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is over 8 Å., and we assume that it is at least as large in $[\text{Ni}(\text{detu})_4\text{Cl}_2]$. Metal-metal bonding is therefore not evident, nor is a path for superexchange interaction apparent in the structure¹⁰ of $[\text{Ni}(\text{tu})_4\text{Cl}_2]$. We also assume its absence here. Furthermore the spectra (Fig. 1) are similar to other compounds with a tetragonal field,¹¹ such as $[\text{Ni}(\text{etu})_4](\text{ClO}_4)_2$. Lastly, the effects of magnetic coupling on spectra are not well known, but appear to be small.¹² The temperature dependence of the spectrum therefore does not appear to be due to exchange effects.

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Orbital Degeneracy and the Electron Spin Resonance Spectrum of the Benzene-1-*d* Negative Ion¹

Sir:

In recent years there has been considerable interest in the Jahn-Teller theorem² and in the simpler molecules such as the negative ion radical of benzene to which it is applicable.^{3,4} The ground electronic state of this radical is doubly degenerate, but the substitution of a methyl group as in the toluene and *p*-xylene anions has a large enough effect to remove the degeneracy.^{4,5} Although the substitution of deuterium for hydrogen in a free radical normally has a negligible effect on the spin-density distribution, it is possible that the degeneracy of the benzene anion would be lifted by deuterium substitution, and we consequently have investigated the electron spin resonance spectrum of the negative ion of benzene-1-*d*.

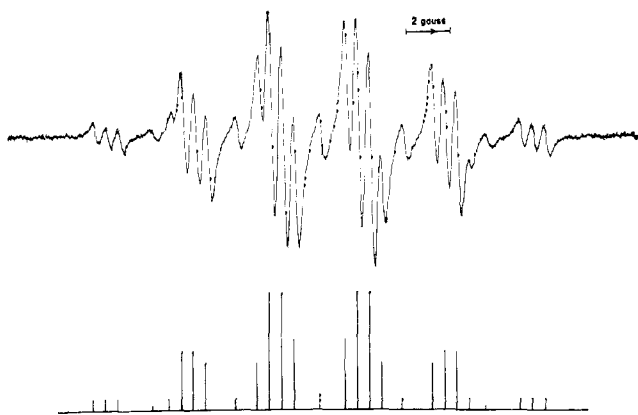


Fig. 1.—First derivative of the e.s.r. spectrum of the benzene-1-*d* anion. The reconstruction includes dotted lines corresponding to a 4% impurity of C_6H_6^- .

The e.s.r. spectrum of the benzene-1-*d* anion is shown in Fig. 1. Benzene-1-*d*, which was prepared by the

(1) Supported in part by the National Science Foundation through Grant NSF-GP-1370.

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method of Weldon and Wilson,⁶ was dissolved in a 1,2-dimethoxyethane-tetrahydrofuran mixture and reduced to the anion radical with a sodium-potassium alloy using the procedure of Bolton.⁷ An X-band superheterodyne spectrometer⁸ was employed with a sample temperature of -100° . The spectrum is readily interpreted as arising from $\text{C}_6\text{H}_5\text{D}^-$ with about a 4% impurity of C_6H_6^- . The latter serves as a convenient internal standard, and the hyperfine splittings relative to benzene, $r^{\text{X}_i} = a^{\text{X}_i}(\text{C}_6\text{H}_5\text{D})/a^{\text{H}}(\text{C}_6\text{H}_6)$, are: $r^{\text{H}_2} = r^{\text{H}_3} = r^{\text{H}_5} = r^{\text{H}_6} = 1.046 \pm 0.002$, $r^{\text{H}_4} = 0.908 \pm 0.005$, and $r^{\text{D}_1} = 0.148 \pm 0.002$. Using $a^{\text{H}}(\text{C}_6\text{H}_6) = 3.75$ gauss^{4,7} gives (in gauss): $a^{\text{H}_2} = 3.92 \pm 0.01$, $a^{\text{H}_4} = 3.41 \pm 0.01$, and $a^{\text{D}_1} = 0.55 \pm 0.01$. The widths of both the deuterated and undeuterated benzene anion absorption lines were the same within experimental error and had the value 0.3 gauss between points of extreme slope. The symmetry of the $\text{C}_6\text{H}_5\text{D}^-$ spectrum about the central line of the C_6H_6^- spectrum implies an equality of the *g*-values of the two radicals to within three parts in 10^6 .

The spectrum of the monodeuteriobenzene anion thus shows that the twofold degeneracy of the ground electronic state of the benzene negative ion is lifted on deuterium substitution. The increase relative to the benzene negative ion of the spin densities from positions 2, 3, 5, and 6, and the decrease at the other positions, indicates that the orbital which is antisymmetric with respect to reflection in the plane through the 1 and 4 positions makes a greater contribution than the symmetric orbital. The antisymmetric orbital is also predominant, and to a much larger extent, in the toluene and *p*-xylene anions.⁵ The direction of the changes that we have found on deuterium substitution is consistent with the secondary isotope effects observed on rates and equilibria.⁹ In the methyl-substituted anions, the stabilization of the antisymmetric orbital is thought to arise from the electron-repelling effect of the methyl groups,^{5,10} but the importance of vibronic interactions is not fully understood. The role of these interactions in the deuteriobenzene anions is currently under investigation.

Adding together the hyperfine splittings in the monodeuteriobenzene anion gives $(1/6)(4r^{\text{H}_2} + 2r^{\text{H}_4}) = 1.000 \pm 0.001$, so that a constant value of $Q_{\text{CH}^{\text{H}}}$ in McConnell's¹¹ relation $a^{\text{H}_i} = Q_{\text{CH}^{\text{H}_i}}^{\text{H}}$ for C_6H_6^- and $\text{C}_6\text{H}_5\text{D}^-$ implies the equality of the spin densities at the 1- and 4-positions in the deuterated radical. There is thus a small but significant isotope effect since $a^{\text{H}_4}/a^{\text{D}_1} = 6.15 \pm 0.11$ while the value of 6.514 is expected if the difference in proton and deuterium splittings is caused only by the magnetic properties of the two isotopes.¹²

The anion of benzene-1,4-*d*₂ has also been observed, but the sample was contaminated with an appreciable amount of benzene-1-*d*. Preliminary studies indicate the spectrum is consistent with predictions based on the spectrum of the benzene-1-*d* anion. Further aspects of the effect of deuterium substitution on the benzene anion spectrum are being actively investigated.

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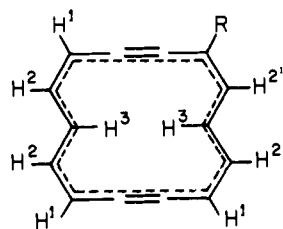
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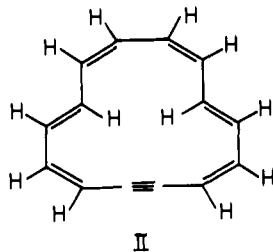
Electrophilic Substitution of Aromatic Fourteen-Membered Ring Cyclic Conjugated Systems¹

Sir:

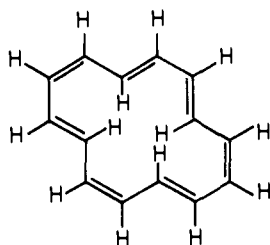
1,8-Bisdehydro[14]annulene (Ia)²⁻⁴ and monodehydro[14]annulene (II or III)^{2,5} have been shown to be aromatic compounds, since they sustain an induced ring current as demonstrated by nuclear magnetic resonance (n.m.r.) spectroscopy.^{3,5} On the other hand, [14]annulene (IV)^{2,6} on this basis is nonaromatic.^{1,5} Aromatic character has usually been associated with the ability to undergo electrophilic substitution reactions (although this need not necessarily be true for all aromatic systems^{1,5,7}). We now report that the two aromatic dehydroannulenes Ia and II (or III) in fact do undergo such substitution reactions, whereas the nonaromatic [14]annulene (IV) under analogous conditions does not.



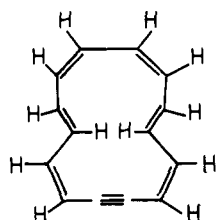
Ia, R=H Ic, R=SO₃Me
b, R=NO₂ d, R=COMe



II



III



IV

1,8-Bisdehydro[14]annulene (Ia) underwent substitution at the position adjacent to the acetylene. Nitration with cupric nitrate in acetic anhydride at room temperature yielded *ca.* 25% of mononitro compound Ib as black needles, which decomposed above 200° on heating [$\lambda_{\text{max}}^{\text{isooctane}}$ 327, 467, and 605 μm (ϵ 85,500, 19,000, and 7800); $\lambda_{\text{max}}^{\text{benzene}}$ 337, 476, and 608 μm ;

(1) This is Part XXXI in the series "Unsaturated Macroyclic Compounds"; for Part XXX, see F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).

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Anal. Found: N, 5.41]. The n.m.r. spectrum (100 Mc./sec., CDCl₃ solution) clearly points to structure Ib; it consists of two symmetrical 1-proton triplets at 15.25 and 14.85 τ ($J = 13.5$ c.p.s.) assigned to the inner H³ protons, a 3-proton multiplet at 1.30 τ assigned to H¹, a 3-proton multiplet at 0.33 τ due to H², and a 1-proton doublet at -0.43 τ ($J = 13.4$ c.p.s.) due to H^{2'} (the proton adjacent to the substituent).

Sulfonation of Ia with oleum in dioxane at room temperature gave a water-soluble sulfonic acid ($\lambda_{\text{max}}^{\text{water}}$ 314, 440, and 590 μm), which was converted to the silver salt with aqueous silver nitrate and then methylated with methyl iodide. The resulting monomethyl sulfonate (Ic), formed in *ca.* 30% yield, crystallized as red needles, m.p. 168–169° dec. [$\lambda_{\text{max}}^{\text{isooctane}}$ 315, 442, and 591 μm (ϵ 179,000, 20,400, and 7700); $\lambda_{\text{max}}^{\text{benzene}}$ 321, 448, and 591 μm ; *Anal.* Found: C, 66.80; H, 4.73]. The n.m.r. spectrum (100 Mc./sec., CDCl₃ solution) consists of two incompletely resolved symmetrical 1-proton triplets at 14.95 and 14.71 τ ($J = 13.2$ c.p.s.) due to the inner H³ protons, a 3-proton singlet at 5.99 τ due to the methyl hydrogens, a 3-proton multiplet at 1.33 τ assigned to H¹, a 3-proton multiplet at 0.25 τ assigned to H², and a 1-proton doublet at -0.11 τ ($J = 13.4$ c.p.s.) due to H^{2'}.

Acylation of Ia with acetic anhydride and boron trifluoride etherate in methylene chloride at room temperature gave an acetyl compound in low yield, to which structure Id is tentatively assigned by analogy; it formed brown crystals [$\lambda_{\text{max}}^{\text{ether}}$ 321, 451, and 608 μm (relative intensities, *ca.* 20:3:1); 2,4-dinitrophenylhydrazone: $\lambda_{\text{max}}^{\text{benzene}}$ 505 and 619 μm]. The amount of material was insufficient for further investigation. Another acetyl compound with unusual ultraviolet properties was also formed, as will be described in a later publication.

Monodehydro[14]annulene (II or III) on nitration under the above-mentioned conditions gave *ca.* 20% of a mononitro compound as dark brown needles, m.p. 185–186° dec. [$\lambda_{\text{max}}^{\text{isooctane}}$ 328 and 425 μm (ϵ 59,500 and 8300); $\lambda_{\text{max}}^{\text{benzene}}$ 335 and 435 μm ; *Anal.* Found: N, 6.67]. The n.m.r. spectrum (56.4 Mc./sec., CDCl₃ solution) consists of two doublets at 10.61 and 10.72 τ assigned to the two inner protons, as well as a complex band in the 2.67–0.91 τ region due to the outer protons. Nitration must have resulted in substitution of one of the outer protons, but the exact point of attack has not been determined.

Sulfonation of monodehydro[14]annulene and subsequent methylation, as above, gave a *ca.* 4:1 mixture of two isomeric monomethyl sulfonates as dark red plates, m.p. 153–154° [$\lambda_{\text{max}}^{\text{isooctane}}$ 314, 367, and 400 μm (ϵ 74,500, 6000, and 5300); $\lambda_{\text{max}}^{\text{benzene}}$ 321, 371, and 406 μm ; *Anal.* Found: C, 65.32; H, 4.99]. That this was in fact a mixture was shown by thin layer chromatography (two spots of very similar polarity) and by the fact that the methyl proton signals in the n.m.r. spectrum (60 Mc./sec., CDCl₃ solution) appeared as two distinct peaks at 6.12 and 5.91 τ . Acylation of monodehydro[14]annulene with acetic anhydride, as above, led in low yield to an acetyl derivative [$\lambda_{\text{max}}^{\text{ether}}$ 329 and 420 μm (relative intensities, *ca.* 7.5:1)].

[14]Annulene (IV) on attempted nitration, sulfonation, and acylation under the conditions used with the dehydro compounds gave no comparable substitution products. In no case did we observe the formation of a substance with a higher wave length maximum in the ultraviolet than the starting material, and decomposition of the latter usually resulted.

1,8-Bisdehydro[14]annulene (Ia) was found to form 1:1 π -complexes with compounds such as 1,3,5-trinitrobenzene; the complex with the latter crystallized as