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INFRARED SPECTRA AND STRUCTURE OF CARBANIONS

XII [*]. DIMERIC DIANIONS DERIVED FROM α,β-DIARYL-ACRYLONITRILES

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Summary

The IR spectra of the products of electrochemical and chemical (alkali metals, naphthalene anion-radical) reduction of substituted α,β-diaryl-acrylonitriles (32 compounds) were studied. It was found that the anion-radicals initially formed dimerize into the corresponding dimeric dianions. Correlations of ν(CN) (dimeric dianions) with ν(CN) (sodium methoxide adducts, ref. 26), as well as with the σ^- constants of the substituents in the α-aromatic rings were found. The effects of the β-substituents, counter ions and solvents on ν(CN) of the dimeric dianions are discussed.

Introduction

The dimerization of anion-radicals, which results in the formation of the corresponding diamagnetic [**] dimeric dianions, is one of the most important anion-radical reactions. The dimerization is rapid in the cases of vinyl and vinylidene monomers, and considerably slower in the other cases studied [1]; the reaction kinetics and equilibrium also depend on the ion aggregation [1]. The anion-radicals of aromatic hydrocarbons do not dimerize because of the considerable loss of resonance stability of the aromatic system, accompanying the formation of the new C—C bond; nevertheless, dimerization has been observed of the anion-radicals of anthracene and some heteroaromatic hydrocarbons [1]. In view of the great importance of the dimerization reactions, they have been the subject of a number of studies ([1], and the references therein); the part played by the dimeric dianions in the course of the anionic polymerization initiation was also been discussed. [1]. A detailed review on the mechanistic and synthetic as-

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[*] Part VIII, see ref. 35; Parts IX—XI have been submitted for publication.

[**] Unlike the paramagnetic dimers of some anion-radicals [1].

pects of the electrochemical hydrodimerization was reported in ref. [2]; the mechanism of the electro-hydrodimerization of activated alkenes and carbonyl compounds was discussed in ref. [3].

A subject of more recent studies has been the dimerization of the anion-radicals of 1,1-diphenylethylene [4—8], some other alkenes [9—11] and acetylenes [12,13], tetracyanoethylene [14,15], tetracyanoquinodimethane [16,17], heteroaromatics [18,19]. Schiff bases [20,21] and carbonyl compounds [22,23]. The routine method for the dimeric dianions preparation is the reaction with alkali metals [4,10,12—16,18—20]; dimeric dianions have also been genrated electrochemically [5,7,11,12] and otherwise [6,23]. The identification of the dimeric dianions has been carried out using data from electronic [5—8,14—19] and NMR [4,13] spectra or voltammetry [22]. The dimeric dianions have not been identified in all cases: their presence has been proved by the decrease in the concentration of the paramagnetic species (by ESR), or by the structure of the products of some further reactions.

A number of recent studies have been devoted to the kinetics [6,11,13,18, 22], mechanism [3,12,22], equilibrium [16,21,23] and some thermodynamic quantities [14,17] characterizing the dimerization reactions, as well as to the structure of the products of protonation (deuteration) [10,12], alkylation and acylation [21] of the dimeric dianions.

It can be noted that there is a very small number of studies on the structure of the dimeric dianions, by themselves: usually their structure has been assumed on the basis of indirect data, viz. the structure of the corresponding dihydro-dimers or the products of some other further reactions. We can mention, as direct studies on the structure of the dimeric dianions, those of Takahashi et al.: the electronic charge distribution in the 1,1-diphenylethylene [4] and α-methylstyrene [13] dimeric dianions has been estimated on the basis of ^{1}H NMR data.

The structure of various anionic systems containing one or more nitrile groups was conveniently studied on the basis of IR spectroscopic data [24—29]. In the present work we used this method to study the structure of the products of cathodic reduction in situ, i.e. in an electrolysis cell for IR (in dimethyl sulphoxide, DMSO), and reduction by alkali metals and naphthalene anion-radical (in hexamethyl phosphoramide, HMPA and 1,2-dimethoxyethane, DME) of a series of α,β-diaryl-acrylonitriles.

Results and discussion

The nitrile group frequencies (ν(CN)) of the products of the electrochemical reduction of the α,β-diaryl-acrylonitriles studied * are reported in Table 1. The

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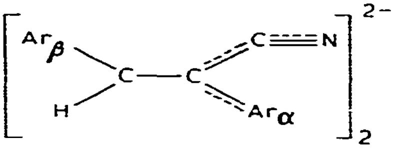
* We carried out similar experiments with some substituted cinnamonitriles. In the case of 4-nitrocinnamonitrile we showed the presence only of its anion-radical (ν(CN) at 2190 cm^{-1}). As expected [11], the anion-radicals of cinnamonitrile and the other substituted cinnamonitriles (p-CH$_3$O, p-(CH$_3$)$_2$N, m-NO$_2$ and β-phenyl) do dimerize, but the corresponding dimeric dianions were not stable under these conditions (absence of the α-aromatic ring, stabilizing the carbanionic structure), taking part in further reactions. The spectra of the products obtained showed bands at ca. 2110—2120 cm^{-1} (probably ν(CN) of fragments of the type of enamino-nitrile anions, cf. [28]) and 2140—2180 cm^{-1} (weaker and wider). On the other hand, the spectra also showed weak bands at ca. 2245 cm^{-1} (ν(CN) of fragments $\gtrdot$CH—CN in oligometic products). These results of ours are in agreement with the data of Trifonov and coworkers ([30] and the references therein), obtained in the course of the ATR-IR investigations of the cathode-initiated polymerization of acrylonitrile.

TABLE 1

FREQUENCIES (cm^{-1}) OF THE NITRILE GROUPS IN THE DIMERIC DIANIONS GENERATED ELECTROCHEMICALLY IN DMSO



Compound	Ar$_\beta$	Ar$_\alpha$	ν(CN)
1	Phenyl	Phenyl	2082
2	Phenyl	4-Tolyl	2077
3	Phenyl	3-Tolyl	2080
4	Phenyl	4-Methoxyphenyl	2079
5	Phenyl	3-Methoxyphenyl	2085
6	Phenyl	3,4-Dimethoxyphenyl	2077
7	Phenyl	4-Dimethylaminophenyl	2075
8	Phenyl	2-Naphthyl	2092
9	Phenyl	4-Biphenyl	2091
10	Phenyl	4-Fluorophenyl	2080
11	Phenyl	4-Chlorophenyl	2089
12	Phenyl	4-Cyanophenyl	2117 2175[a]
13	Phenyl	3-Cyanophenyl	2101 2216[a]
14	Phenyl	4-Nitrophenyl	2150
15	Phenyl	4-p-Benzoylphenyl	2125
16	Phenyl	1-Naphthyl	2086 2108[c]
17	Phenyl	1-Pyrenyl	2098 2114[c]
18	4-Tolyl	Phenyl	2082
19	4-Methoxyphenyl	Phenyl	2081
20	4-Dimethylaminophenyl	Phenyl	2081
21	4-Biphenyl	Phenyl	2084
22[d]	4-Cyanophenyl	Phenyl	2085 2224[b]
23	1-Naphthyl	Phenyl	2086
24	9-Phenanthryl	Phenyl	2087
25[d]	1-Pyrenyl	Phenyl	2087
26[d]	4-Cyanophenyl	4-Dimethylaminophenyl	2072 2224[b]
27[d]	1-Pyrenyl	4-Dimethylaminophenyl	2071
28	4-Dimethylaminophenyl	4-Cyanophenyl	2115 2174[a]
29	4-Cyanophenyl	4-Cyanophenyl	2113 2180[a] 2224[b]
30	4-Methoxyphenyl	4-Nitrophenyl	2152
31	4-Dimethylaminophenyl	4-Nitrophenyl	2152
32	1-Naphthyl	1-Naphthyl	2084 2107[c]

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[a] Frequency of the nitrile group in the α-aromatic ring. [b] Frequency of the nitrile group in the β-aromatic ring. [c] Doublet character of the band of the α-nitrile group (cf. refs. 26,27). [d] Frequencies of the dimeric dianion only; there are some other bands in the spectra in these cases, which are probably due to the simultaneous presence of anion-radicals in the solutions studied.

TABLE 2

ν(CN) OF DIMERIC DIANIONS, PREPARED BY REDUCTION WITH ALKALI METALS AND NAPHTHALENIDES IN DME AND HMPA

Compound No.	Solvent	ν(CN), counter ion
1	DME	2087, Li^+; 2082, Na^+; 2079, K^+
	HMPA	2093, Li^+; 2089, K^+
12	DME	2116 and 2118 [a], Li^+; 2110 and 2185 [a], K^+
	HMPA	2120 and 2180 [a], K^+
14	DME	2171, Li^+; 2169, Na^+; 2164, K^+
32	DME	2120, 2191 [a], Li^+
40	DME	2080 and ν 2222 [b], Li^+; 2072 and ν 2222 [b], K^+
41	DME	2117, 2192 [a] and ν 2225 [b], Li^+; 2112, 2185 [a] and ν 2222 [b], K^+
	HMPA	2122, 2182 [a] and ν 2225 [b], K^+; 2121, 2182 [a] and ν 2223 [b], Et_4N^+ (electrochemically generated)

[a,b] See footnotes to Table 1.

spectra of the compounds which contain additional nitrile groups (in the aromatic rings) are strongly diagnostic with respect to the structure of the corresponding anionic systems [24,26,28]; on that account, additional experiments were carried out in these cases (compounds 12, 14, 32, 40 and 41): we recorded the spectra of the products of the alkali metal and alkali naphthalenide reduction; the results are reported in Table 2. Regardless of the method of preparation and the solvents, the spectra of the products are similar (Fig. 1a, b) and the ν(CN) values are close (cf. the data in Tables 1 and 2).

According to Szwarc [1], when a molecule of a vinyl or vinylidene monomer (M) acquires an extra electron, the resulting anion-radical ($M^{\overline{\cdot}}$) has a fleeting existance only: as a result, some of the following products are formed:

$$M + e^- \rightarrow M^{\overline{\cdot}} \text{ anion-radical} \tag{1}$$

$$2\,M^{\overline{\cdot}} \rightarrow {}^-MM^- \text{ dimeric dianion} \tag{2}$$

$$M^{\overline{\cdot}} + M \rightleftharpoons {}^-MM^{\cdot} \text{ dimeric anion-radical} \tag{3}$$

$$2\,M^{\overline{\cdot}} \rightleftharpoons M^{2-} + M \text{ disproportionation: monomeric dianion} \tag{4}$$

We carried out the identification of the products obtained, as follows:

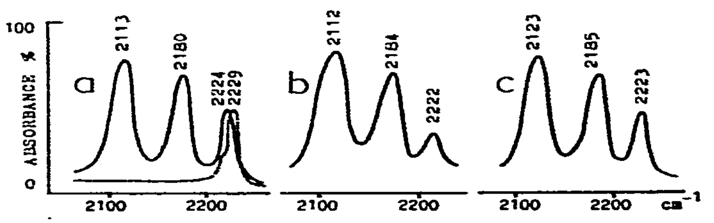


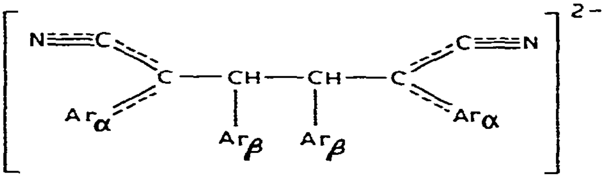
Fig. 1. IR spectra of: (a) (• • • • • •) compound 29, 0.03 *M* in DMSO; (———) its dimeric dianion, electrochemically generated in DMSO. (b) Dimeric dianion of compound 29, prepared by reduction with naphthalene-potassium in DME. (c) Sodium methoxide adduct of the same compound, 0.03 *M* in DMSO. Band assignment: 2229 cm^{-1}, superposition of the three types ν(CN); 2112—2123 cm^{-1}, ν(CN) of the α-nitrile group; 2180—2185 cm^{-1}, ν(CN) of the α-p-nitrile group; 2222—2224 cm^{-1}, ν(CN) of the β-p-nitrile group.

The particles obtained are neither anion-radicals (eq. 1), nor dimeric anion-radicals (eq. 3), since their solutions are almost inactive in the ESR: 1 active particle among 10^3—10^6 ionic particles in the solutions (cf.: less than 10^6 in the case of 1,1-diphenylethylene [31]).

The particles studied are not monomeric dianions, which could be formed as a result of the possible disproportion reaction 4, or directly (by two-electron transfer) [32], since it was found that practically fully converted solutions (absence of the bands of the parent compounds) contained 1 ± 0.1 equivalents of metal cations * for 1 mole of the parent compounds. On the other hand, the spectra of the monomeric dianions of the compounds studied show ν(CN) bands in the lower frequency region [29].

Measurable amounts of olygomeric dianions (living olygomer) were not present in the system, since they would show bands at ca. 2245 cm^{-1} (ν(CN) of unconjugated nitrile groups), and such bands were not detected in the spectra.

An assumption, that the species studied are dimeric dianions (eq. 2) does not contradict the data mentioned above. The probable structure corresponds to I,

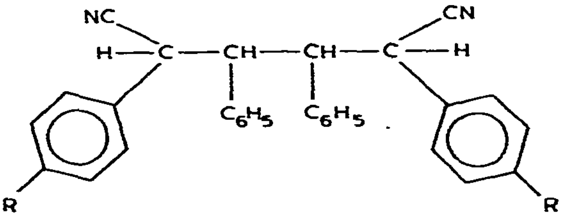


(I)

and this structure can be confirmed by the following considerations:

This mode of dimerization (by recombination of the radical ends) is thermodynamically the most favored, since it gives the best possibilities for delocalization of the anionic charge [1]: in the present case, over the aromatic ring and the strong electron-acceptor C≡N.

On the other hand, the protonation carried out in the cases of the dimeric dianions of compounds 1 and 7 (Table 1) resulted in the formation of products, whose structure (according to IR, ^{1}H NMR, molecular weight and elemental analysis) correspond to the dihydro-dimeric one (structure II).



IIa: R = H, m.p. 250°C;
IIb: R = $(CH_3)_2N$, m.p. 260°C

The frequencies ν(CN) of the dimeric dianions obtained are very close to those of the corresponding sodium methoxide adducts [26] (structure III) of the same

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* These experiments were carried out in the cases of samples prepared by alkali metal reduction.

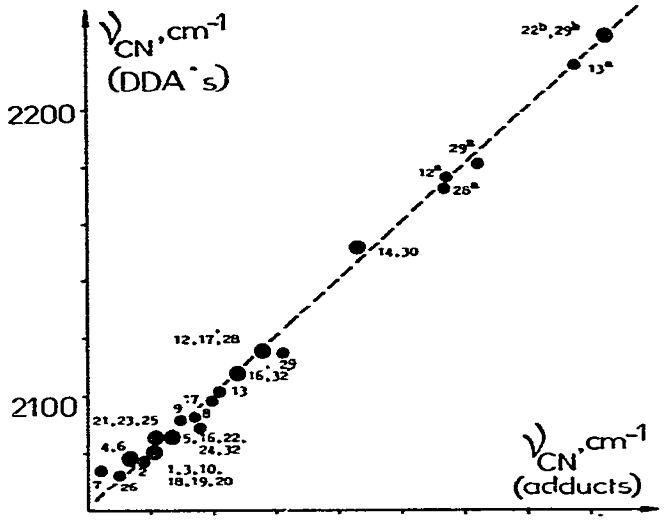
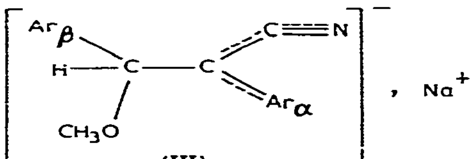


Fig. 2. Plot of ν(CN) of the dimeric dianions (DDA's) against ν(CN) of the sodium methoxide adducts [26]. Correlation equation: ν(CN) (DDA's) = (0.979 ν(CN) (adducts) + 2.4) cm^{-1}; r = 0.9964 (correlation coefficient).

α,β-diaryl-acrylonitriles, as well as to ν(CN) of the carbenoids of the correspondingly substituted arylacetonitriles [27]. The comparison of ν(CN) of the dimeric dianions with ν(CN) of the corresponding sodium methoxide adducts (III) gave



(III)

an excellent correlation (Fig. 2). We used [27] a similar correlation to prove the structure of the arylacetonitrile carbanions; as in that case [27], the full analogy in the ν(CN) region spectra of (I) and (III) (Fig. 1) is due to the identity of the fragments, conjugated with the carbanionic center (cf. structures I and III). ν(CN) of the dimeric dianions are on average 2.4 cm^{-1} higher than those of the corresponding adducts (III), which points to a very weak mutual influence of the two negative charges across two sp^3 carbon atoms.

Similarly to the cases of the adducts (III) [26] and the phenylacetonitrile carbanions [27], the bands of the α-nitrile groups in the dimeric dianions appear in a very broad frequency region, viz. 2071—2152 cm^{-1}. The correlation of ν(CN) of the dimeric dianions of α-aryl-β-phenylacrylonitriles (compounds 1—15) showed best fit with the σ^- values (according to Tseng [33]; the value of +1.1 [26] was used as σ of the benzoyl group) (Fig. 3). The present correlation is very similar to the corresponding correlations for the sodium methoxide adducts (III) [26] and the arylacetonitrile carbanions [27], which fact also confirms

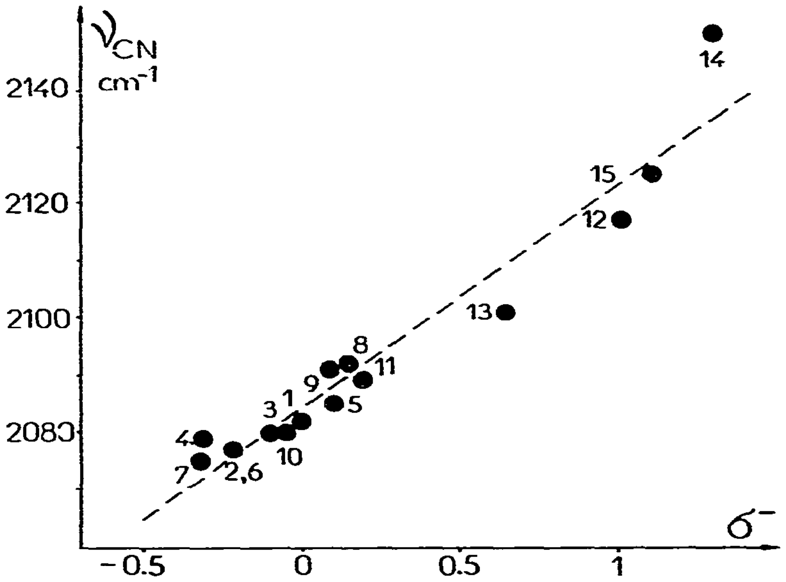


Fig. 3. Plot of ν(CN) of the dimeric dianions against σ^-. Correlation equation: $\nu(CN) = (39.0\ \sigma^- + 2084.5)$ cm^{-1}; $r = 0.964$.

structure I. The steep correlation slope ($\rho = 39.0$) and the σ constants fit are caused by the presence of the carbanionic center between the α-substituents and the indicator nitrile group, or in fact by the possibility of competitive conjugation of the very mobile charge of the carbanionic center with the α-nitrile group on the one hand, and on the other, with the electron-withdrawing substituents in the α-aromatic ring.

The influence of the β-substituents on ν(CN) of the dimeric dianions can be seen by comparing ν(CN) in the following series: α-phenyl-β-aryl-acrylonitriles (compounds 1, 18—25; ν(CN) = 2081—2087 cm^{-1}), α-p-dimethylaminophenyl-β-aryl-acrylonitriles (Compounds 7,26,27; ν(CN) = 2071—2072 cm^{-1}), α-p-cyanophenyl-β-aryl-acrylonitriles (Compounds 12, 28, 29; ν(CN) = 2113—2117 cm^{-1}) and α-p-nitrophenyl-β-aryl-acrylonitriles (Compounds 14, 30 31; ν(CN) = 2150—2152 cm^{-1}). It is seen that the effects of the β-substituents on ν(CN) do not exceed 6 cm^{-1}, which fact is in full agreement with structure I: absence of conjugation between Ar$_\beta$ and the indicator nitrile group.

As seen in Table 2, the spectra of the products obtained by reduction with alkali metals and naphthalenides of the studied compounds in HMPA and DME are very similar to each other, and are at the same time very similar to the spectra of the products, electrochemically generated in DMSO (cf. Table 1 and Fig. 1a, b). These data enabled us to assume that regardless of both the preparation method and the solvents, in all the cases studied, the structure of the products corresponds to I. It is also seen in Table 2 that all ν(CN) of the dimeric dianions studied in DME increase with the decrease of the counter ion size in the order Li$^+$, Na$^+$, K$^+$. By analogy to some similar cases [24,25,27,28], these ν(CN) variations can be ascribed to the electrostatic anion-counter ion interactions in the corresponding ion pairs.

Regardless of the method of generation, the ν(CN) bands of the dimeric dianions are 1—2 orders more intense than those of the neutral parent compounds. The very high ν(CN) band intensity, as in the cases of some other carbanions containing nitrile groups [25—28], can be explained by the strong migration of the very mobile carbanionic charge over the conjugated system in the ν(CN) vibration course.

Experimental

The preparation of the parent α,β-diaryl-acrylonitriles was described earlier [26,34]. The electrochemical generation of the dimeric dianions was carried out in a special IR electrolysis cell with CaF_2 windows [24] to an UR-20 Zeiss spectrophotometer; supporting electrolyte: 0.1 *M* $(C_2H_5)_4N^+ClO_4^-$. The alkali metal derivatives were prepared by reacting the parent compounds with alkali metals in dry HMPA and DME, or by adding the substrate solution to an equivalent amount of alkali naphthalenide in the corresponding solvent, under pure argon [28]; substrate concentrations: 0.01—0.05 *M*. The dihydro-dimers (II) were prepared by protonation of the corresponding dimeric dianions (alkali derivatives) with diluted hydrochloric or acetic acids.

References

1 M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Wiley-Inerscience, New York, 1968, Chpts. 6—8; M. Szwarc, in A Streitwieser Jr. and R.W. Taft, (Eds.). Progress Phys. Org. Chem., Wiley-Interscience, New York, 1968, Chpt. 5; M. Szwarc, Acc. Chem. Res., 5 (1972) 169.

2 M.M. Baiser and J.P. Petrovich, in A. Streitwieser Jr. and R.W. Taft, (Eds.), Progress Phys. Org. Chem., Vol. IX, Wiley-Interscience, New York, 1972, Chpt. 6.

3 L. Nadjo and J.M. Savéant, J. Electroanal. Chem., 33 (1971) 419; 73 (1976) 163; E. Lami, L. Nadjo and J.M. Savêant, J. Electroanal. Chem., 42 (1973) 189; Yu.D. Smirnov, S.K. Smirnov and A.P. Tomilov, Zh. Org. Khim., (1974) 1597.

4 K. Takahashi and R. Asami, Bull. Chem. Soc. Jap., 41 (1968) 231.

5 L.D. McKeever and R. Waack, J. Organometal. Chem., 17 (1969(142.

6 T.L. Staples, J. Jagur-Grodzinski and M. Szwarc, J. Amer. Chem. Soc., 91 (1969) 3721.

7 S.N. Bhadani, Trans. Soc. A.E.S.T., 8 (9173) 24.

8 L. Christmann-Lamande, C. Mathis, R. Nuffer and B. Francois, J. Chim. Phys. Phys.-Chim. Biol., 72 (1975) 322.

9 K. Takahashi, M. Takaki and R. Asami, J. Phys. Chem., 75 (1971) 1062.

10 D.Y. Myers, R.R. Grabbe and P.D. Gardner, Tetrahedron. Letters, (1973) 533.

11 I.B. Goldberg, D. Boyd, R. Hirasawa and A.J. Bard, J. Phys. Chem., 78 (1974) 295.

12 Z. Cs¯ ur¯ os, P. Caluwe and M. Szwarc, J. Amer. Chem. Soc., 95 (1973) 6171.

13 D. Dadley and A.G. Evans, J. Chem. Soc., (B1967) 418; E. Franta, J. Chandhuri, A. Csthegyt, J. JagurGrodzinski and M. Szwarc, J. Amer. Chem. Soc., 89 (1967) 7129.

14 R. Chang, J. Phys. Chem., 74 (1970) 2029.

15 M. Itoh, Bull. Soc. Chem. Jap., 45 (1972) 1947.

16 L. Alcacer, B.J.V. Saramago and A.M.P. Soares, Phys. Status Solidi, A20 (1973) K151.

17 T. Sakata, A. Nakane and H. Tsubomura, Bull. Chem. Soc. Jap., 48 (1975) 3391.

18 R.S. Hay and P.J. Pomery, Aust. J. Chem., 24 (1971) 2287.

19 V. Kalyanaraman, C.N.R. Rao and M.V. George, J. Chem. Soc., (B1971) 2409.

20 J. Smith and I. Ho, J. Org. Chem., 37 (1972) 653.

21 J. Smith and I. Ho, J. Org. Chem., 38 (1973) 2776.

22 A. Lasia, J. Electroanal. Chem., 42 (1973) 253.

23 W.P. Neumann, B. Schröder and M. Ziebarth, J.L. Ann. Chem., (1975) 2279.

24 I.N. Juchnovski, Ch. Tsvetanov and I. Panayotov, Monatsh. Chem., 100 (1969) 1980; I.N. Juchnovski and I.G. Binev, Chem. Phys. Letters, 12 (1971) 40; idem, C.R. Acad. Bulg. Sci., 24 (1971) 483; idem, J. Mol. Structure, 7 (1971) 495.

25 I.N. Juchnovski, Teoret. Eksp. Khim., 3 (1967) 410; I.N. Juchnovski and I.G. Binev, C.R. Acad. Bulg. Sci., 26 (1973) 659.

26 I.N. Juchnovski and I.G. Binev, Tetrahedron Letters, (1974) 3645; I.G. Binev and I.N. Juchnovski, Commun. Dept. Chem. Bulg. Acad. Sci., 9 (1976) 33.

27 I.N. Juchnovski, I.G. Binev and Ts. M. Kolev, Tetrahedron Letters, (1976) 1519; I.G. Binev, I.N. Juchnovski and Ts.M. Kolev, Commun. Dept. Chem. Bulg. Acad. Sci., in press.

28 I.N. Juchnovski and I.G. Binev, J. Organometal. Chem., 99 (1975) 1; I.G. Binev, R.I. Todorova-Momcheva and I.N. Juchnovski, C.R. Acad. Bulg. Sci., 29 (1976) 1301; Z.I. Demireva, I.G. Binev and I.N. Juchnovski, Tetrahedron Letters, (1976) 1523.

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

30 A.Z. Trifonov, Z. Phys. Chem. (Leipzig), 254 (1973) 156.

31 J. Jagur-Grodzinski and M. Szwarc, Proc. Roy. Soc. (London), A288 (1965) 224.

32 T. Asahara, M. Seno and M. Tsushiya, Bull. Chem. Soc. Jap., 42 (1969) 2416.

33 Tseng Kuang-Chih, Acta Chim. Sinica, 32 (1966) 107.

34 I.N. Juchnovski and Ts. Popov, Commun. Dept. Chem. Bulg. Acad. Sci., 2 (1969) 373; I.G. Binev and I.N. Juchnovski, Commun. Dept. Chem. Bulg. Acad. Sci., 6 (1973) 595.

35 I.N. Juchnovski, V.B. Radomirstea, I.G. Binov and E.A. Grekova, J. Organometal. Chem., 128 (1977) 139.