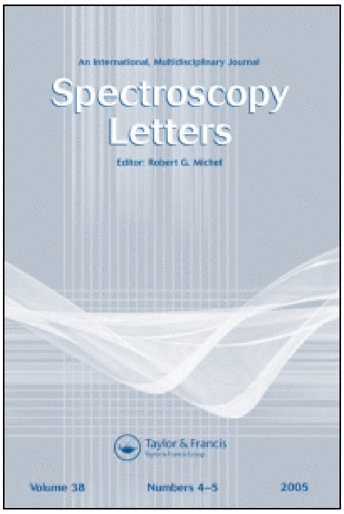

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A NEW APPROACH TO THE DETECTION AND DETERMINATION OF o-CHLOROBENZYLIDENE-MALONONITRILE (CS) AND ITS CHEMICAL RELATIVES

Ivan G. Binev[a]; Yuri I. Binev[a]; Ivan N. Juchnovski[a]
[a] Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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A NEW APPROACH TO THE DETECTION AND DETERMINATION OF o-CHLOROBENZYLIDENE-MALONONITRILE (CS) AND ITS CHEMICAL RELATIVES

Ivan G. Binev,* Yuri I. Binev, and Ivan N. Juchnovski

Institute of Organic Chemistry, Bulgarian Academy of
Sciences, 1113 Sofia, Bulgaria

ABSTRACT

o-Chlorobenzylidenemalononitrile (CS-gaz) has been found to react with KCN in DMSO and to form practically quantitatively a stable 1:1 adduct of carbanionic structure. The conversion results in the appearance of two very strong $\nu^{s}_{C\equiv N}$ and $\nu^{as}_{C\equiv N}$ IR bands of the dicyanomethide fragment of the adduct at 2161 cm^{-1} and 2106 cm^{-1}, respectively. These bands can be used to detect selectively and to determine quantitatively CS and its chemical relatives, including in the presence of large quantities of other substances.

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*Corresponding author. E-mail: binev@orgchm.bas.bg

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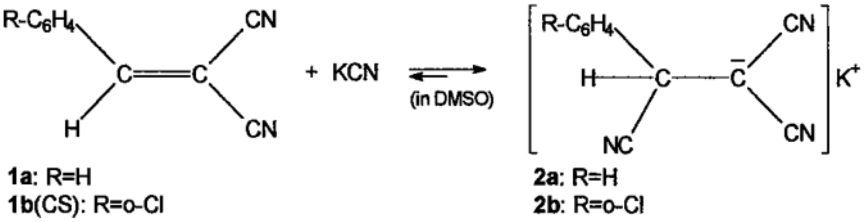
Key Words: o-Chlorobenzylidenemalononitrile (CS); Adduct; Carbanion; Infrared spectra; Detection; Determination

INTRODUCTION

Ylidenemalononitriles, a large series of compounds easily accessible by synthesis [1–3], have shown a variety of physiological activities and have been used for various purposes, e.g., from anti-cancer and X-ray protective medicines to pesticides, rodent repellents, hair-growth stimulating agents, etc.[1–6] However one of these compounds, viz. o-chlorobenzylidenemalononitrile (CS, **1b** in Sch. 1), has turned to be a strong irritant and has been used as the active principle in numerous military antipersonnel devices (lachrymators, tear gases) [1–3,6,7]. There is information about 13,736 t of CS applied in South Vietnam within the years 1964—1969 [8]. CS is nowadays the most common riot-control agent [1–3,6,7], used also for self-defense in various gas-maces, etc.

It is obvious therefore, that there should be a simple, reliable, selective and sensitive method of detection and determination of this widespread and dangerous substance. The classical methods of detection and determination of CS are based on colour reactions of itself or of its hydrolysis products, followed by photoabsorption[9–12] or luminescence[13,14] measurements. Some of these methods are highly sensitive[11,12,14] but all of them have many limitations and suffer from lack of selectivity[6]. Direct IR measurements in the $\nu_{C\equiv N}$ region[6,13,15] have low selectivity, as numerous nitriles show singlet bands near 2230 cm^{-1} [16]. The complex approach, based on IR, NMR, Mass spectra etc.[6,17–19] increases, of course, the selectivity, but it needs considerable amounts of the *pure* substance. At present CS is detected by means of gas chromatography/mass spectrometry[20–22]. The "yellow powder",



Scheme 1. Synthesis of the potassium cyanide adducts (**2a**,**2b**) of benzylidenemalononitrile (**1a**) and its o-chloro derivative (CS,**1b**).

having caused pupils' intoxication in Curituba (Brazil), has been identified as CS in the same manner[23].

EXPERIMENTAL

CS was prepared by Knoevenagel condensation[2,3] between malononitrile and o-chlorobenzaldehyde (Fluka) in dry ethanol solvent, using sodium ethoxide as catalyst. After double recrystallization from ethanol, its melting point was 94 °C, in agreement with Ref. 24. The potassium cyanide adduct of CS was prepared, as follows (see Scheme 1): 1 mL of 0.001–0.070 $\mathrm{mol \cdot L^{-1}}$ dimethyl sulphoxide (DMSO) solutions of CS were added in small glass tubes to an excess of potassium cyanide (Merck). The reaction mixtures were stirred for a minute and then filtered through a syringe-filter. The adduct obtained (**2b** in Sch. 1) is in fact a carbanion, but a very stable one, so the use of an argon protection[25] could be recommended, but this is not necessary.

The IR spectra were measured on Bruker IFS 113v and Vector 22 spectrophotometers in a CaF_2 cell of 0.13 mm path length at a resolution of 1 $\mathrm{cm^{-1}}$ and 50 scans. The spectral measurements were restricted within the 1460–2700 $\mathrm{cm^{-1}}$ region, in view of the transparency of both the cell windows and solvent. The peak wavenumbers were reproducible within ± 0.1 $\mathrm{cm^{-1}}$.

RESULTS AND DISCUSSION

We have recently found[25] that the unsubstituted benzylidenemalononitrile (**1a**) reacts with potassium cyanide in DMSO to form practically quantitatively the adduct **2a** (Sch. 1). The structures of both the parent nitrile and its adduct have been determined, and the assignment of their IR bands have been performed on the basis of ab initio force field calculations[25]. We supposed that a similar reaction should take place also with its o-chloro derivative (CS, **1b**). Our present experiments (see Experimental) confirmed completely this supposition. In fact CS reacted with potassium cyanide in a similar way to form the adduct **2b** (Sch. 1). The conversion was practically complete: no bands of the parent CS were seen in the spectra of the reaction mixtures (Fig. 1, Table 1). The 2000–2300 $\mathrm{cm^{-1}}$ spectrum of the adduct **2b** (Fig. 1(B)) is very close to that of **2a**[25] and this result guarantees a close similarity in the structures of the adduct **2a** and **2b** (Sch. 1). The bands in the spectra of both CS and its adduct (Table 1) are assigned by analogy with those of **1a** and **1b**[25]. The moderate band at 2232 $\mathrm{cm^{-1}}$ in the spectrum

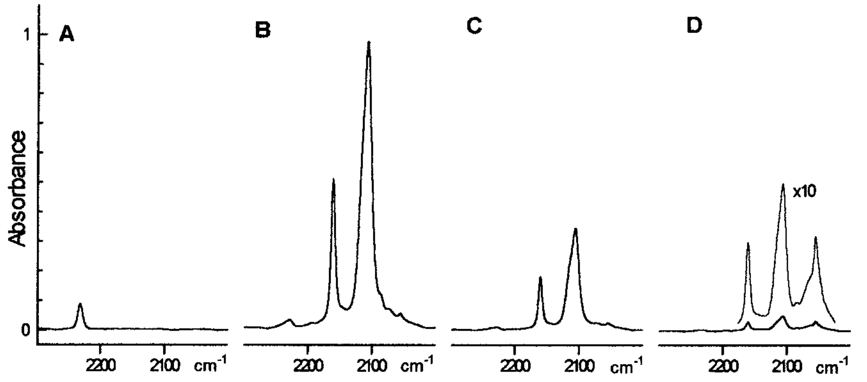


Figure 1. IR spectra (ν_{CN} region, solvent DMSO): (A) CS, 0.070 mol·L^{-1}; (B) KCN adduct of CS, 0.070 mol·L^{-1}; (C) the same adduct, 0.021 mol·L^{-1}; (D) the same adduct, 0.0035 mol.L^{-1}.

of CS (Fig. 1, Table 1) corresponds to both $\nu^{s}_{C\equiv N}$ and $\nu^{as}_{C\equiv N}$ vibrations in the molecule: e.g., for the **1a** molecule the predicted, but not measurable splitting between the corresponding bands is 4 cm^{-1} only. The conversion of the CS molecule into the adduct results in a strong enhancement of the C≡N/C≡N vibrational coupling (ν_{CN} splitting of 54 cm^{-1}, Table 1), like in the cases of other species containing dicyanomethide groups, e.g., malononitrile carbanion (54 cm^{-1} [25]), alkali-metal methoxide, potassium cyanide and heptylamine adducts of **1a** (52–57 cm^{-1} [25]), butyldimethylammonium dicyanomethylide (49 cm^{-1} [26]), etc.

Table 1. Infrared Data for the CS Molecule and Its Potassium Cyanide Adduct

Molecule			Adduct			
ν^{a}	ε^{b}	A^{c}	ν^{a}	ε^{b}	A^{c}	Assignment^{d}
			2230.8	22	3	$\nu_{C\equiv N}$
2232.2	93	10	2160.8	552	62	$\nu^{s}_{C\equiv N}$ $\nu^{as}_{C\equiv N}$
			2106.4	1057	260	
1597.0	112	17				ν_{CC}
1587.7	127	15	1588.5	67	37	ring 8a^{f}
1469.0	61	11	1472.5	86	16	ring 19a^{f}

[a] Frequency in cm^{-1}. [b] Molar absorbance in L.mol^{-1}·cm^{-1}. [c] Integrated intensity in km·mol^{-1}. [d] By analogy to Ref. 25. [e] The band of the new (added) cyano group in the adduct. [f] Wilson's notation.

The position of the weak band at 2230.8 cm^{-1} in the spectrum of the adduct is close to the ν_{CN} band of the parent CS (Fig. 1, Table 1), Thus, having in mind the equilibrium character of the reaction (Sch. 1), this band could be incorrectly ascribed to the incomplete conversion of the parent CS into the adduct. However we have rejected the same assumption in the previous case **2a**[25] by using $KC^{15}N$ instead of $KC^{14}N$ in the reaction (Sch. 1). The ^{15}N isotopic shift of 31 cm^{-1} of this band proved unambiguously, in agreement between theory and experiment, that the third, weak band near 2230 cm^{-1} corresponded to the third (new, added) cyano group of the adduct.

The enhanced spectra of very low-concentrated (with respect to CS) solutions (Fig. 1(D)) show additional bands below 2100 cm^{-1}. They correspond to the potassium cyanide ion-pairs[27], as their concentration is constant in all solutions studied (saturated with respect to KCN).

Comparing both spectra on Fig. 1 and numerical data in Table 1 for CS and for its potassium cyanide adduct gives reasons for the following statements:

i) The conversion of CS into the adduct is accompanied by a strong increase in the ν_{CN} band intensity. For example: the $\nu^{as}_{C\equiv N}$ band of the adduct is 11 fold stronger (by molar absorbance) or 26 fold stronger (by integrated intensity) than ν_{CN} of CS. So, this conversion leads to an essential increase (by an order or more) in the sensitivity of the IR detection and determination of CS.

ii) The $\nu^{s}_{C\equiv N}$ and $\nu^{as}_{C\equiv N}$ frequencies of the adduct are away from the cyano stretching frequencies of all the nitrile molecules (2180–2260 cm^{-1} [16]). Bands $\nu^{s}_{C\equiv N}$ (strong) near 2160 cm^{-1} and $\nu^{as}_{C\equiv N}$ (very strong) near 2100 cm^{-1} are typical only for anions, dianions and zwitterions, containing dicyanomethide group[25,26,28,28]. Hence similar, but not exactly the same spectral patterns could give only CS and its chemical relatives. Having in mind, that no ylidenemalononitriles other than CS have actually been used for offensive purposes[1], we can state that the above spectral measurements are highly selective.

iii) The procedure described (see Experimental) can be preceded by a simple extraction of the sample available with chloroform, ether or another volatile solvent, and evaporation of the extragent. In this manner samples of soil, foliage, mud, etc., can be also studied. Because of the high selectivity of the IR measurements described, other soluble substances, eventually present in the samples, could neither block nor hinder both the detection and determination of CS and of its chemical relatives.

CONCLUSION

We hope the procedure described in this paper, can be used as a simple, reliable, highly selective and sufficiently sensitive method for both detection and determination of CS and its chemical relatives, including in samples containing large quantities of by-substances.

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