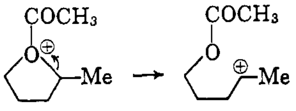
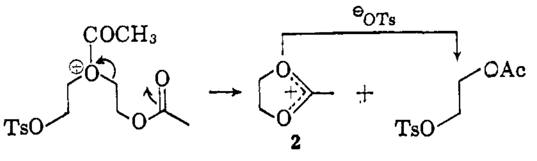


1

The weakness of tosylate anion as a nucleophile serves to inhibit the possibility of SN2-type cleavage of the acylated species **1**, thus favoring cleavage of the alternative O–C bond to yield mixed products.[8]

The remarkably specific cleavage of 2-acetoxyethyl 2′-tosyloxyethyl ether, a diprimary ether which on cleavage with acetyl *p*-toluenesulfonate gives only ethylene glycol acetate tosylate (Table I), may be explained by the assistance to cleavage in this direction rendered by neighboring acetate participation.[9]



2

The preparation, from cyclic ethers, of mixed acetate sulfonate diesters by reaction with mixed sulfonic–carboxylic anhydrides promises to have useful synthetic applications. Subsequent nucleophilic displacement of the labile sulfonate group by nucleophiles such as halide or amine moieties has enabled high-yield syntheses of a number of novel substituted acetates to be achieved. Full details of these reactions together with further regions of application of these versatile mixed anhydrides will be discussed in forthcoming publications.

(8) The reluctance of $^-$OTs to engage in nucleophilic attack is shown by the preponderance of isobutylene formation in the cleavage of *t*-butyl ethyl ether with acetyl *p*-toluenesulfonate, such formation being a consequence of the longer lifetime of the *t*-butylcarbonium ion generated by cleavage. In contrast cleavage of *t*-butyl ethyl ether with acetyl chloride–zinc chloride is reported to give a quantitative yield of *t*-butyl chloride: J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, **54**, 2088 (1932).

(9) Such AcO-5 participation invoking formation of the stabilized 2-methyl-1,3-dioxolenium ion **2** is well known; *cf.* B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(10) Weizmann Fellow, 1967–1968.

Michael H. Karger,[10] Yehuda Mazur
Department of Chemistry, Weizmann Institute of Science
Rehovoth, Israel
Received April 26, 1968

The Dicyanoethylene Anion Moiety. A New Spin Label

Sir:

The number of spin labels in rigid, bridged polycyclic compounds is growing rapidly.[1-3] An important new member of this class is the dicyanoethylene moiety. This communication presents preliminary results obtained with this useful spin-density probe in the anion radicals of two compounds, 2,3;5,6-dibenzo-7,8-dicyanobicyclo[2.2.2]oct-7-ene (I) and 2,3-dicyanobicyclo-[2.2.2]octa-2,7-diene (II).

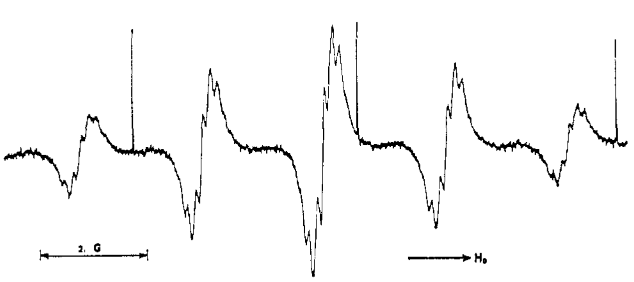
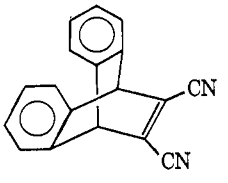
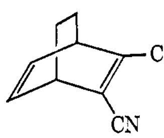


Figure 1. Anion radical from the reduction of compound I; 0.81 m*M* solution in acetonitrile.



I

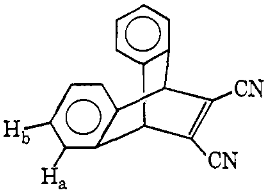


II

The parent compounds are easily synthesized by the facile Diels–Alder addition of dicyanoacetylene to anthracene and 1,3-cyclohexadiene, respectively.[4] Each compound is easily reduced electrochemically in acetonitrile. The half-wave potentials (*vs.* saturated calomel electrode) are −1.4 V for I and −1.59 V for II, and in each case the wave is polarographically reversible.

The electron spin resonance (esr) spectrum of the anion radical of I is shown in Figure 1. Its assignment is open to some question. The major splitting is due to coupling of the unpaired electron with two equivalent nitrogen nuclei; the nitrogen coupling constant is 2.30 G. The remaining hyperfine structure appears to be due to coupling with six equivalent protons. However, there are not six symmetrically equivalent hydrogen atoms present in the molecule, and so it was proposed that the two bridgehead protons had a coupling constant which was accidentally the same as that of four equivalent aromatic protons, 0.15 G.

In order to test this hypothesis, 9,10-dideuterioanthracene was prepared[5] and allowed to react with dicyanoacetylene. A spectrum of the 1,4-dideuterio anion of I shows coupling with two equivalent nitrogens and further quintet splitting, presumably due to coupling with four equivalent ring protons. At this time it is impossible to state which group of hydrogens, H_a or H_b, is responsible for this splitting. In all likelihood,



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(1) Semidiones: (a) G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); (b) G. A. Russell, K. Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965); (c) G. A. Russell, E. T. Strom, E. R. Talaty, K. Y. Chang, R. D. Stephens, and M. C. Young, *Record. Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 3 (1966); (d) G. A. Russell, G. Holland, K. Y. Chang, and L. H. Zulkow, *Tetrahedron Letters*, 1955 (1967); (e) G. A. Russell, G. Holland, and K. Y. Chang, *J. Am. Chem. Soc.*, **89**, 6629 (1967).

(2 Semiquinones: (a) L. M. Stock and J. Suzuki, *ibid.*, **87**, 3909 (1965); (b) D. Kosman and L. M. Stock, *ibid.*, **88**, 843 (1966); (c) S. F. Nelson and B. M. Trost, *Tetrahedron Letters*, 5737 (1966); (d) D. Kosman and L. M. Stock, *ibid.*, 1511 (1967).

(3) Semifuraquinones: S. F. Nelson and E. D. Seppanen, *J. Am. Chem. Soc.*, **89**, 5740 (1967).

(4) C. D. Weis, *J. Org. Chem.*, **28**, 74 (1963).

(5) Anthraquinone was reduced in the presence of D_2O according to the method of E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1438 (1936).

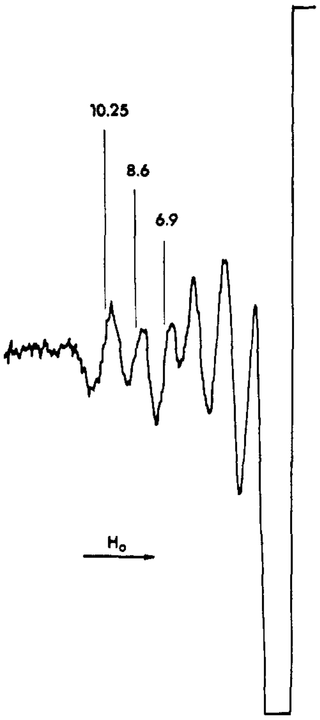


Figure 2. Low-field ^{13}C satellites of the anion of compound I; 1.25 m*M* solution in acetonitrile.

coupling to both groups does occur, giving rise to the relatively large line width (105 mG) of the undeuterated anion.[6]

The observation of apparent coupling with the bridgehead protons raises another interesting point. Since these protons are in the nodal plane of the π-orbital containing the unpaired electron, the hyperconjugative coupling mechanism can be ruled out. The consecutive polarization mechanism must be invoked,[7] which argues for a high spin density on the ethylenic carbons and also for relatively high spin densities on the bridgehead carbons as well. This is borne out by the observation of three different ^{13}C coupling constants as seen in Figure 2, which shows the low-field satellites. The three lines at lowest field are the ^{13}C satellites from the $|M_{\mathrm{IN}}| = 2$ line and the next group of three lines arises from the $|M_{\mathrm{IN}}| = 1$ nitrogen line. The intensities of the ^{13}C lines, with respect to the parent nitrogen lines, are the correct values for doubly degenerate carbon sites. The values of the ^{13}C coupling constants are 10.25, 8.6, and 6.9 G and are presumably due to the cyano, ethylenic, and bridgehead carbon atoms, respectively; molecular orbital calculations have not yet been initiated to confirm this assignment.

Returning momentarily to the question of bridgehead proton coupling, it may be that the dicyanoethylene spin label concentrates significantly more spin density at the bridgeheads than do the previously reported labels. Thus, the other bicyclo[2.2.2]octane anions[1e,2a,3] do not exhibit coupling with the bridgehead protons.

An example in which bridgehead proton coupling is unequivocal appears in the anion radical of compound II. A spectrum of this radical together with the computed reconstruction appear in Figure 3. The parameters used in the computed spectrum along with the provisional assignments are as follows: 2.34 (two nitrogens); 1.805 (two ethylenic hydrogens); 1.255 (two *anti* hydrogens); 0.45 (two *syn* hydrogens); 0.225 (two bridgehead hydrogens); and a Lorentzian line width of 0.14 (values in gauss).

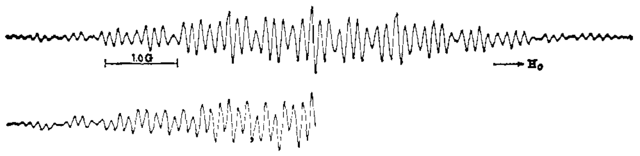
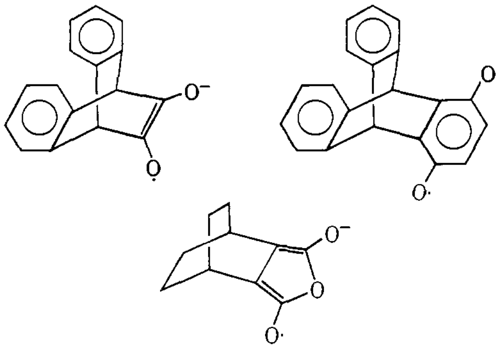


Figure 3. Anion radical from the reduction of compound II; 0.72 m*M* solution in acetonitrile. One-half of spectrum simulated using parameters in the text.



Further deuteration experiments will be undertaken to elucidate these preliminary observations. Other radicals containing the dicyanoethylene spin label will be discussed subsequently, as will the question of through-space *vs.* through-bond delocalization mechanisms.

Ted M. McKinney
Department of Chemistry, University of California
Riverside, California 92502

Received April 22, 1968

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[6] In the analogous semidione anion radical,[1e] all eight ring protons were observed to couple equally and no bridgehead proton coupling was discernible.

[7] J. P. Colpa and E. de Boer, *Mol. Phys.*, 7, 333 (1964).

Magnetic Ordering of Poly-γ-benzyl-L-glutamate Solutions

Sir:

The liquid crystalline nature of concentrated solutions of poly-γ-benzyl-L-glutamate (PBLG) in solvents such as CH_2Cl_2, $CHCl_3$, dichloroacetic acid, and N,N-dimethylformamide (DMF) has been well established by optical, microscopic,[1] and X-ray[2] studies. In these anisotropic phases, rigid (α helix) polymer molecules are aligned in a parallel fashion.[2] Because of the optically active nature of the polymer, each molecule is tilted slightly relative to its neighbor, and a helical structure develops that is manifested optically as a series of equidistant, parallel lines with a spacing equal to half the helical pitch. This structure is similar in many respects to that of thermotropic cholesteric melts.[3]

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[1] C. Robinson, *Trans. Faraday Soc.*, 52, 571 (1956).

[2] C. Robinson, J. C. Ward, and R. B. Beevers, *Discussions Faraday Soc.*, 25, 29 (1958); D. A. D. Parry and A. Elliott, *J. Mol. Biol.*, 25, 1 (1967).

[3] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., New York, N. Y., 1962.