Tetrahedron Letters,Vol.24,No.15,pp 1567-1568,1983 0040-4039/83/151567-02$03.00/0
Printed in Great Britain

OCTACYANOTETRAMETHYLENECYCLOBUTANE DIANION AND ITS ANION-RADICAL

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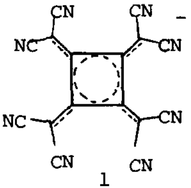
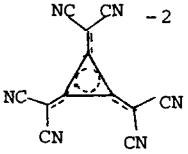
SUMMARY: A new synthesis of the novel octacyanotetramethylenecyclobutane dianion 1 is presented; electron spin resonance spectroscopy of its anion radical and cyclic voltammetry are used to elucidate its electronic properties.

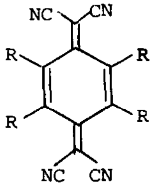
A recent communication by Seitz *et. al.*[1] reporting the synthesis of dianion 1, prompts us to report our own synthesis and studies of this interesting new pseudooxocarbon. Dianion 1 represents a higher homolog of Fukunaga's series of trimethylenecyclopropane dianions.[2] Our synthesis of 1 is analogous to Fukunaga's synthesis of hexacyanotrimethylenecyclopropandiide 2; 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene was reacted with four equivalents of malononitrile in THF, in the presence of eight equivalents of NaH. Dianion 1 was isolated as the bis(tetra-*n*-butylammonium) salt, mp 99°, in 40% yield. The low yield of 1 relative to that reported for 2 probably reflects the increased steric crowding experienced by 1.



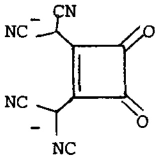
1



2



3 R = CN
4 R = H



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Our spectral data for 1 are generally similar to those reported earlier,[1] but there are significant differences. IR (Na^+ salt, KBr): 2205 (CN), 1500-1490, 1360, 1270, 1100 cm^{-1}. ^{13}C nmr (Bu_4N^+ salt): 160.8 (ring) 114.4 and 114.3 (CN), 45.7 (methylidene), 58.9, 23.7, 19.5, 13.2 (butyl). We observe a uv spectrum notably different from that previously reported.[1] UV (H_2O): λ_{max} = 400 nm (log ε = 5.07).

The ^{13}C nmr chemical shifts show the expected concentration of negative charge on the exocyclic methylidene carbons, leaving the ring relatively electropositive. Interestingly, we observe two nitrile carbon resonances, rather than just one,[1] separated by only 0.1 ppm. This indicates that the chemically distinct nitriles observed in the solid state[1] are also apparent in solution.

The esr spectrum of $1^{\overline{\cdot}}$ (Bu_4N^+ salt, electrolytic generation) exhibits the 17 line pattern expected for eight equivalent nitrogens ($a_{^{14}N}$ = 1.06 G), and one set of ^{13}C sidebands ($a_{^{13}C}$ = 22.5 G), with g = 2.00398. The ^{14}N coupling of $1^{\overline{\cdot}}$ is comparable to coupling found in related compounds 2-5 (Table 1). Using the methods of Rieger and Fraenkel,[2] the spin density of each nitrogen in $1^{\cdot -}$ is calculated to be 0.0556 (McLachlan) or 0.0530 (Hückel). The ^{13}C coupling observed is attributed to the exocyclic methylidene carbon by comparison with related compounds 2-5;[2-6] the spin density for this carbon is estimated to be approximately 0.1. Thus, about 80% of the odd electron density is _exo_ to the ring. This is in accord with intuition as well as with the ^{13}C nmr data above.

Table 1

Cmpd	E_1	E_2	$a_{^{14}N}$ (G)	λ_{max}(nm)	Log ε
1	+1.25	>+2.1	1.05	400	5.07
2	+0.34	+1.13	0.906[5]	315	4.52
3	+0.639	+1.187	1.09[3,7]	-	-
4	-	-	1.10[4]	392	4.8
5	+0.95	+1.77	1.03[6]	380	4.53

E_1: dianion/anion radical
E_2: anion radical/neutral

Whereas the esr data shows similarities between 1 and related compounds 2-5, an important difference becomes apparent with cyclic voltammetry. Upon oxidation 1 gives only a single reversible wave at +1.25 v (all potentials vs SCE), corresponding to the dianion/radical anion couple. A wave corresponding to the radical anion/neutral couple apparently occurs above +2.1 v, the limit of our acetonitrile/$LiClO_4$ system. By contrast, compounds 2, 3 and 5 show two waves each; in each case the E_1 wave occurs at significantly lower potential than that for 1 (Table 1). The high E_1 and E_2 potentials of 1 relative to 2 and 5 can be explained as due to additional stabilization of the dianion (and anion radical) of 1 by electron delocalization onto a larger number of cyano groups. However, as 3 is a structural isomer of 1, this explanation is not sufficient. The esr of $3^{\cdot -}$ [3] shows that only the dicyanomethylidene nitriles have appreciable odd electron densities. It is thus the number of dicyanomethylidene groups, rather than the number of nitrile groups, that is most important in stabilizing the radical anion and dianion of 1.

Acknowledgements. This work was supported by Grant CHE-8026714 from the National Science Foundation. The authors acknowledge the assistance of Kimberly Stearley, Daniel Wellman and Cynthia Wadsworth.

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(Received in USA 2 December 1982)