAN and DMAMB by C-acids 1–5 in  $[^2\text{H}_3]$ acetonitrile

C-Acid	DMAN		DMAMB	
	1:1	1:2	1:1	1:2
1	26	58	60	100
2	22	45	52	100
3	16	37	38	82
4	7	20	33	56
5	1	2	18	40

the highest degree of deprotonation. For comparison the spectra of the respective bases are also given. The intensity of Bohlmann bands decreases when C-acid is added to a solution of the base and these bands vanish completely in the spectrum of the 1:2 mixture of DMAMB with C-acid 1. This could be explained in terms of the  $\text{p}K_a$  values of the bases; the  $\text{p}K_a$  value of DMAMB is higher and, as a consequence, it is protonated to a higher degree than DMAN. The determined degrees of protonation of DMAN and DMAMB are given in Table 1. This table shows that in the case of 1:2 mixtures of DMAMB with C-acids 1 and 2 the base is fully protonated.

From  $^1\text{H}$  NMR spectra we can determine the structure of protonated bases in mixtures with C-acids. These  $^1\text{H}$  NMR data are collected in Table 2. For comparison the  $^1\text{H}$  NMR data of free bases and their monosalts with  $\text{HClO}_4$  are also given.

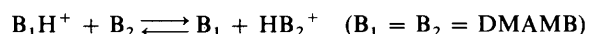
The chemical shifts of the hydrogen-bonded  $(\text{NHN})^+$

protons in the case of DMAN mixtures with all C-acids are almost the same and the intensities of these signals are proportional to the degrees of protonation (Table 1).

The protonation of DMAN influences the charge distribution in the naphthalene ring and in the methyl groups, and this in turn affects the  $^1\text{H}$  NMR chemical shifts. In the case of the 1:2 mixture of DMAN with C-acid 1 one can find signals characteristic for ring protons of both protonated and non-protonated forms of this base. Furthermore, only one, very broad, signal of the methyl group protons is observed. These results indicate that chemical exchange between protonated and non-protonated forms of DMAN must be relatively slow. In the case of the DMAN (1:2) mixture with C-acid 2 only very broadened signals of ring protons and methyl groups were observed, which indicates that the chemical exchange reaction is slightly faster than in the corresponding mixture with C-acid 1.

In the  $^1\text{H}$  NMR spectrum of 1:2 mixtures of DMAMB with C-acid 1 (100% protonation of DMAMB), the signals of the hydrogen-bonded  $(\text{NHN})^+$  proton, ring and methyl protons are sharp. In the case of DMAMB 1:2 mixtures with C-acid 2 (also 100% protonation of the base) the signals of the ring and methyl group protons are also sharp, whereas the  $\text{NHN}^+$  proton signal is broadened and shifted slightly towards higher field. Its integration value is higher than for one proton. This observation indicates that a relatively fast chemical exchange between hydrogen-bonded  $(\text{NHN})^+$  proton and other protons occurs; this will be discussed below.

In the  $^1\text{H}$  NMR spectrum of 1:2 mixtures of DMAMB with C-acid 5 (DMAMB is only 40% protonated) the signal of the hydrogen-bonded proton is very broadened whereas other signals of DMAMB protons (ring, methyl groups) are sharp. Taking into account all the above observations we may conclude that in this case fast chemical exchange between protonated and non-protonated DMAMB occurs:



More information about the equilibria existing in the acetonitrile mixtures of DMAN and DMAMB with C-acids has been obtained from the analysis of the  $^1\text{H}$  NMR signals of the acids. The  $^1\text{H}$  NMR chemical shifts of the C-acids 1 and 2 and their mixtures with DMAN or DMAMB, *i.e.* the mixtures with 100% proton transfer, are summarized in Tables 3 and 4, respectively.

The  $^1\text{H}$  NMR spectrum of C-acid 1 in  $[^2\text{H}_3]$ acetonitrile solution (Table 3) points clearly to an equilibrium existing in the solution. The type of this equilibrium can be deduced from the signals of the  $\text{CH}_2$  protons. For these protons we observe two very closely placed signals at 4.77 and 4.79 ppm. The signal at 4.77 ppm may be assigned to the structure 1, and the signal at 4.79 ppm to the structure 1a, in which one of the  $\text{CH}_2$  group protons is involved in intramolecular hydrogen bonding (Scheme 1). Such assignments are in good agreement with previous  $^1\text{H}$  NMR investigations of other C-acids, *e.g.*  $\text{H}-\text{CCl}_3$  in mixtures with various proton acceptors.<sup>21,22</sup> The existence of the structure 1a in the solution explains also the stronger shift of the 3-H ring proton signal to lower field. This shift is due to the deshielding effect of the  $\text{NO}_2$  groups in the *ortho* position which should be planar to the aromatic ring. The integration of the signals indicates that the structure 1 is the predominant one in solution.

The signals in the  $^1\text{H}$  NMR spectrum of the 1:2 mixture of DMAMB with C-acid 1 can be assigned to the structure 1, and to two new structures 1b and 1c (Scheme 1). The presence of the  $\text{CH}_2$  signal at 4.75 ppm and two new singlets at 8.40 and 7.29 ppm of the  $\text{HC}=\text{C}$  protons confirm this supposition.

The  $^1\text{H}$  NMR spectrum of the 1:2 mixture of DMAN with C-acid 1 is far more complex than that of DMAMB. In this

**Table 2**  $^1\text{H}$  NMR chemical shifts (ppm) and coupling constants (Hz) of (a) DMAN and (b) DMAMB, their (1:1) complexes with  $\text{HClO}_4$  and their (1:2) mixtures with C-acids **1**, **2**, **5** in  $[\text{D}_2\text{H}_3]\text{acetonitrile}$ 

(a)	NHN <sup>+</sup>	2,7-H	3,8-H	4,5-H	CH <sub>3</sub>	J(2,3)	J(3,4)	J(2,4)	
DMAN	—	6.93	7.25	7.32	2.75	7.2	7.8	1.8	
DMAN + $\text{HClO}_4$	18.67	8.03	7.69	7.89	3.11	5.6	5.1	0.9	
DMAN + <b>1</b>	18.60	8.02	7.68	7.48	2.88 <sup>a</sup>	6.9	6.0	1.1	
		6.94 <sup>a</sup>	7.35 <sup>a</sup>	7.35 <sup>a</sup>					
DMAN + <b>2</b>	18.60	7.82 <sup>a</sup>	7.35 <sup>a</sup>	7.35 <sup>a</sup>	2.85 <sup>a</sup>				
DMAN + <b>5</b>	—	6.94	7.25	7.33	2.75	7.2	7.7	1.8	
(b)	NHN <sup>+</sup>	3,6-H	4,5-H	CH <sub>2</sub>	CH <sub>3</sub>	J(3,4)			
DMAMB	—	7.26	7.18	3.47	2.15	18.3			
DMAMB + $\text{HClO}_4$	14.19	7.41 <sup>b</sup>	4.00	2.57	—				
DMAMB + <b>1</b>	13.88	7.39 <sup>b</sup>	3.85	2.45	—				
DMAMB + <b>2</b>	13.77	7.40 <sup>b</sup>	3.87	2.46	—				
DMAMB + <b>5</b>	13.34	7.33 <sup>b</sup>	3.66	2.22	—				

<sup>a</sup> Very broad. <sup>b</sup> Multiplet.**Table 3**  $^1\text{H}$  NMR chemical shifts (ppm) and coupling constants (Hz) of C-acid **1** and its 2:1 mixtures with DMAN and DMAMB in  $[\text{D}_2\text{H}_3]\text{acetonitrile}$ 

Compound	3-H	5-H	6-H	CH <sub>2</sub>	HC=	J(3,5)	J(5,6)	Structure	Contribution (% ± 5)
<b>1</b>	8.82	8.40	7.49	4.77s	—	2.0	8.5	<b>1</b>	65
	9.04	8.32	7.23	4.79s	—	2.0	8.5	<b>1a</b>	35
DMAMB + <b>1</b>	8.79	8.37	7.47	4.75	—	2.2	8.4	<b>1</b>	30
	8.67	8.04	7.21	—	8.42s	2.1	8.4	<b>1b</b>	40
	8.67	8.04	7.21	—	7.29s	2.1	8.4	<b>1c</b>	30
DMAN + <b>1</b>	8.78	8.35	7.46	4.75		masked	8.6	<b>1</b>	46
	9.01	8.30	7.22	4.78		masked	8.6	<b>1a</b>	10
	8.66	8.03	7.20		8.35s	masked	8.6	<b>1b</b>	24
	8.66	8.03	7.20		7.29s	masked	8.6	<b>1c</b>	20

**Table 4**  $^1\text{H}$  NMR chemical shifts (ppm) and coupling constants (Hz) of the C-acid **2** and its 2:1 mixtures with DMAMB and DMAN in  $[\text{D}_2\text{H}_3]\text{acetonitrile}$ 

Compound	2,6-H	3,5-H	CH	J(2,3)	Structure	Contribution (% ± 5)
<b>2</b>	7.97	8.50	4.38	8.6	<b>2</b>	95
	7.50	8.18	—	8.5	<b>2a</b>	5
DMAMB + <b>2</b>	7.94	8.31	4.45	8.7	<b>2</b>	20
	7.64	8.22		8.5	<b>2a</b>	30
	7.32	7.86		8.5	<b>2b/c</b>	50
DMAN + <b>2</b>	7.95	8.28	4.45	8.7	<b>2</b>	50
	7.64	8.22		8.5	<b>2a</b>	15
	7.32	7.86		8.5	<b>2b/c</b>	35

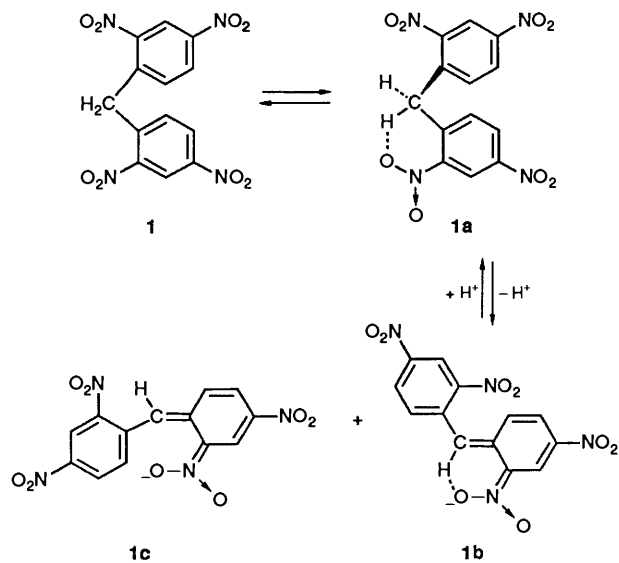
spectrum we can find signals proving the presence of all four structures **1–1c** in the solution (Table 3, Scheme 1).

The  $^1\text{H}$  NMR spectrum of the  $[\text{D}_2\text{H}_3]\text{acetonitrile}$  solution of C-acid **2** exhibits proton signals of both high and low intensity. This result proves that the C-acid **2** in  $[\text{D}_2\text{H}_3]\text{acetonitrile}$  occurs in two nitro-*aci*-nitro tautomeric forms, the nitro being predominant (Table 4). Unfortunately, the N-OH (*aci*-nitro) proton signal was not visible in the spectrum, probably owing to the low concentration of this form in the solution and to the relatively slow tautomerization.

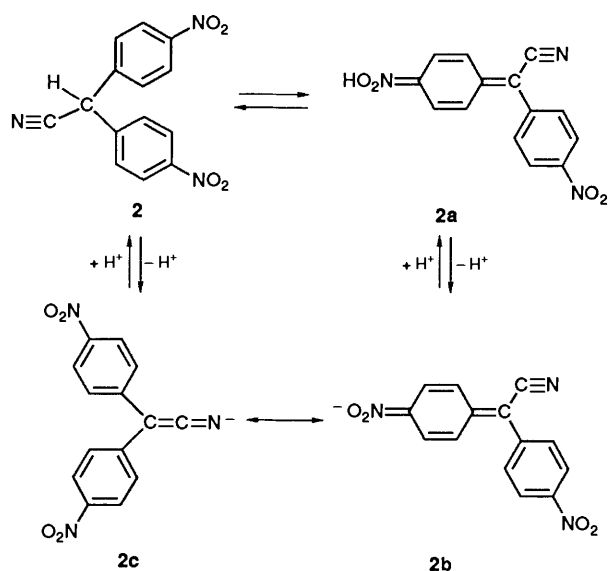
The  $^1\text{H}$  NMR spectrum of the 1:2 mixture of DMAMB with C-acid **2** is very complex. This spectrum exhibits signals which can be assigned to the structures **2**, **2a** and **2b/c** (Scheme 2; assignments and percentages of these structures are given in Table 4). The presence of the structure **2a** in the solution explains the increase of the intensity, broadening, and shift towards higher field of the (NHN)<sup>+</sup> signal (Table 2). Such interpretation is further justified by the fact that, in the spectrum of the 1:2 mixture of DMAN with C-acid **2**, when the degree of protonation is only 45%, the contribution of the signals assigned to the structure **2a** is much smaller.

The presence of the structures **1b/1c** and **2b/2c** in  $[\text{D}_2\text{H}_3]\text{acetonitrile}$  is shown also in FTIR spectra (Figs. 2, 3). Figs. 2(a) and 2(b) show IR spectra in the region 1800–1000  $\text{cm}^{-1}$  of the 1:2 mixtures of DMAMB with C-acids **1** and **2**, respectively. For comparison the IR spectra of bases and C-acids are also presented.

The IR spectra of C-acids **1** and **2** (Fig. 2) show very intense  $\nu_{\text{as}}(\text{NO}_2) = 1530 \text{ cm}^{-1}$  and  $\nu_{\text{s}}(\text{NO}_2) = 1350 \text{ cm}^{-1}$  bands. In 1:2 mixtures the intensity of these bands decreases significantly. This is particularly distinctly visible in Fig. 2(b) In the spectra of the mixtures a new band at  $1580 \text{ cm}^{-1}$  is observed, which can be assigned to a  $\nu(\text{C}=\text{C})$  vibration in a conjugated system.<sup>23,24</sup> The most characteristic and very intense bands are observed in the region 1320–1100  $\text{cm}^{-1}$  (1320, 1250  $\text{cm}^{-1}$ ), which can be ascribed to the  $\nu_{\text{s}}(\text{NO}_2^-)$  and  $\nu_{\text{as}}(\text{NO}_2^-)$  vibrations, respectively. Such intense bands in this region were previously observed for  $\text{NaNO}_2$  salt<sup>25</sup> and for nitro complexes in which the nitro groups were co-ordinated to a metal.<sup>26</sup> Furthermore, an intense continuous absorption for the mixtures in the region 1600–1000  $\text{cm}^{-1}$  is observed. In this continuous absorption besides the proton (NHN)<sup>+</sup> vibration other types of easily



Scheme 1



Scheme 2

polarizable hydrogen bonds must contribute, because the continuum caused by  $(\text{NHN})^+$  intramolecular hydrogen bonds of protonated DMAMB is itself of low intensity.<sup>27</sup> The observed continuum is caused presumably by the homoconjugated  $\text{ONO}^- \cdots \text{H}-\text{ONO}$  (nitronic acid–nitronic ion) strong intermolecular hydrogen bonds. Such very intense absorption in the region  $1600\text{--}1000\text{ cm}^{-1}$  was also observed for other systems, containing strong intra- or inter-molecular hydrogen bonds, *i.e.* phenol–phenolate and carboxylic acid–carboxylate.<sup>6,28</sup>

Fig. 3 shows IR spectra in the  $\nu(\text{C}\equiv\text{N})$  vibration region. The  $\nu(\text{C}\equiv\text{N})$  vibration of the acid **2** in  $[\text{D}_2\text{O}]$  is masked by the respective solvent band. In the IR spectrum of the 1:2 mixture of DMAMB with C-acid **2** this band is strongly shifted to  $2170\text{ cm}^{-1}$ . Similar behaviour of this band was previously observed for the complexes of  $\text{H}-\text{C}\equiv\text{N}$  with various proton acceptors, indicating increase of the electron density on the  $\text{C}\equiv\text{N}$  group.<sup>29</sup> In our case the presence of this band is additional evidence for the structure **2c** in  $[\text{D}_2\text{O}]$ .

The following conclusions can be drawn from the obtained results. Firstly, the higher protonation degree of DMAMB with C-acids mixtures is due to the difference in  $\text{p}K_a$  values of DMAMB and DMAN. Secondly, in the case of C-acid **1**, containing a nitro group in the *ortho* position to the C–H group

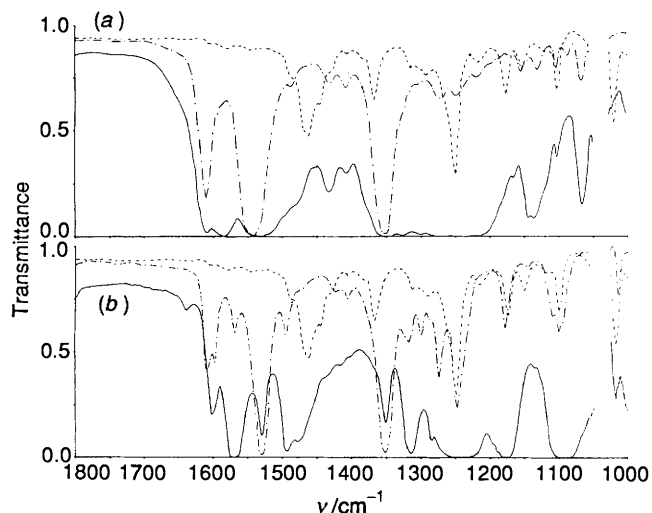


Fig. 2 IR spectra in the region  $1800\text{--}1000\text{ cm}^{-1}$  of DMAMB (---) and its 1:2 mixtures (—) with C-acids (---): (a) C-acid **1**; (b) C-acid **2**

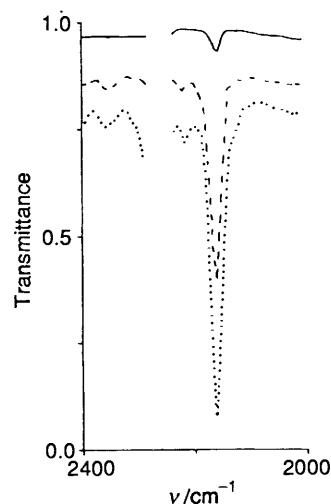


Fig. 3 IR spectra in the region of  $\nu(\text{C}\equiv\text{N})$  vibrations of mixtures of DMAMB and C-acid **2**: 1:1 (---); 1:2 (····); C-acid **2** (—)

in the benzene ring, intramolecular  $\text{C}-\text{H}\cdots\text{O}-\text{N}$  hydrogen bonds are formed. In the case of C-acid **2** an equilibrium between nitro and *aci*-nitro tautomers in  $[\text{D}_2\text{O}]$  was observed. Thirdly, the deprotonation of C-acids leads to complex equilibria. The formation of the structures with deprotonated  $\text{NO}_2^-$  groups strongly influences the nitro–*aci*-nitro equilibrium with the formation of homoconjugated  $\text{NOO}^- \cdots \text{H}-\text{ONO}$  hydrogen bonds. This observation suggests that the deprotonation reaction of the investigated C-acids may in fact be the deprotonation of their *aci*-nitro tautomers.

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