BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3274—3276 (1970)

The Electron Spin Resonance Spectra of Dicyanobiphenyl Radical Anions

Hideo SHIKATA,[*1] Kazuhiko ISHIZU,[*1] Yasuo DEGUCHI and Hideo TAKAKI

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

(Received February 19, 1970)

Some of the radical anions of biphenyl and its derivatives, produced by the reduction with alkali metals, show ESR spectra which can be interpreted in terms of the pairing of the alkali metal cation with the anion. As a remarkable case, the dinitrobiphenyl radical anions[1)] have their unpaired electron localized only one of the nitrophenyl rings. In the course of several previous studies,[1—3)] the ESR spectra have been observed for the radical anions of several dicyanobiphenyls, substances which possess substituents with a weaker electron-withdrawing tendency than that of the nitro groups.

Experimental

Dicyanobiphenyls were synthesized by the following procedures:

2,2′-Dicyanobiphenyl. Diphenic acid[4)] obtained from anthranilic acid with a Sandmeyer reaction was converted to its diamide by repetition of the anhydration with acetic anhydride and by treatment with ammonium hydroxide,[5)] the diamide was finally anhydrated with acetic anhydride to its dinitrile, 2,2′-dicyanobiphenyl,[6)] mp 177°C.

3,3′-Dicyanobiphenyl. 3,3′-Dinitrobiphenyl[7)] was synthesized from *m*-iodonitrobenzene[8)] by Ullmann's method. It was then reduced to 3,3′-diaminobiphenyl in the presence of Raney nickel. 3,3′-Diaminobiphenyl was tetrazotized and added to the hot KCN–$CuSO_4$ solution to obtain 3,3′-dicyanobiphenyl, mp 201°C.

4,4′-Dicyanobiphenyl. 4,4′-Dicyanobiphenyl[9)] was prepared from benzidine by the same procedures as those used in the last step used in obtaining 3,3′-dicyanobiphenyl, mp 221°C.

All the final products were purified by vacuum sublimation or by recrystallization from ethanol several times.

The radical anions were prepared by reduction with potassium, sodium, lithium, or cecium in some solvent such as 1,2-dimethoxyethane, tetrahydrofuran, or tetrahydropyran. The reduction of 4,4′-dicyanobiphenyl gave a fairly stable radical anion at room temperature, whereas 2,2′-dicyanobiphenyl and 3,3′-dicyanobiphenyl radical anions were found to be stable only at the temperature of an acetone-dry ice bath. Therefore, the ESR spectra were examined in detail for only the 4,4′-diycanobiphenyl radical anions.

The ESR spectra were measured using a JEOL-3B X-band-type ESR spectrometer with a 100 kc/sec field modulation.

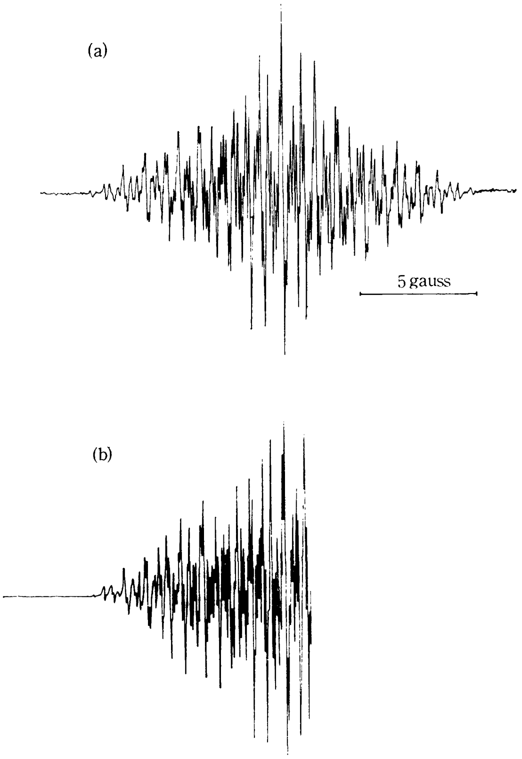


Fig. 1

(a) (2,2′-dicyanobiphenyl)$^-$ K^+ in DME
(b) the simulated spectrum of (a),

[*1] Present address: Department of Chemistry, Faculty of Science, Ehime University, Matsuyama.

1) Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, This Bulletin, **39**, 847 (1966).

2) K. Ishizu, *ibid.*, **36**, 938 (1963); **37**, 1093 (1964); **42**, 2808 (1969).

3) H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, *J. Chem. Phys.*, **40**, 241 (1964); H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, *Mol. Phys.*, **9**, 153 (1965).

4) E. R. Atkinson and H. J. Lawler, "Organic Syntheses," Coll. Vol. I, p. 222 (1941).

5) Underwood and Kochmann, *J. Amer. Chem. Soc.*, **46**, 2075 (1924).

6) Underwood and Kochmann, *ibid.*, **51**, 584 (1929).

7) R. C. Fuson and E. A. Cleveland, "Organic Syntheses," Coll. Vol. III, p. 339 (1955).

8) Ferriss and Turner, *J. Chem. Soc.*, **117**, 1149.

9) Dannett and Turner, *ibid.*, **1926**, 480.

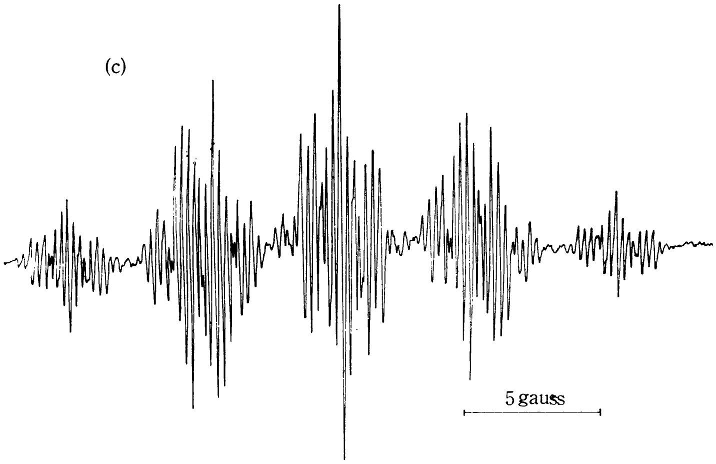


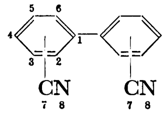
Fig. 1. (c) (3,3′-dicyanobiphenyl)$^-$ K$^+$ in DME.

Table 1. The hyperfine splitting constants and the experimental and the theoretical spin densities

Position*	h.f.s.c. (gauss)	ρ_{exp}	$\rho_{Hückel}$	$\rho_{McLachlan}$
	4,4′-Dicyanobiphenyl			
1			0.1059	0.1174
2	1.86	0.0785	0.0658	0.0767
3	0.26	0.011	0.0315	0.0075
4			0.1288	0.1591
7			0.0271	0.0143
8	1.05	0.0528	0.0437	0.0409
	3,3′-Dicyanobiphenyl			
1			0.1026	0.1058
2	0.91	0.039	0.0333	0.0238
3			0.0387	0.0258
4	5.59	0.236	0.1672	0.2113
5	0.52	0.022	0.0064	−0.0489
6	4.69	0.1965	0.1258	0.1649
7			0.0108	0.0065
8	0.26	0.013	0.0153	0.0113
	2,2′-Dicyanobiphenyl			
1			0.1151	0.1263
2			0.1174	0.1470
3	1.41	0.0595	0.0002	−0.0459
4	3.39	0.143	0.1112	0.1455
5	0.57	0.024	0.0471	0.0357
6	0.84	0.035	0.0408	0.0394
7			0.0267	0.0139
8	0.91	0.046	0.0415	0.0384

parameter values: $\alpha_N=\alpha+1.0\beta$, $\beta_{CN}=2.0\beta$, $\beta_{CC'}=0.9\beta$, $\lambda=1.2$

*



Results and Discussion

The observed spectra for dicyanobiphenyls are shown in Fig. 1. Rieger *et al.*[10] have reported that the radical anion produced by the electrolytic reduction of *p*-cyanoaniline showed the ESR spectrum of the 4,4′-dicyanobiphenyl radical anion. Our observation for synthesized 4,4′-dicyanobiphenyl supports their interpretation.

The hyperfine splitting constants for the proton summarized in Table 1, were assigned by taking into account the results of the McLachlan MO calculation, though those results are not unarbitrary. The experimental spin density for the ring carbon atoms is calculated from the McConnell relation, $a_H=Q\rho_C$, where $Q=23.7$ gauss, while for the nitrogen atom of the cyano group, $A_N=K\rho_N$ is used (according to Rieger and Fraenkell[11]), where $K=$ 19.8 gauss. The experimental spin density is then compared with that obtained from either the simple Hückel MO or the McLachlan MO calculation.

In contrast to the dinitrobiphenyl ion pairs, no alkali metal splitting was found for the 4,4-dicyanobiphenyl radical anion, though we repeatedly observed solutions with a variety of solvents, using different alkali metal and at temperatures from 20°C to −90°C. Moreover, the unpaired spin distribution was found to be symmetrical for two cyanophenyl rings of dicyanobiphenyl. These results suggest that the ion pairing, if any, is rather weaker in this case. The difference may be the weaker electron-withdrawing tendency of the cyano group than that of the nitro group.

When terephthalonitrile, which has a structure analogous to 4, 4′-dicyanobiphenyl, is reduced with lithium, it is known that the ESR spectrum

---

[10] P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963).

[11] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

shows an extra-hyperfine splitting of lithium and results in an asymmetric spin distribution of the anion.[12] In order to explain the difference in the ion pairing between the two cases, the π electron energy of these anions was estimated by the Hückel MO method on the following assumption: the accession of the alkali metal to one of the cyano groups leads to the variation of the Coulomb integral parameter, h_N, at its nitrogen atom, where $\alpha_N = \alpha + h_N\beta$. As the result of the calculations,

$$\left[\frac{\partial E}{\partial h_N}\right]_{h_N=1.0}(\text{terephthalonitrile}) - \left[\frac{\partial E}{\partial h_N}\right]_{h_N=1.0}(\text{4,4}'\text{-dicyanobiphenyl}) = 0.042\beta,$$

where E is the total π electron energy of the anion and where β is the resonance integral. This may mean that the 4,4′-dicyanobiphenyl radical anion is less stabilized by the ion-pair formation than is the terephthalonitrile radical anion. Though no consideration was made of the energy of the lone-paired electrons and of the solvation, this calculation can explain the experimental results qualitatively.

The authors are grateful to Drs. Kazuo Nakamura, Hiroaki Nishiguchi, and Kazuo Mukai for their kind discussions throughout the work. The authors also wish to thank Mr. Hideo Hasegawa for his simulation of the spectra.

---

12) K. Nakamura, This Bulletin, **40**, 1019 (1967).