pentane. The pentane extracts were combined and dried over magnesium sulfate. The pentane was evaporated and the residue distilled to give 6.7 g (74%) of **24**, bp 75° (10 mm).

4-Bromo-2-butyl-2-cyclopentenone (25). A mixture of 3.00 g (0.0217 mole) of **24**, 3.19 g (0.0217 mole) of N-bromosuccinimide, 0.10 g of benzoyl peroxide, and 30 ml of carbon tetrachloride was refluxed for 1 hr. The mixture then was washed with water and aqueous sodium thiosulfate, and finally dried. The solvent was evaporated under vacuum and the residue distilled. After a forerun of 0.6 g, a center cut of 2.2 g (47%) of pure **25** was collected, bp 75° (1.0 mm). A pot residue of 1.1 g was saved. Analysis by nmr showed that the forerun contained 29% **24**, in addition to **25**, and that the pot residue contained 8.5% of another compound. In a run using an 8.0% excess of NBS, the distilled product contained 11.6% of this compound. The presence, in the nmr spectrum of the mixture, of sharp singlets at τ 2.54 and 6.47 in a relative area of 1:2, in addition to a *t*-butyl resonance at τ 8.19 suggests that the compound is 4,4-dibromo-2-*t*-butyl-2-cyclopentenone.

***endo*-4,4-Di-*t*-butyltricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione (27).** A solution of 0.20 g of **25** in 2.0 ml of triethylamine was allowed to stand for 0.5 hr. The resulting paste was taken up in pentane and water. The pentane solution was washed with 10% aqueous sulfuric acid and water, and dried. The pentane was evaporated to give 0.14 g (100%) of white solid, mp 134–140°. An analytical sample, prepared by recrystallization from pentane, melted at 141–143° dec.

Acknowledgment. We are appreciative of support of this work by the National Science Foundation (Grant GP-5806).

Organometallic Electrochemistry. XV.[1] Electron–Nuclear Spin–Spin Coupling Involving Mercury. Organomercurial Radical Anions

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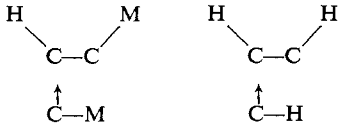
Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia 24061. *Received February 6, 1969*

Abstract: A series of organomercurial radical anions have been prepared, and hyperfine splitting constants for mercury, a_{Hg}, measured. It appears that a McConnell-type equation holds: $a = Q_{\mathrm{HgC}}{}^{\mathrm{Hg}}\rho_{\mathrm{C}}$, with $Q_{\mathrm{HgC}}{}^{\mathrm{Hg}} \cong -200$ G.

Simple consideration of the Fermi contact interactions which are the heart of the electron–nuclear coupling in the esr experiment and the nuclear–nuclear coupling in the nmr experiment suggest that it would be of interest to take two systems and measure the indicated parameters, comparing these with optical hyperfine structure constants, which derive from spectroscopic studies on H and M, and which were first explained by Fermi using the contact interaction which now bears his name.



$J_{\mathrm{M-H}}$ *vs.* $J_{\mathrm{H-H}}$ $\qquad$ a_{M} *vs.* a_{H}

Hydrogen is a natural choice as one of the nuclei because of its low electronegativity and rather straightforward bonding to carbon, which is well understood theoretically. The choice of a comparison nucleus is rather more difficult, and preliminary work on organoboron and organophosphorus systems has uncovered rather formidable synthetic and theoretical barriers. This paper therefore focuses on a series of stable organomercurial radical anions, and compares the observed electron–nuclear coupling with the available literature data to make the suggested juxtaposition.[2,3]

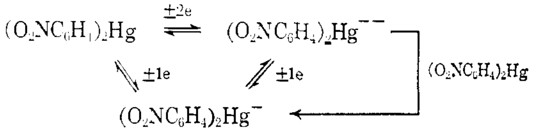
Results

It has been previously reported[4] that diphenylmercury reduces at a mercury cathode in a two-electron step to yield two phenyl anions and mercury metal.

$$(C_6H_5)_2Hg \xrightarrow[-3.2\ \mathrm{V}]{2e} 2C_6H_5:^- + Hg \qquad (1)$$

The low bond strength of carbon–mercury linkages and the high negative charge at carbon in the presumed anion intermediate are together presumably responsible for the cleavage. Attempts to reduce spin density at the C–Hg site and to stabilize the anion intermediates by means of naphthyl or biphenyl groups failed. However, mono- and bis(nitroaryl)mercury compounds reduce to yield radical species.

When bis(*p*-nitrophenyl)mercury is reduced in dimethoxyethane, employing tetrabutylammonium perchlorate as a supporting electrolyte, there seems little doubt that the system can be represented as



(2)

The following observations were made. (1) The compound exhibited a well-defined polarographic wave at -1.84 V *vs.* 10^{-3} *M* Ag$^+$–Ag . (2) Triangular voltammetry at 1 V/sec sweep speeds showed an *i*/*e* plot characteristic of an electrochemically reversible process. (3) Controlled potential reduction at -2.0 V gave a

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[1] For previous papers in this series see R. E. Dessy, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4963 (1969).

[2] R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, 30, 1422 (1959).

[3] J. V. Hatton and W. G. Schneider, *ibid.*, **39**, 1330 (1963).

[4] R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Amer. Chem. Soc.*, **88**, 460 (1966).

coulometric count of $n = 2.1$. The resulting solution was pink-violet in color and showed a very weak esr signal near $g = 2$. Ultraviolet spectroscopy gave the results shown in Table I. The solution did not contain any nitrobenzene, as evidenced by gas chromatography, either on direct aliquots or water-quenched aliquots. (4) The solution generated in point 3 exhibited an oxidative polarographic wave at -1.84 V. Controlled potential oxidation at -1.5 V with the removal of *one electron per molecule*, by coulometric count, gave a solution which had an esr signal similar to that shown in Figure 1. Ultraviolet spectroscopy gave the data shown in Table I. A similar solution resulted (a) by a one-electron reduction of the neutral parent, or (b) by addition of an equivalent amount of neutral parent to the solution resulting from the actions of point 3 (eq 2). (5) Further oxidation at -1.5 V, removing another electron/molecule, gave a solution whose polarographic behavior and ultraviolet spectra were identical with neutral parent. The presence of neutral parent was established by thin layer chromatography. No nitrobenzene or *p,p'*-dinitrobiphenyl could be detected. Oxidation processes conducted at a platinum electrode or *via* chemical oxidants (I_2) gave identical results. It is well known that some carbon and metalloidal anions are oxidized at a mercury pool to yield the symmetrical organomercurial.[5] The lack of evidence for nitrobenzene, derivable from nitrophenyl anion, or the nitrophenyl radical, eliminates the possibility of fragmentation of the molecule upon reduction, as does the fact that chemical oxidation, or oxidation at platinum, regenerates starting material.

Table I. Electronic Spectra of *p*-Nitrophenylmercury Species[a]

Compound		λ_{max}, mμ	A^b	λ_{max} mμ	A^b	λ_{max}, mμ	A^b
$(O_2NC_6H_4)_2Hg$	○	280	1.6				
	⊖	280	0.7	335	1.0	520	0.4
	⊜			335	1.9	524	0.7
$O_2NC_6H_4HgC_6H_5$		278	1.0				
				336	1.1	519	0.3
$O_2NC_6H_5$		260	0.8				
				315	1.0	455	0.3

[a] ○, neutral; ⊖, radical anion; ⊜, dianion. [b] Actual absorbance values recorded at millimolar substrate concentrations with 1-mm path length cells in dimethoxyethane with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte.

The extremely weak, but still well-defined esr signal upon two-electron reduction and a lack of half-field signal at any temperature down to the freezing point of the solution suggest a singlet-state dianion, the residual signal being due to small amounts of radical anion.

The ultraviolet spectra of bis(*p*-nitrophenyl)mercury, its radical anion and dianion, and related compounds are particularly revealing. Approximate calculations of the equilibrium constant for the process

$$\bigcirc + ⊜ \overset{K}{\rightleftharpoons} 2\ominus \qquad (3)$$

can be made from the values of $E_{1/4} - E_{1/4}$ as described by Maki.[6] As indicated in Table II, $K = 15$, and this should allow direct observation of the radical anion, upon addition of one electron per molecule by controlled potential reduction, or alternately by exhaustive reduction and addition of 1 equiv of neutral parent. Table I lists λ_{max} and absorbance values (all substrates at millimolar concentration) for bis(*p*-nitrophenyl)mercury, *p*-nitrophenylphenylmercury, and nitrobenzene, as well as their related radical anions and dianions. The neutral species are characterized by the typical short wavelength band centering around 260–280 mμ. *Two-electron reduction of the bis(p-nitrophenyl)mercury or one-electron reduction of p-nitrophenylphenylmercury* both eliminate the 280-mμ band and yield solutions absorbing at 335 and 520 mμ. The absorption intensities in the mononitrophenyl case are one-half that in the bisnitrophenyl example, as might be expected if the aromatic rings were operating independently. Partial reduction of the bis(*p*-nitrophenyl)mercury to the radical anion gives a solution absorbing at 280, 335, and 520 mμ, again with the expected intensities if both rings were operating independently, and spin density was localized in one ring only.

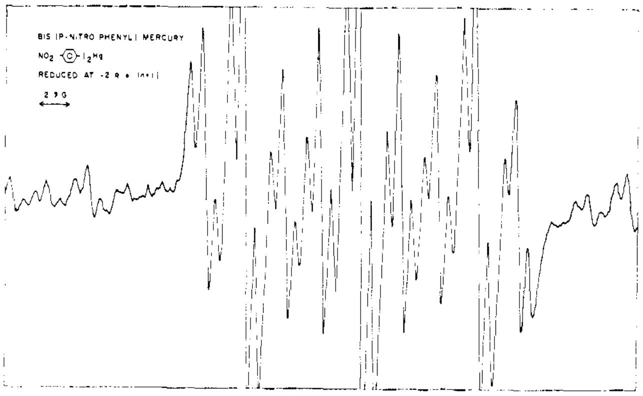

Figure 1.

The esr spectra of the anion radical does show hyperfine coupling with the nuclei in one ring only; one nitrogen, and two sets of two equivalent protons. The hyperfine couplings are very similar to those found for nitrobenzene radical anion under these conditions. The esr results are tabulated in Table II.

Bis(*m*-nitrophenyl)mercury and bis(4-nitronaphthyl)-mercury gave electrochemical, spectral, and paramagnetic resonance characteristics similar to that described. Bis(*o*-nitrophenyl)mercury showed a split polarographic wave (-1.70 and -1.80 V) with excellent separation of two successive one-electron steps on triangular voltammetry. The spatial proximity of the two *nitro* groups in the *ortho* derivative apparently facilitates the introduction of the first electron. The *K* values (eq 3) appearing in Table II for the nitrophenyl cases indicate a monotonic increase in K ($p < m < o$), as progressive steps in the series is made. This would be expected from the large electron charges residing on and near the *nitro* group, and the consequent charge and dipole–dipole interactions. The *ortho* derivative also shows some evidence of anomalous line-width phenomena.[7]

The present data can be compared to the *para*- and *ortho*-substituted nitrophenyl ethers, sulfides, and methanes.[6,8]

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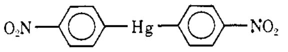
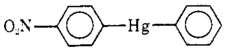
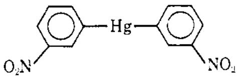
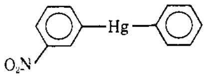
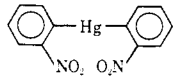
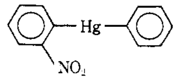
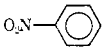
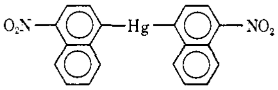
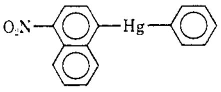
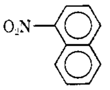
(5) R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 471 (1966).

(6) (a) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963); (b) D. H. Geski and A. H. Maki, *J. Amer. Chem. Soc.*, **82**, 2631 (1960); (c) A. H. Maki and D. H. Geski, *ibid.*, **83**, 1852 (1961).

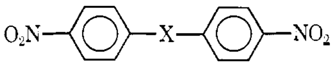
(7) J. M. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

Table II. Electrochemical and Esr Spectral Data for $O_2NC_6H_4Hg$ and $O_2NC_{10}H_6Hg$ Derivatives

Compound	$-E_{1/2}$ (*n*)	*K*[c]	a_N, G	$a_{o\text{-H}}$, G[a]	$a_{m\text{-H}}$, G[a]	$a_{p\text{-H}}$, G[a]	a_{Hg}, G
	1.83 (2)	15	9.29	3.25	1.00	...	42.3
	1.82 (1)		9.29	3.25	1.00	...	39.2
	1.88 (2)	40	9.72	3.30	1.08	4.06	10.8
	1.83 (1)		9.72	3.30	1.08	4.06	9.8
	1.7 (1) 1.9 (1)	10^3	10.5	3.30	1g	3.30	33.0
	1.79 (1)		10.5	3.70	1.00	3.30	28.0
	2.0 (1)		9.5	3.20	1.10	4.00	...
	1.75 (2)		7.37	5.20	*b*	...	58.0
	1.76 (1)		7.30	5.08	*b*	...	52.3
	1.76 (1)		7.43	5.24	*b*	5.24	...

[a] Positions relative to the nitro group. [b] Indistinguishable from H couplings in remaining part of ring system. [c] *K* = 2⊖/○·⊖.

In bis(*p*-nitrophenyl)methane radical anion, the two rings are equivalent due to fast electron-transfer processes, and the nitrogen hyperfine coupling leads to the expected quintet. In the corresponding ether and sulfide, the intramolecular electron transfer rate is of the same order of magnitude as the hyperfine interval. In the *ortho* series, the sulfide has the two rings equivalent, while the ether has rings which are magnetically equivalent as far as protons are concerned, but are inequivalent with respect to nitrogens. This is due to an intramolecular transfer rate intermediate between hydrogen and nitrogen hyperfine intervals. The dianions of these species are unknown, and are reported to be unstable. The mercurials reported here show, by previously described criteria,[6,8] very slow intramolecular electron-transfer rate with respect to the hyperfine intervals and resemble 4,4′-dinitrobibenzyl radical anion.



X = CH_2, S, O

In order to examine the effect of the presence of one ring upon the other in these disubstituted compounds, the corresponding mononitrophenylphenylmercury and 4-nitronaphthylphenylmercury were prepared. All of these show well-defined *one*-electron reductions, and gave radical anions whose main esr spectra were identical with those derived from one-electron reduction of the disubstituted compounds. This agreed with the apparent lack of conjugation mentioned above. The hyperfine coupling constants are recorded in Table II.

All of the radical anions mentioned thus far exhibited satellite spectra to the high- and low-field side of the main spectrum using high-gain-low-modulation sweep conditions (Figure 2). These appeared identical with the line shapes of the main spectra, where overlap did not obscure the satellite spectra. The intensities are about 10% of that of the main spectra. This is what would be expected of hyperfine coupling with the naturally occurring (16% abundant) Hg^{199}, with $I = {}^1/_2$. The most abundant isotope, Hg^{200}, has no spin. These satellite spectra are inconsistent with coupling with the other naturally occurring isotope of Hg, Hg^{201}, which has $I = {}^3/_2$. Previous nmr studies have failed to see this coupling due to this isotope. The Hg hyperfine coupling constants for the eight radical anions studied appear in Table II.

Discussion

Mercury is an excellent choice as a test atom in the proposed comparison for several reasons. (1) Its electronegativity is near that of H, so that charge distribution in the neutral molecule and unpaired spin density in the radical anion are not drastically altered by its presence in comparison with the parent nitroarene. (2) Its high atomic number, coupled with a large optical hyperfine structure constant, will increase the values of

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(8) R. K. Gupta and P. T. Narasimhan, *J. Chem. Phys.*, **48**, 2453 (1966).

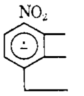
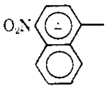
the observed coupling parameters, making analysis simple, and reducing the possibility of d_π–p_π bonding. (3) Its long covalent radius will reduce dipole–dipole and polarization interactions. (4) Its valency is low, easing synthesis, and reducing also undesired intramolecular interactions. (5) The linearity of its molecules and the weak coordinating ability of mercury should tend to minimize solvent effects and render them isotropic since coordinating ligands would occupy the equatorial belt.

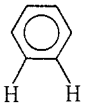
Close analysis of the data in Table II indicates that for the phenyl derivatives, $a_{o\text{-H}} + a_{m\text{-H}} = -2.25 \pm 0.05$ G (assuming ρ_o is positive and ρ_m is negative). This is the value reported by Maki[6] for a large series of substituted nitroaromatics and suggests that the total spin magnetization in the π orbitals of the radical ions of Table II is constant, in agreement with the first point made above.

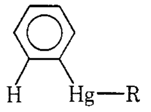
There is a monotonic increase in a_{N} as one progresses the series bis(*p*- to bis(*o*-nitrophenyl)mercury. Since there appears to be little change in the unpaired spin density in the ring system this is probably due to a change in the mixture of orbitals defining the character of the hybrid orbital around nitrogen. This phenomenon has been discussed by Ayscough.[9]

Of most interest, however, is an analysis of the hyperfine splitting constants for mercury. These are best evaluated from Table III. One first notices the large splitting constants for Hg *vs.* H. It is also of some import that a comparison of nuclear–nuclear spin–spin coupling between H^1–Hg^{199} and H^1–H^1 shows[3,10] roughly the same ratio as does the electron–nuclear spin–spin coupling, $\overset{\uparrow}{\mathrm{C}}$–H *vs.* $\overset{\uparrow}{\mathrm{C}}$–Hg, as reflected by the values in Table III.

Table III

	Hyperfine splitting, G			
	H	$\mathrm{HgC_6H_5}$	$\mathrm{HgC_6H_4NO_2}$	$\mathrm{HgC_{10}H_6NO_2}$
	3.2 1.1 4.0	28.0 9.8 39.2	33.0 10.8 42.3	
	5.25	52.3		58.0
$\alpha_{\mathrm{H}}^{\mathrm{Hg}} = a_{\mathrm{Hg}}/a_{\mathrm{H}}$		9.3 ± 0.5	10.2 ± 0.4	11.0





$J_{\mathrm{H-H}} \cong$ 8–10 cps $\qquad J_{\mathrm{H-Hg}} \cong$ 100 cps

$$J_{\mathrm{H-Hg}}/J_{\mathrm{H-H}} = 10\text{–}12$$

Schneider,[3] as well as others,[11,12] has shown that the nuclear–nuclear spin–spin couplings in organomercurials are largely controlled by the Fermi contact mechanism. He has extended Ramsey and Purcell's[13] basic development for H–H coupling to alkali-like atoms and fractional bonds, where

$$J_{\mathrm{NN'}} = \tfrac{1}{2}h a_{\mathrm{N}}' a_{\mathrm{N'}}' F_{\mathrm{NN'}}/\Delta E$$

(a_{N}' is the optical hyperfine structure constant, $F_{\mathrm{NN'}}$ measures the fractional bond order between N and N′, and ΔE is the excitation energy). The a_{N}' values of interest are H -0.14×10^{10}Mcps; Hg(6s6p, ^{3}P) -1.5×10^{16}Mcps; $\mathrm{Hg}^+(6s, {}^2S_{1/2})$ -4.05×10^{10} Mcps. The magnitude of the observed H–Hg nuclear coupling compared to H–H coupling is therefore expected. Since the nuclear–nuclear coupling is Fermi contact controlled, the electron–nuclear couplings which comprise it are also likely to be Fermi contact controlled. It is satisfying that the observed ratio of hyperfine coupling constants $a_{\mathrm{Hg}}/a_{\mathrm{H}}$ derived from the mononitrophenylphenylmercury radical anions (9.3 ± 0.5) is near the ratio of optical hyperfine structure constants (10.7).[14]

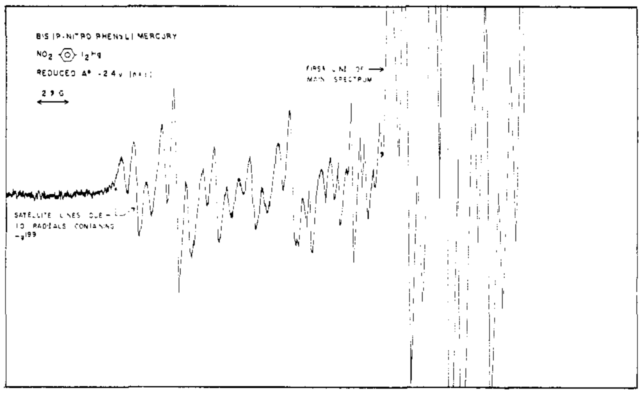


Figure 2.

Secondly, the constancy of the $a_{\mathrm{Hg}}/a_{\mathrm{H}}$ ratios in Table III indicate that a McConnell equation[15] is applicable to organomercurials. For aromatic hydrogens, associated with a radical anion

$$a_{\mathrm{H}} = Q_{\mathrm{CH}}{}^{\mathrm{H}}\rho_{\mathrm{C}}$$

where ρ_{C} is the unpaired spin density on a carbon of the aromatic system and $Q_{\mathrm{CH}}{}^{\mathrm{H}}$ is a constant. $Q_{\mathrm{CH}}{}^{\mathrm{H}}$ varies from molecule to molecule, but has an average semiempirical value of −23 G. In aromatic systems $^3J_{\mathrm{Hg-H}}$ and $^3J_{\mathrm{H-H}}$ couplings are positive in sign.[10c] It is suggested that for aromatic mercurials the equation that is satisfied is

$$a_{\mathrm{H}} = Q_{\mathrm{CHg}}{}^{\mathrm{Hg}}\rho_{\mathrm{C}}$$

with $Q_{\mathrm{CHg}}{}^{\mathrm{Hg}} \cong -200$ G.

One possible utilization of this empirical observation is to evaluate extremely small hydrogen hyperfine splitting constants in the presence of a number of larger splitting constants each involving several equivalent

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[9] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

[10] H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Amer. Chem. Soc.*, **79**, 4596 (1957).

[11] (a) D. F. Evans, P. M. Ridout, and I. Wharf, *J. Chem. Soc.*, 2127 (1968); (b) J. P. Maher and D. F. Evans, *ibid.*, 637 (1965); (c) W. McFarlane, *ibid.*, *A*, 2280 (1968).

[12] G. D. Shier and R. S. Drago, *J. Organometal. Chem.*, **5**, 330 (1966).

[13] N. F. Ramsey and E. M. Purcell, *Phys. Rev.*, **85**, 143 (1952).

[14] In the bis(nitrophenyl)mercury radical anions, the ligand bonded to the nitrophenylmercury radical anion core has been changed from phenyl to the more electronegative nitrophenyl group. This will tend to make the mercury more positive, and in line with the optical hyperfine structure constants listed above would be expected to lead to an increase in the observed electron–nuclear hyperfine coupling constant. This expectation is realized. Similar increases in $J_{\mathrm{M-H}}$ coupling have been reported as the change of *M* is increased or more s character is injected into hybrid bonds.[3,10c–12]

[15] H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

nuclei in the set ("a_H" = a_{Hg}/α_H^{Hg}). Previously this has involved exhaustive computer application or endor techniques.

Experimental Section

The electrochemical studies were performed as previously described.[1] Electron spin resonance spectra were simulated using a program similar to SESR described by Stone and Maki,[16] with suitable modifications to permit use on the Virginia Polytechnic Institute's Computing Center IBM 360/40-50 with associated Calcomp plotter.

All three isomers of the bis(nitrophenyl)mercury and bis(4-nitronaphthyl)mercury were prepared through symmetrizing of the corresponding RHgCl compound according to the method of Hein.[17] The RHgCl compounds were prepared from the corresponding anilines *via* the mercury diazonium double salt according to Nesmeyanov.[18] The nitrophenylphenylmercury isomers and 4-nitronaphthylphenylmercury were obtained by phenylating the appropriate RHgCl compound with $(C_6H_5)_2SnCl_2$, again according to Nesmeyanov.[19] All of the compounds analyzed correctly for C, H, N.

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Chemical Shifts for Bicyclic Fluorides[1]

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Abstract: The ^{19}F chemical shifts of four series of bicyclic molecules have been determined. There are major differences in the ^{19}F chemical shifts of fluorine atoms bonded to the bridgehead carbon atoms of different bicyclic molecules. These chemical-shift differences may be related to the change in p character of the endocyclic bonding orbitals of the bridgehead carbon atom. The SCS[2] for 4-substituted-1-fluorobicyclo[2.2.2]octanes are anomalous in the sense that electron-withdrawing groups produce large upfield shifts. These results suggest that substituent-induced structural changes modify the shielding environment of the fluorine nucleus thereby altering the chemical shift importantly. The magnitude of dipolar substituent effects (σ induction, electric field effects, and van der Waals interactions) on the ^{19}F substituent chemical shifts for several other quite rigid bridged anthracene derivatives, II–IV, were determined. The SCS for these molecules are small and negative in accord with the view that structural variations are responsible for the upfield shifts in the octane series. The data for the bridged anthracenes reveal that, for ^{19}F magnetic resonance, substituent effects propagated through σ bonds and through the dielectric medium are much less important than substituent effects propagated through π bonds.

Fluorine nuclear magnetic resonance spectroscopy has been used to study substituent-induced chemical shift (SCS),[2] to assay the substituent's influence on the distribution of electron density, and to unravel the mechanisms by which the substituent alters the distribution of electron density. Studies of this kind are appropriate because, although the theory for the chemical shift is complex,[3] the fluorine chemical shifts are dominated by the paramagnetic term of the Ramsey equation[4] and, as such, are interpretable within the framework of the conventional localized bond model.[5] Several theoretical treatments have been presented for the interpretation of SCS for complex molecules.[5–7] The changes in shielding have been related principally to substituent-induced changes in the ionic character and π bond order of the carbon–fluorine bond and to changes in the hybridization of the bonding oribtal of the fluorine atom.[5] In addition, changes in the π electron density on the carbon atom[6] of the carbon–fluorine bond and on more remote carbon atoms[7] have been reasoned to influence the chemical shift. The Prosser–Goodman treatment for π electron density variations has been coupled with an electric field theory[8a] considering both dipolar electric field and van der Waals contributions to account for SCS in aliphatic and aromatic fluorocarbons.[8b–g]

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[2] The ^{19}F substituent chemical shift (SCS) is defined as the difference between the resonance frequency of a ^{19}F nucleus in a substituted molecule and that of the same nucleus in a molecule in which a hydrogen atom replaces the substituent. Positive values mean that the resonance signal for the substituted compound is upfield of the signal for the hydrogen-bearing reference compound.

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