

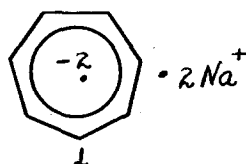
CYCLIC CONJUGATED DIANION RADICALS II  
 THE FLUORENIDE AND CARBAZOLIDE DIANION RADICALS

N. L. Bauld, J. H. Zoeller, Jr.  
 Department of Chemistry  
 The University of Texas  
 Austin, Texas 78712

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The first hydrocarbon dianion radical (1) was reported recently (1).

Since the cycloheptatrienyl system is such a favorable one for dianion radical



formation (the final electron enters an HMO of energy  $E = \alpha - 0.44\beta$ ) it seemed desirable to seek other examples of dianion radicals, particularly in systems simple enough to provide tests of current pi electronic theories. The purpose of the present report is to describe two more examples of the aforementioned type in which, now, HMO's of energy about  $E = \alpha - 0.8\beta$  are utilized; additionally, we hope to illustrate the good agreement between theoretically calculated and experimentally determined spin densities for these novel species.

Fluorene reacts with sodium-potassium alloy in DME to form the fluorene anion radical, which has a biphenyl-like pi system. At ambient temperatures this radical instantly decomposes to the fluorenyl anion, as reported (2). The latter anion can also be prepared starting with 9-bromofluorene. The further reaction

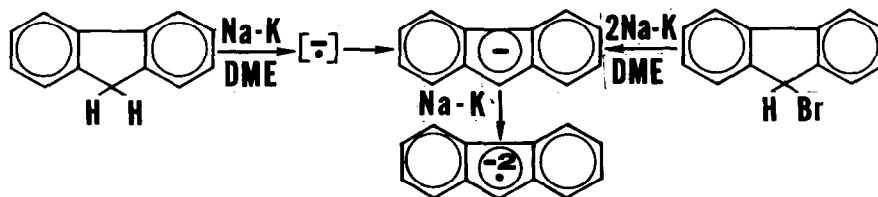


TABLE 1

Position	<sup>a</sup> <sub>exp.</sub>	<sup>a</sup> <sub>calc.</sub> (Hückel) <sup>a</sup>	<sup>a</sup> <sub>calc.</sub> (McLachlan)	<sup>a</sup> <sub>calc.</sub> (SCF)
(Fluorenylide)				
1	3.20	-3.13	-3.70	-3.56
2	3.20	-3.04	-3.49	-2.89
3	0.36	-0.13	+1.13	+0.88
4	4.74	-4.11	-5.22	-5.00
9	0.36	-0.57	-0.37	-0.71
(Carbazolide) <sup>b</sup>				
1	2.96	-2.85	-3.38	
2	3.58	-3.20	-3.19	
3	0.60	-0.50	+1.36	
4	4.85	-4.00	-5.17	
N	0.00	c		

<sup>a</sup>All calculations of  $a$  were performed using the Colpa-Bolton equation,  $a_1 = (-27 - 12.8q_1)\rho_1$ , where  $q_1$  is the charge density and  $\rho_1$  is the odd electron or spin density at atom 1.

<sup>b</sup>The Hückel calculations were made using  $\beta_{CN} = \beta_{CC}$  and  $\alpha_N = \alpha_C + 0.5\beta$ .

<sup>c</sup>Owing to the uncertainty in the effective value of  $Q$  here, no  $a_N$  has been calculated; however, the calculated spin density<sup>1</sup> at nitrogen (0.019) is an order of magnitude less than those at carbon. Thus a small or vanishing  $a_N$  is reasonable.

of the anion with alloy results in the formation of the stable (at room temperature) green fluorenylide dianion radical. The esr spectrum (Fig. 1) is readily analyzed into the isotropic hyperfine splitting constants ( $a_1$ ) given in Table 1. It is gratifying to note that even the simple Hückel calculations give a good account of the spin densities as reflected by the  $a_1$  (3). The assignment of splitting constants to particular positions has been fully verified by the esr spectra of the 2,9-, 3,9-, 4,9-, and 9-deutero dianion radicals.

The analogous carbazolide dianion radical has been obtained in like manner and its spectrum is given in Fig. 2. We did not, however, succeed in

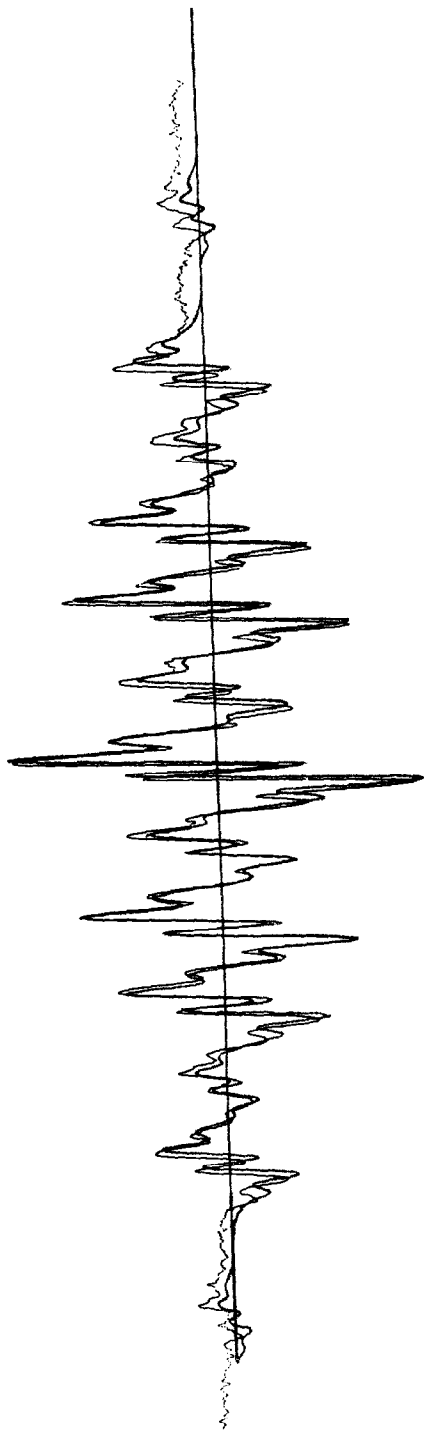


Fig. 1 Experimental (boldface) and simulated  
ESR spectra of the fluorenyl dianion  
radical ( $-30^\circ$ , DME, Na-K alloy)

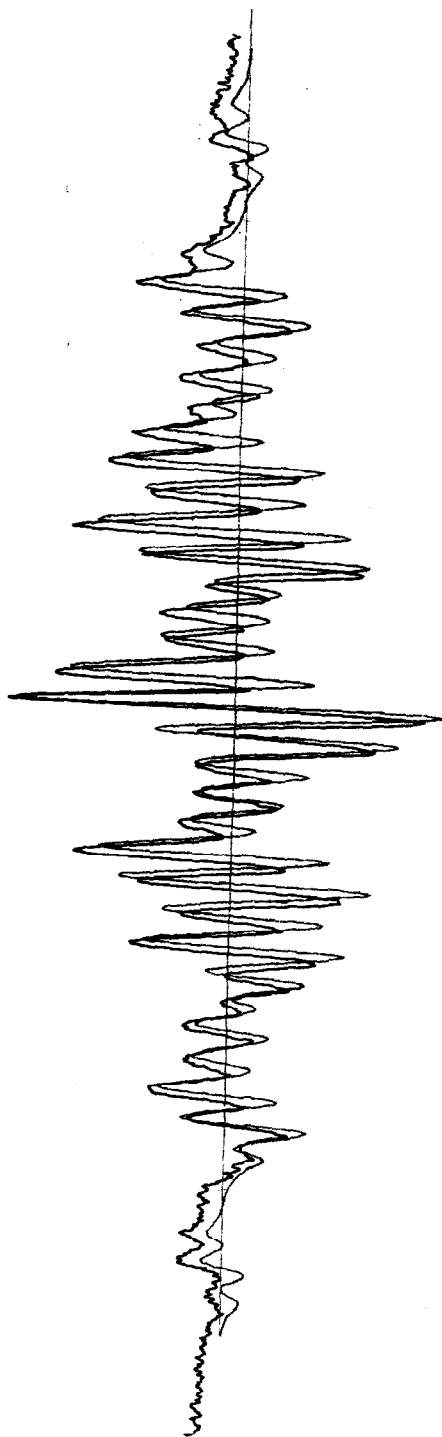


Fig. 2 Epr spectra of the carbazolidine dianion radical (ambient, DME, Na-K alloy)

obtaining any esr signal from indole except that of the benzene anion radical.



Indene yielded a spectrum which appears almost certain not to be that of the indene dianion radical. The latter two systems have  $E = \alpha - 0.9\beta$ . A reasonable working hypothesis might therefore be that a cyclic conjugated anion must have a vacant HMO of energy not much greater than  $\alpha - 0.8\beta$  in order to form a dianion radical. We have also noticed the lack of dianion radical formation with cyclo-nonatetraenide ion which has relevant  $E = \alpha - 1.00\beta$ . It may be recalled that neutral molecules are, at least in some cases (benzene anion radical) able to utilize ABMO's energy as high as  $\alpha - 1.00\beta$  or higher. It is felt that the additional repulsions present in a dianion radical as contrasted to an anion radical could account for the apparent difference in their respective thresholds of reactivity.

#### REFERENCES

1. N. L. Bauld and M. S. Brown, J. Amer. Chem. Soc. 87, 4390 (1965). Since then, two additional reports of more complex hydrocarbon dianion radicals have appeared: P. Dowd, J. Amer. Chem. Soc. 87, 4968 (1965) on the tetraphenylallyl dianion radical and E. G. Jansen and J. C. Pacifici, J. Amer. Chem. Soc. 87, 5504 (1965) on the bisindenylphenylmethide dianion radical.
2. R. L. Kugel, W. G. Hodgson, and H. R. Allcock, Chem. Ind. 1962, 1649.
3. The SCF calculations were of the open shell type recently described by A. T. Amos and L. C. Snyder, J. Chem. Phys. 42, 3670 (1965). Thanks are due to Dr. Snyder for these results. The open shell method without annihilation of unwanted spin components is grossly inaccurate.