The π-Trianion Radical of 2,3,6,7-Tetracyanobenzo[1,2-b:4,5-b']bisdithiole-4,8-dione. Observation of ESR with ^{13}C-Satellites in Natural Abundance

Masatoshi Hirayama,* Manabu Itasaka, Takanori Suzuki,† Yoshiro Yamashita,†† and Tsutomu Miyashi†
Department of Chemistry, Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito 310
†*Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-77*
††*Institute for Molecular Science, Myodaiji, Okazaki 444*

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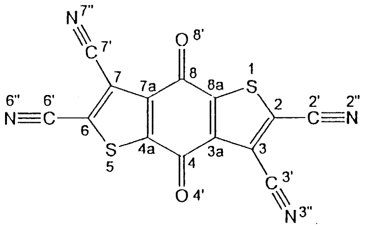
The π-trianion radical of the title compound was formed by electrolysis in acetonitrile and its ESR spectrum with ^{13}C satellites in natural abundance was observed, which was clearly identified by MO calculation.

Precise measurement of ESR hfsc's of π-trianion radicals is very instructive for theoretical consideration on electronic structue of these molecules, especially characteristics of next lowest unoccupied molecular orbital (NLUMO). However, for the formation and observation of stable π-trianion radical it has been considered that some conditions are required: The energy of NLUMO is sufficiently low, three excess charges are dispersed in a radical molecule, a π-trianion is kept planar , a π-trianion is stabilized by forming an ion pair with some counter ions.[1] In view of the trianion radicals having observed so far,[2] it appears likely that some additional factors are related to the feasibility of formation of these trianion radical. The title compound 1 has a large electron affinity as well as other quinones fused with sulphur-heterocycles,[3] while the third reduction potential E_3 has been measured to be -1.60V, although this wave seems irreversible. Considering such conditions, several characteristics of this compound enables us to expect that π-trianion radical 1^{3-} may be generated. We report here the formation of 1^{3-} by the electolysis in acetonitrile and the analysis of its ESR spectrum. 1 was synthesized in according to the literature.[4] The electrolysis of 1 was carried out using a Pyrex cell with two platinum-wire electrodes in acetonitrile with n-Bu_4NClO_4 as a supporting electolyte at room temperature. At about 2.5V (appearance voltage, Va), a blue solution was obtained, which gave ESR spectrum identified to the π-anion radical of 1. Furthermore, elevating the votage to about 3.1V the solution turned to green, which displayed a new spectrum shown in Fig.1. On decreasing slightly the voltage this spectrum gradually superseded that of the anion radical. These changes were completely reversible. Therefore, this spectrum can be expected to arise



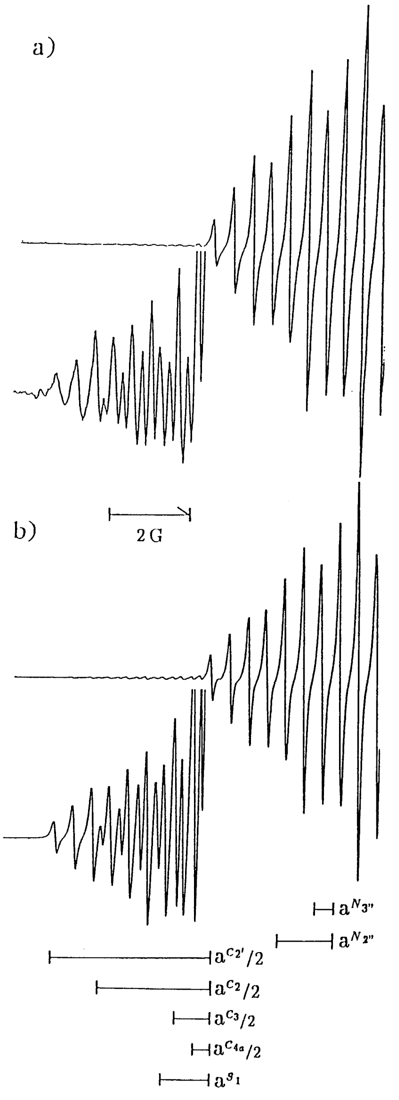


Figure 1. ESR spectrum of 1^{3-} generated by electrolysis in acetonitrile and measured at -30°C (a) and its simulation (b). In (a), the low-field part is reproduced under high amplification, which renders the ^{13}C satellite lines more evident. In (b), the magnitudes of hfsc's of $C_{3'}$ and C_{3a} were tentatively taken as to be equal to that of C_3.

from 1^{3-}, which consists with two nitrogen hfsc's arising from two equivalent nitrogens, respectively. With high amplification, several satellite lines were detected at both sides of the main spectrum and were found to arise mainly from two kinds of two equivalent ^{13}C's (7.86G, 5.54G) by measuring precisely their intensities relative to the main spectrum. Furthermore, the addition of a ^{33}S hfsc (1.22G, two equivalent ^{33}S's) and a ^{13}C hfsc (1.78G, six equivalent ^{13}C's) to the simulation led to better fit to the experimental spectrum as shown in Fig. 1b. Thus, the analysis of the spectrum by simulation together with the MO calculation of spin density distribution clearly supports the formation of 1^{3-}.

In the calculation of π-spin densities by McLachlan'method, several appropriate values of MO-parameters used were those from the literatures for a cyano group,[5] a quinone moiety,[6] and a C-S bond.[7] For evaluating hfsc's on the basis of the Karplus-Fraenkel equation, the values of polarization parameters used were those from the literatures for a cyano group[8] and a quinone moiety.[9] However, the value of Q_{cs} was tentatively taken as to be equal to that of Q_{cc}, because an appropriate value of Q_{cs} for -C-S-C- fragment in a five-membered ring has not clearly been established so far. The calculated results obtained from the McLachlan's procedure are compared with observed ones in Table 1. Thus, the largest observed a^c was assigned to a cyano carbon $C_{2'}$ and the next largest one to C_2. The third hfsc was therefore assignable to the residual three carbons, C_3, $C_{3'}$, and C_{3a}. It may be found from Table 1 that the hfs pattern induced from this π-spin distribution corresponds relatively well to experimental one. On the other hand, π-charge distribution of 1^{3-} implies that about 74% of unit charge is at each of oxygen atoms, about 33% at each of $N_{2''}$, and about 30% at each of $N_{3''}$. It may be plausible to consider that such the charge separation largely contributes to the stabilization of 1^{3-}.

Table 1. π-Spin densities and experimental and calculated hfs constants (in gaüss) of 1^{3-}

Position	ρ^π	a_{obs}	a^a_{cal}
1	0.0590	1.22	1.95
2	0.2104	5.54	4.31
2'	0.0341	7.86	-6.02
2"	0.0665	1.36	1.30
3	0.0494	1.78	-1.63
3a	-0.0073	1.78	-1.54
3'	0.0139	1.78	-1.50
3"	0.0221	0.48	0.42
4	0.0148		0.09
4a	0.0306	0.84±0.2G[b]	0.36
4'	0.0066		

[a] Estimated using π-spin densities calculated by McLachlan's method and Karplus-Fraenkel Equation with several Q-values. [b] The simulation seems to be improved to some extent by the further addition of 0.84±0.2G arising from two equivalent ^{13}C's but this is less reliable.

References and Notes

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