Journal of Organometallic Chemistry, 128 (1977) 139—144

INFRARED SPECTRA AND STRUCTURE OF CARBANIONS

VIII *. MONO- AND DI-ALKALI METAL DERIVATIVES OF SOME BIS(CYANOMETHYL)ARENES

I.N. JUCHNOVSKI *, V.B. RADOMIRSKA, I.G. BINEV and E.A. GREKOVA
Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia (Bulgaria)
(Received August 20th, 1976)

Summary

Infrared spectral data were obtained for the mono- and di-alkali metal derivatives of 1,4-bis(cyanomethylbenzene, 1,4-bis(cyanomethyl)naphthalene and 9,10-bis(cyanomethyl)anthracene, as well as data for their electrochemically generated carbanions. It was found that the mono-alkali metal derivatives of the title nitriles exist as "free" carbanions in dimethyl sulphoxide and hexamethyl phosphoramide. The di-alkali metal derivatives are dicarbanions, and they can be considered as dianions of dicyano-quinodimethane and its polycyclic analogues.

It was reported earlier that the IR spectra of the carbanions of substituted arylacetonitriles [1—5] and some of their derivatives [4,5] are characterized by the very strong bands of the nitrile group (ν(CN)) in the 2070—2150 cm^{-1} region. The strong ν(CN) lowering (up to 180 cm^{-1}), caused by conversion of the neutral molecules into the corresponding carbanions, is in agreement with the concept of the mesomeric character of these carbanions. The ν(CN) values correlate with the C≡N bond orders, calculated by the Hückel and the self-consistent field methods [2,4,5].

The subject of the present study are the alkali metal and tetraethylammonium derivatives of 1,4-bis(cyanomethyl)benzene (I), 1,4-bis(cyanomethyl)naphthalene (II) and 9,10-bis(cyanomethyl)anthracene (III); it is likely that mono- and di-alkali metal derivatives should be formed in these cases.

Results and discussion

We measured the IR spectra (1900—2300 cm^{-1} region) of the products of metalation (lithium, sodium and potassium; see Experimental) of the nitriles I,

---

[*] For Part VII see ref. 9; and for Part VI see ref. 4b.

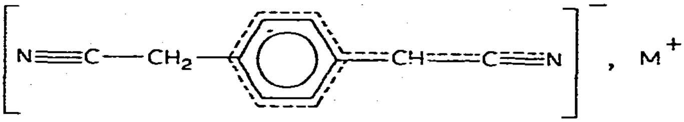
II, and III in tetrahydrofuran (THF) and hexamethyl phosphoramide (HMPA); we also recorded the spectra of the electrochemically generated carbanions (counter ion: tetraethylammonium cation; see Experimental) of the same nitriles. The wave number data and the relative intensities of the bands observed are given in Table 1.

A. Mono-derivatives

As seen from Table 1, all the mono-derivatives of the studied bis(cyanomethyl)-arenes are characterized by two types of bands in the ν(CN) region: very strong bands at 2087—2120 cm^{-1} and weak bands at 2233—2243 cm^{-1}.

It was not difficult to assign the very strong bands in the spectra of the mono-derivatives of I, viz. 2094—2096 cm^{-1} (in HMPA) and 2087 cm^{-1} (in DMSO) as bands of the nitrile group directly bonded to a carbanionic center; having in mind the small σ value of the $-CH_2CN$ group * and the correlation $\nu(CN)/\sigma^-$ for the substituted arylacetonitrile carbanions [4,5], one can expect that ν(CN) of the carbanion of I will be close to that of phenylacetonitrile (2096 cm^{-1} in HMPA, 2080 cm^{-1} in DMSO; counter ions Li^+, Na^+, K^+ and Et_4N^+ [4,5]).

The data in Table 1 for I show that a structure of type IV can be ascribed to the mono-derivatives of I in these solvents.



(IV)

($M^+ = Li^+, Na^+, K^+$ and Et_4N^+)

The fact that ν(CN) of IV in HMPA and DMSO does not depend (within experimental error of ±1 cm^{-1}) on the counter ion shows that no measurable effects of ion aggregation are present, i.e. in these solvents, IV exists as "free" ions and not ion pairs.

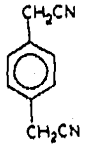
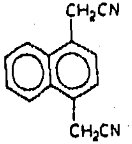
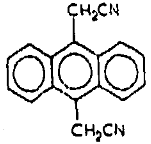
A similar kind of analogy concerning the band assignment can be found by comparing the ν(CN) data for the mono-derivatives of II, with the data for the α-naphthylacetonitrile carbanion (2096 cm^{-1} in HMPA and 2088, 2109 cm^{-1} in DMSO; the same counter ions [4,5]). The ν(CN) data obtained for the mono-derivatives of II and III (Table 1) are also in favour of a structure of type IV for these organometallic compounds, i.e. "free", delocalized carbanions.

The increase in ν(CN) of the carbanions in the order I < II < III is due to an increase in the possibility of conjugation (and delocalization) of the carbanionic charge over the aromatic residues in the same order: phenyl < 1-naphthyl < 9-anthracyl (the conjugation coefficients are 0.315, 0.345 and 0.39, respectively [7]). These data show that the influence of the a priori expected steric hindrance to the conjugation is not of major importance. On the basis of the correlation between ν(CN) of the carbanions $Ar{-}\bar{C}H{-}CN$ and the conjugation coefficients of the radicals [8], and assuming a planar structure of the phenylacetonitrile

---

* $\sigma = 0.007$; in the cases of substituents showing predominantly inductive effect $\sigma^- \cong \sigma$ [6].

TABLE 1

No.	Compound	ν(CN) (cm^{-1}) Neutral molecule	ν(CN) (cm^{-1}) Mono-derivatives		ν(CN) (cm^{-1}) Di-derivatives		Counter ion
			in HMPA	in DMSO	in HMPA	in THF	
I		2246 [a]	2096vs 2239w	—	2047vs 2065w	2044s	Li^+
		2247 [b]	2096vs 2239w	2087vs 2243w	2047vs 2065w	2040s	Na^+
		2251 [c]	2094vs 2239w	—	2050vs 2060w	2044s	K^+
			2095vs 2240w	2087vs 2242w	—	—	Et_4N^+
II		2247 [a]	2113vs 2238w	—	2058vs 2075vs	2050s	Li^+
		2248 [b]	2112vs 2237w	2107vs 2238w	2057vs 2076vs	2045s	Na^+
		2253 [c]	2112vs 2237w	—	2050vs 2075vs	2044s	K^+
			2113vs 2237w	2106vs 2238w	—	—	Et_4N^+
III		2247 [a]	2120vs 2234m	—	2055vs 2078(sh)	2044s	Li^+
		2246 [b]	2119vs 2235m	2112vs 2233m	2056vs 2075w	2036s	Na^+
		2249 [c]	2120vs 2234m	—	2050vs 2074w	2041s	K^+
			2120vs 2234m	2112vs 2233m	—	—	Et_4N^+

[a] In HMPA. [b] In DMSO. [c] In THF. All the ν(CN) bands of the neutral compounds are weak. vs, very strong; s, strong; m, moderate; w, weak; sh, shoulder.

carbanion, it can be supposed that the torsion angle between the sp^2 hybride carbon atom of the cyanomethyl group and the aromatic ring is less than 18° in the case of the carbanion of II, and considerably less than 27° for the carbanion of III.

The weak bands in the 2233—2243 cm^{-1} region in the spectra of the mono-derivatives, must be assigned as ν(CN) of the second (unionized) cyanomethyl group. The ν(CN) lowering of 4—13 cm^{-1} *, in comparison with the parent neutral nitriles, can be ascribed to the strong inductive influence of the carbanionic charge on the cyanomethyl groups (see Formula IV). ν(CN) of these groups decreases in the order I > II > III (carbanions); it is possible that the stronger ν(CN) decrease in the case of the carbanion of III is due to the proximity of parts of the negatively charged anthracene ring (being a di-ortho substituted benzene ring) to the cyanomethyl group.

Some of the spectra show weak bands or "shoulders" in the 2110—2140 cm^{-1} region, over the main strong bands (see Fig. 1). We suppose that their appearence is caused by the presence of the alkali metal derivatives of the dimerization products of the parent nitriles, as impurities, by analogy with [4,5,9].

We also recorded the spectra of the mono-derivatives of I, II and III in tetrahydrofuran (THF); the spectra show strong bands in the 2078—2096 cm^{-1} region; the frequencies depend upon the counter ion, viz. they increase in the order $K^+ < Na^+ < Li^+$. These data show that the mono-alkali metal derivatives of the bis(cyanomethyl)arenes studied exist as ion aggregates in THF. The latter is in agreement with the literature data for some related systems in ethereal solvents [10]. An increase in ν(CN) in the same order is characteristic of the previously studied alkali metal derivatives of saturated nitriles, arylacetonitriles, etc. [4,5] and also of the anion-radicals of aromatic nitriles [11]; these effects are caused by the electrostatic anion—counter ion interactions in the ion aggregates [4,5].

B. Di-derivatives

The spectra of the solutions of the bis(cyanomethyl)arenes studied, metalated

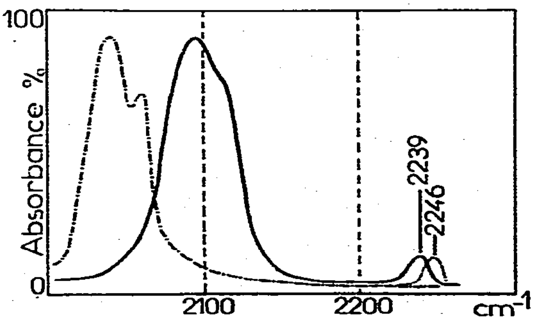
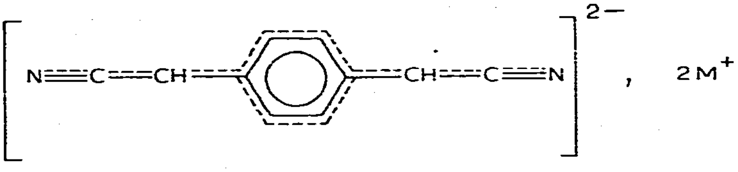


Fig. 1. IR spectra of: (··········) 1,4-bis-cyanomethyl-benzene (I); (———) mono-lithium derivative of I; (· — · —) di-lithium derivative of I.

---

* In agreement with the data for some related systems [5].

by an excess metalating agents (see Experimental), show strong bands in the 2036—2075 cm^{-1} region (Table 1). These very low ν(CN) values may be compared with the ν(CN) values of the saturated nitrile carbanions [4,5] and the aromatic nitrile dianions [12]; they agree qualitatively with a structure including two carbanionic centers, i.e. the dicarbanions obtained can be considered as dianions of dicyano-quinodimethane (Formula V) and its polycycic analogues.



(V)

$(M^+ = Li^+, Na^+ \text{ and } K^+)$

In order to prove the above assignment, the following experiments were carried out: equimolar amounts of the parent nitriles were added to solutions of the corresponding di-derivatives; the spectra of the solutions obtained showed that the corresponding mono-derivatives were formed, i.e. the reaction

$$A^{2-} + AH_2 \rightarrow 2\ AH^-$$

had taken place.

On the other hand, the protonation of the di-derivatives with an excess of diluted hydrochloric acid leads to regeneration of the parent neutral compounds I, II and III.

It is not very probable that the doublet character of the ν(CN) bands of the di-derivatives (Table 1, Fig. 1) should be due to the simultaneous presence of "free" ions and ion pairs, since the variations in the counter ion concentrations do not lead to changes either in the frequencies or relative intensities of the doublet bands. A possible explanation of the doublet character of the ν(CN) bands of the di-derivatives could be the existence of their *s-cis* and *s-trans* forms in HMPA, i.e. the bands could correspond to the synphase and antiphase vibrations of the two nitrile groups, by analogy to the anion-radicals of some aromatic dinitriles [5,11]. This assumption agrees with the fact that the ν(CN) doublet of II (di-derivatives) consists of bands of similar intensity; in the other cases the second bands, which can be ascribed to ν(CN) of the *s-cis* forms, are much weaker (Table 1).

Steric hindrance to conjugation may be expected in the polycyclic bis(cyanomethyl)arene di-derivatives; despite this, as in the case of mono-derivatives (Section A), their ν(CN) values are higher than those of the di-derivatives of I. A probable reason for the phenomenon observed is the greater possibility for delocalization of the negative charges over the larger (anthracene and naphthalene) rings. A similar increase in ν(CN) with increasing the size of the conjugated system was observed [12] in the spectra of the aromatic nitrile dianions.

The very high ν(CN) band intensities of the studied mono- and di-alkali metal derivatives, as in the other cases of anionic systems containing nitrile groups, [4,5,9,11], is due to the strong migration of the anionic charges over the conjugated system in the course of the ν(CN) vibration.

Experimental

We obtained the neutral compounds I, II and III from the corresponding bischloromethyl derivatives after reaction with potassium cyanide [13,14]. The mono-alkali metal derivatives were obtained by adding 1.1 equiv. of naphthalene dianion in HMPA and THF (counter ions Li^+, Na^+ and K^+), and dimsyl-sodium in DMSO, to the solutions of I, II and III in the corresponding solvent, under pure argon; in order to obtain the di-derivatives, 2.2 equiv. of naphthalene dianion were added. The experiments in THF were carried out as rapidly as possible, since the di-derivatives are unstable in this solvent, changing even in the absence of moisture and air.

The electrochemical generation of the carbanions was carried out in a special electrolysis cell with platinum electrodes, viz. a cathode in the measuring beam and two anodes, all built in the polythene spacer [15]. DMSO and HMPA contained 0.1 mol l^{-1} tetraethylammonium perchlorate as supporting electrolyte. By applying 4.5 V, an evolution of hydrogen was seen in the cathode space and the spectra of the electrolyzed solutions showed bands of the corresponding carbanions.

The spectra were recorded by UR-20 "Zeiss" spectrophotometer in calcium fluoride cells.

References

1 H. Feuer, Ch. Savides and C.N.R. Rao, Spectrochim. Acta, 19 (1963) 431.

2 I.N. Juchnovski, Theor. Exp. Chem., (Kiev), 3 (1967) 410.

3 C. Crüger, J. Organometal. Chem., 9 (1967) 125.

4 (a) I.N. Juchnovski and I.G. Binev, Tetrahedron Lett., (1974) 3645; J. Organometal. Chem., 99 (1975) 1; C.R. Acad. Bulg. Sci., 26 (1973) 659; (b) I.N. Juchnovski, I.G. Binev and Ts.M. Kolev, Tetrahedron Lett., (1976) 1519; (c) I.G. Binev and I.N. Juchnovski, Commun. Dept. Chem. Bulg. Acad. Sci., 9 (1976) 33.

5 I.G. Binev, Thesis, Inst. Org. Chem., Bulg. Acad. Sci., Sofia 1975.

6 Yu. A. Zhdanov and V.I. Minkin, Correlation Analysis in Organic Chemistry (Russ.), Rostov-na-Donu, 1966, p. 85 and Ch. II-1.

7 Kh.S. Bagdasaryan, Theory of Radical Polymerization, (Russ.), Nauka, Moskva, 1966, p. 293.

8 Our unpublished data.

9 I.G. Binev, R.I. Todorova-Momcheva and I.N. Juchnovski, C.R. Acad. Bulg. Sci., 29 (1976), in press.

10 M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Interscience, New York, 1968, Ch. 5; M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, Vol. 1, Wiley-Interscience, New York, 1972, Ch. 3; A.A. Solov'yanov, P.I. Dem'yanov, I.P. Beletzkaya and O.A. Reutov, J. Org. Chem. (USSR), 22 (1976) 718, 725.

11 I.N. Juchnovski and I.G. Binev, Chem. Phys. Lett., 12 (1971) 40; J. Mol. Struct., 7 (1971) 490.

12 I.N. Juchnovski, Ch. Tsvetanov and I. Panayotov, Monatsh. Chem., 101 (1970) 1271.

13 G.M. Barger, J.W. Cook and G.W. Crosbie, J. Chem. Soc., (1947) 1432.

14 M. Miller, R. Amidon and P. Tawnev, J. Amer. Chem. Soc., 77 (1955) 2845.

15 I.N. Juchnovski and I.G. Binev, C.R. Acad. Bulg. Sci., 24 (1971) 483.