proton, although directed away from the fluorine, also couples with it. Coupling could conceivably occur through the bonds, but it seems more likely that spin information is relayed either through the agency of the *syn* proton or by overlap of the fluorine with the small rear lobe of the *anti* C_8–H bond.[15] Whatever the mechanism, it is now certain that the satisfaction of the space criterion for a proximal proton will ensure that the geminal, apotropic proton couples as well. Consequently, for the cases of $^5J_{HF}$ coupling involving methyl groups, it has to be considered probable that *all* three methyl protons are simultaneously coupled. It remains to be seen whether other fixed proximal arrangements, for example, that shown by Figure 3b, which do not obey Cross's rule, also undergo coupling through space.

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[15] This mechanism is reminiscent of that postulated for coupling through oxygen; K. C. Ramey and J. Messick, *Tetrahedron Lett.*, 4423 (1965); F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 5249 (1965).

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Nuclear Magnetic Resonance Spectra of the Dianions of Anthracene and Other Polynuclear Aromatic Hydrocarbons

Sir:

We report here the nmr spectra of a series of dianions obtained by two-electron reduction of planar aromatic hydrocarbons[1] and note some anomalies which arise in an attempt to compare empirically estimated electron densities in these species with those in the corresponding radical anions.

Nmr spectra[2] of the dianions of anthracene (**1**), tetracene (**2**), acenaphthylene (**3**), fluoranthene (**4**), and perylene (**5**), prepared by reduction of the hydrocarbons in tetrahydrofuran-d_8 with metallic sodium or lithium, are shown in Figure 1. Chemical shift data taken from these spectra are summarized in Table I. In all compounds studied, electron exchange[3] broadened the nmr lines of the parent hydrocarbon into the base line as soon as a visually detectable amount of the highly colored radical anion was formed. The spectrum of the dianion appeared only when essentially quantitative two-electron reduction had been achieved.

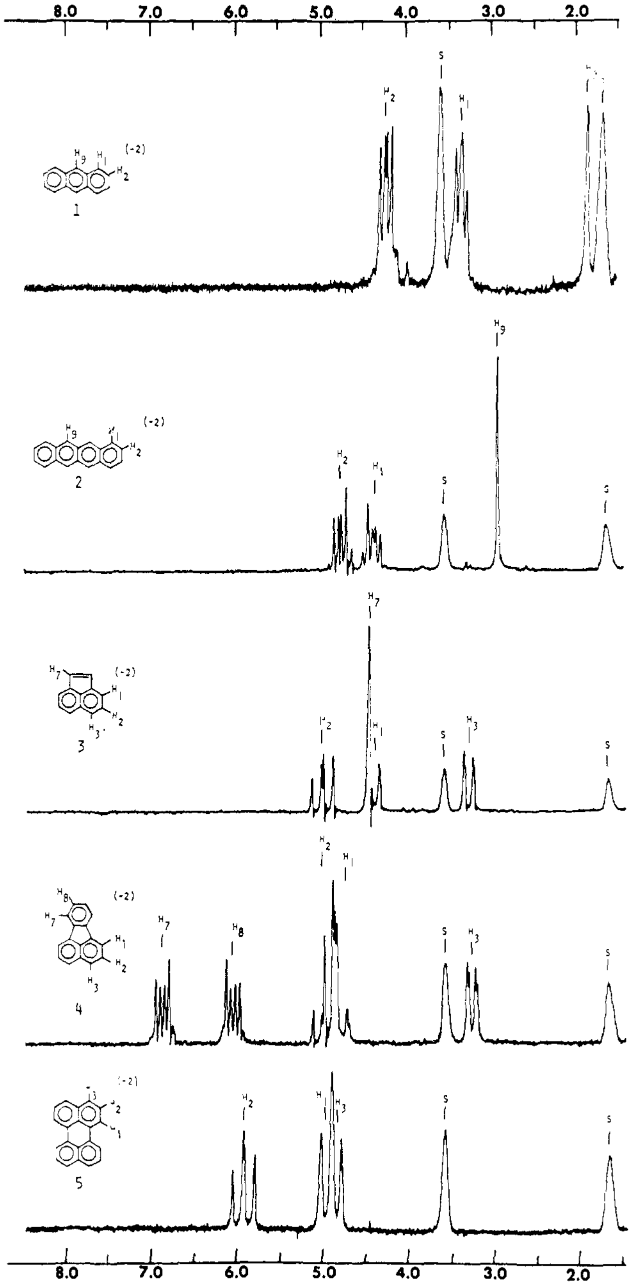

Figure 1. 60-MHz nmr spectra of aromatic hydrocarbon dianions in tetrahydrofuran-d_8. The counterion is lithium in **1** and sodium in all other spectra. Peaks at 1.7 and 3.6 ppm indicated by S arise from the protons in tetrahydrofuran-d_7 present in the deuterated solvent.

The differences in charge-induced chemical shift[4] between protons in the dianions and in their neutral precursors are shown in Table I. The excess charge,

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[1] (a) G. J. Hoijtink, *Rec. Trav. Chim.*, 74, 1525 (1955); (b) G. J. Hoijtink, P. Balk, and J. W. H. Schreurs, *ibid.*, 76, 813 (1957).

[2] All spectra were obtained at 37 ± 1° using an A-60A spectrometer purchased with funds from the National Science Foundation.

[3] (a) E. deBoer and H. van Willigen, *Progr. NMR Spectros.*, 2, (1967). (b) Both uniform and nonuniform broadening of the lines of the neutral and dianionic species have been observed depending on whether the conditions for "strong" or "weak" exchange are met.[3a] In the weak pulse limit, broadening is least for protons such as H_2 and H_7 in fluoranthene and H_2 in perylene which are weakly coupled to the unpaired electron in the radical anion. Further aspects of these electron-exchange effects are currently being investigated.

[4] (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 82, 5846 (1960); (b) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); (c) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963); (d) T. J. Katz, *J. Amer. Chem. Soc.*, 82, 3784 (1960); (e) W. G. Schneider in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 63.

Table I. Comparison of Charge-Induced Chemical Shifts and Hyperfine Splittings in Aromatic Dianions and Radical Anions

Compound	Position $(r)^a$	δ (dianion), ppm^b	$\Delta\delta_r$, ppm^c	$\|a_r^H\|$, G^d
Anthracene (**1**)	1	3.36	4.61	2.74
	2	4.25	3.18	1.51
	9	1.89	6.56	5.34
Tetracene (**2**)	1	4.46	3.54	1.54
	2	4.85	2.65	1.16
	9	3.00	5.63	4.23
Acenaphthylene (**3**)	1	4.50	3.08	4.51
	2	5.04	2.46	0.45
	3	3.33	4.37	5.64
	7	4.46	2.59	3.09
Fluoranthene (**4**)	1	4.81	2.97	3.91
	2	5.04	2.47	0.15
	3	3.27	4.63	5.28
	7	6.89	0.95	0.08
	8	6.06	1.25	1.21
Perylene (**5**)	1	4.99	3.28	3.09
	2	5.93	1.52	0.46
	3	4.87	2.83	3.55

[a] See Figure 1 for numbering systems. [b] All chemical shifts were determined relative to the low-field multiplet of THF and related to internal TMS by assuming a value of δ 3.60 ppm for the solvent peak. [c] $\Delta\delta_r = \delta_r(\text{neutral}) - \delta_r(\text{dianion})$. For analysis of nmr of parent hydrocarbons see B. P. Dailey, S. Gordon, and N. Jonathan, *J. Chem. Phys.*, **36**, 2443 (1962), for **1** and **5**; R. H. Martin, N. Defay, F. Geerts-evrard, and S. Delavarenne, *Tetrahedron* 1073 (1964), for **2**; and M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2704 (1963), for **3**. [d] $|a_r^H|$ = absolute value of hyperfine splitting at position r in radical anion. Large values have negative signs, and values less than 0.5 G are probably positive. Hyperfine splitting data were taken from the following references: G. K. Fraenkel, and J. R. Bolton, *J. Chem. Phys.*, **40**, 3307 (1964), for **1**; G. K. Fraenkel, M. Kaplan, and B. G. Segal, *ibid.*, **43**, 4191 (1965), for **2** and **4**; F. Gerson, *Helv. Chim. Acta*, **49**, 1837 (1966), for **3**; and A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947, (1959), for **5**.

q_r, at a trigonally hybridized position, r, in conjugated ions has been generally assumed[4] to be related by eq 1 to the charge-induced chemical shift, $\Delta\delta_r$, of a proton attached to that carbon. The constant, K, is usually taken to be approximately 10 ppm per unit

$$\Delta\delta_r = -Kq_r \qquad (1)$$

charge. The data in Table I indicate, however, that this value of K is much too low to explain the large upfield shifts observed in most of the dianions reported here. For example, the sums of charge-induced chemical shifts over all positions bearing protons for dianions **1** through **5** are 44.3, 47.3, 25.0, 24.5, and 30.5 ppm, respectively. Inasmuch as the *maximum* value of q_r in the dianions summed over all positions is -2, the *minimum* value of K which will fit these data, assuming that no carbon atom in the dianion bears a formal positive charge, ranges from 12 to 23 ppm per electron. The upper limit is approximately twice the generally accepted value obtained empirically from the nmr spectra of monocyclic polyene ions.[4a–d] Although the lower limit is in better agreement, it carries the unrealistic implication that the proton-free positions of **3** and **4** bear no negative charge. Inclusion of a term quadratic in q_r in eq 1, as has been suggested,[5] only leads to a still larger value of K. Furthermore, the probability that the dianions are present as ion triplets or higher aggregates would also be expected to have an effect on chemical shifts which is opposite to that observed.[4a,c]

Whether the apparent high sensitivity of chemical shifts to charge in the polycyclic dianions is actually the result of additional shielding effects such as anomalous paramagnetic ring current contributions or shielding from charge on adjacent atoms[4e] must await detailed theoretical analysis of the results. It is clear, however, that despite the good correlation obtained for monocyclic ions,[4] eq 1 must be used with caution in "evaluating" charge densities.

If one simply *assumes* proportionality between chemical shifts and π-charge densities in the dianions reported here, a comparison with esr hyperfine splittings in the corresponding radical anions indicates a qualitatively more uniform electron distribution in the dianions (see Table I). The effect is especially apparent at positions which have a small spin density in the radical anion but exhibit a substantial upfield shift of the proton resonance in the dianion. This observation, based on a comparison of two empirical quantities, is consistent with the apparent necessity for explicit consideration of electron repulsion effects in calculating π-electron densities in benzylic anions[4c,6] and azulene dianion.[4c]

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(5) J. I. Musher, *J. Chem. Phys.*, 37, 34 (1962).

(6) H. H. Freedman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

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The Structure of Nucleocidin. III (a New Structure)

Sir:

Nucleocidin, an antitrypanosomal antibiotic, was first isolated[1a] and described[1b] in 1957. Partial structure **1** was proposed[2] based on an empirical formula of $C_{11}H_{16}N_6SO_8$ which had been derived from ir and uv spectra, elemental analysis, and chemical degradation studies. This structure was recently revised to 9-(4-O-sulfamoylpentofuranosyl)adenine[3a] ($C_{10}H_{14}N_6SO_7$) on the basis of additional chemical and spectroscopic evidence.

New spectroscopic evidence, including 100-MHz ^{1}H nmr, ^{19}F nmr, and mass spectral data, has now provided

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(2) C. W. Waller, J. B. Patrick, W. Fulmor, and W. E. Meyer, *J. Am. Chem. Soc.*, **79**, 1011 (1957).

(3) (a) J. B. Patrick and W. E. Meyer, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, MEDI-024; (b) J. B. Patrick, private communication (previous analysis of the 60-MHz spectrum had suggested that hindered rotation was the cause of the doubling in the $C_{3'}$-H and the $C_{5'}$ methylene).