Substituent Effects in Diphenylmercury Radical Cations: A Very Clear Distinction between σ- and π-States

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$^{199/201}$Hg 'satellite' features have been resolved in electron paramagnetic resonance (EPR) spectra recorded from radical cations of diphenylmercury and its bis-*ortho*-allyloxy derivatives as isolated in solid freon matrices at 77 K. In accord with our previous work, we confirm that the parent radical cation of diphenylmercury is a σ-species with substantial electron loss from the C–Hg–C bonding region of the molecule: studies of the perdeuteriated analogue reveal a complex superhyperfine structure which persists in $CFCl_3$ and CCl_4 matrices, and is assigned to coupling from a single matrix chlorine atom.

In marked contrast, the allyloxy derivatives are π-radicals, and show well resolved, nearly isotropic, mercury satellite features that are of the magnitude expected for this assignment. Thus the electron-releasing power of the oxygen atom is sufficient to stabilise the π-state over the σ-state.

The relationship of these results to the mechanism of reactions involving the single-electron oxidation of these organomercurials is discussed.

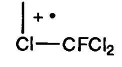
We have recently made a study[1,2] of radical cations of dibenzylmercury and diphenylmercury derivatives. In general, these radicals correspond to σ_u (C–Hg–C) species, although there is appreciable delocalisation of spin density onto the organic units: particularly for the diphenylmercurials. Clear Hg features were observed for the dibenzylmercurials which showed the presence of a large ^{19}F superhyperfine interaction from a single-matrix $CFCl_3$ molecule; while no evidence for this effect was obtained in the diphenylmercury series, the lines were very broad so that we could not eliminate definitely the possibility of matrix interaction, nor could we be certain of the presence of ^{201}Hg features. The remaining uncertainty concerns the form of the g tensor: while clearly axial, with a narrow $g_\perp$ feature of *ca.* 1.85 in the dibenzylmercury radical cation spectra, given the greater breadth of all the lines in the $Ph_2Hg^{\cdot+}$ spectrum, it was not possible to say whether g_x and g_y were actually degenerate. To probe further these questions, we have now studied the perdeuteriated analogue, $(C_6D_5)_2Hg$, the results of which are discussed below. We have also investigated the properties of some allyloxyphenylmercury radical cations, which provide a striking contrast to the unsubstituted version.

Results and Discussion

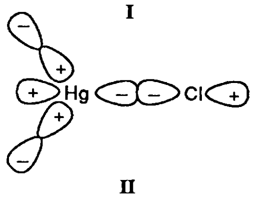
Diphenylmercury Radical Cations.—The spectrum recorded at 77 K from the unlabelled material is shown in Fig. 1(*a*), following γ-irradiation in a solid $CFCl_3$ matrix. As mentioned above, the features are all broad, but Hg satellite peaks are apparent in the high- and low-field regions. We decided to try to reduce the intrinsic linewidth of the spectrum by using the perdeuteriated material, since this substantially eliminates the contribution from long-range, unresolved, proton couplings.[3] As can be seen from Fig. 1(*b*), the reason for the very broad lines in Fig. 1(*a*) is at once clear, since a complex substructure is now observed, but which would coalesce into the band profile of Fig. 1(*a*) given an appropriate increase in the linewidth, as caused by unresolved proton coupling. Since it is possible that some of this structure arises from ^{19}F interactions (particularly, considering the results for dibenzylmercury radical cations[1,2]) we repeated the experiments using CCl_4 as a solid matrix: the resulting spectrum is shown in Fig. 2, from which it is quite clear that all the features of Fig. 1(*b*) are still present, and also that the spectrum is slightly better resolved.

It seems to us that there are two possibilities, namely, either that there are multiple trapping sites present, or that the additional structure stems entirely from superhyperfine coupling with a matrix atom. In the former case, it appears unlikely that precisely the same effective sites would be adopted in the different matrices, and we note that multiple trapping effects have not been observed previously for radical cations in freon matrices. That no difference in the number of features is found between CCl_4 and $CFCl_3$ rules out the involvement of a fluorine atom; however, inspection of the central 'perpendicular' feature seems to show the presence of 'doublets' which is characteristic of a $^{35/37}$Cl interaction, and, indeed, the overall structure of this feature may be accounted for in terms of the formation of a specific Cl–Hg adduct. It appears that the g-tensor is indeed axial as assumed previously,[2] in accord also with the results for the dibenzylmercury radical cations.[1,2]

We propose the structure **I** to account for these observations, in which bonding has occurred between the 3p orbital on chlorine and the 6p orbital component on mercury, leading to a singly occupied molecular orbital (SOMO) of type **II** with a substantial spin density on the chlorine atom. In this structure, the 'parallel' axis for the chlorine coupling now coincides with one of the 'perpendicular' axes of the g-tensor. One of the 'perpendicular' axes of the chlorine hyperfine tensor coincides with the other perpendicular g-axis so that the chlorine interaction appears on the $g_\perp$ feature as an overlapping parallel



I



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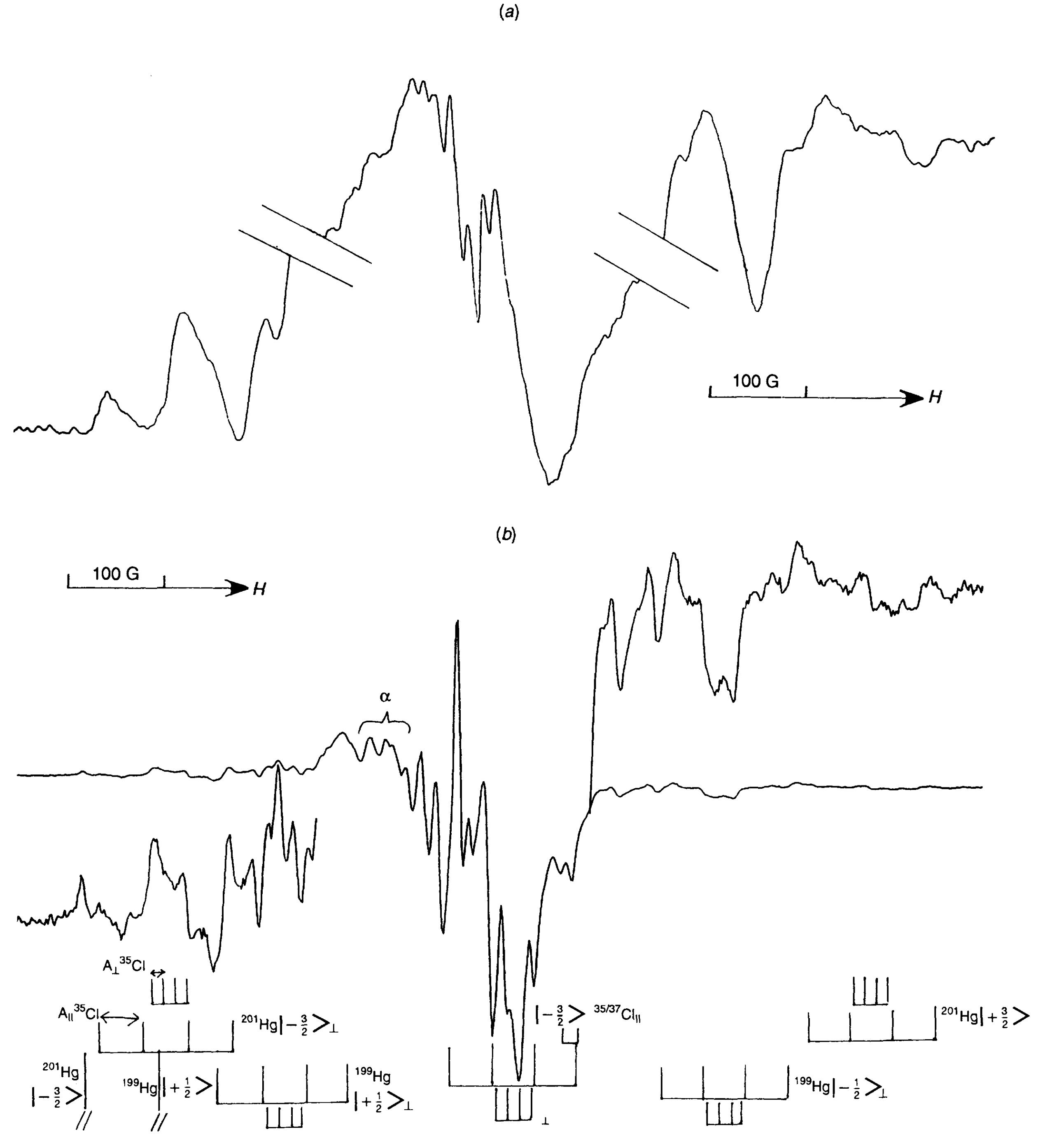


Fig. 1 EPR spectra from (*a*) $(C_6H_5)_2Hg^{\cdot +}$ radical cations and (*b*) $(C_6D_5)_2Hg^{\cdot +}$ radical cations isolated in a $CFCl_3$ matrix at 77 K

Table 1 EPR parameters for organomercury radical cations in a $CFCl_3$ matrix, measured at 77 K

Radical	Coupling constants[a]	*g*-Values
$III^{\cdot +}$	*a* (3 H) 13, *a* (Hg)[b] 43	g_{av} = 2.002
$IV^{\cdot +}$	*a* (1 H) 10, *a* (Hg)[b] 47	g_{av} = 2.002
$(C_6D_5)_2Hg^{\cdot +}$	$A_\perp(^{199}Hg)$ 400 $A_\perp(^{201}Hg)$ 146 $A_\parallel(^{35}Cl)$ 38 $A_\perp(^{35}Cl)$ 9 $A_\parallel(^{199}Hg)$ 514 $e^2Qq_z = -1000 \pm 40$ MHz	$g_\perp$ = 1.959

[a] In G. [b] ^{199}Hg nuclei.

and a barely resolved, perpendicular quartet: the $^{35/37}Cl$ pattern is clear on the $|-\frac{3}{2}\rangle$ 'parallel' peaks. In further support of this interpretation, we are able to locate the same structure on both ^{199}Hg $|-\frac{1}{2}\rangle$ and ^{201}Hg $|+\frac{3}{2}\rangle$ features. As shown in Fig. 1(*b*), perpendicular features are detected for both mercury isotopes: the hyperfine and *g*-tensor data are given in Table 1.

At 400 G, the perpendicular ^{199}Hg coupling is reduced from that deduced previously for $Ph_2Hg^{\cdot +}$ radical cations,[2] but is now more in line with that for the diethyl and dimethyl derivatives:[2] $g_\perp$ is also very slightly reduced. Surprisingly, it appears that 38% of the spin density is localised in the chlorine 3p orbital, with a normally very small admixture of the 3s component. As found in our previous study,[2] substantially less of the spin density resides on the Hg atom than is the case for all the dibenzylmercury radical cations studied so far. As indicated in the figure, we have detected low-field features which we

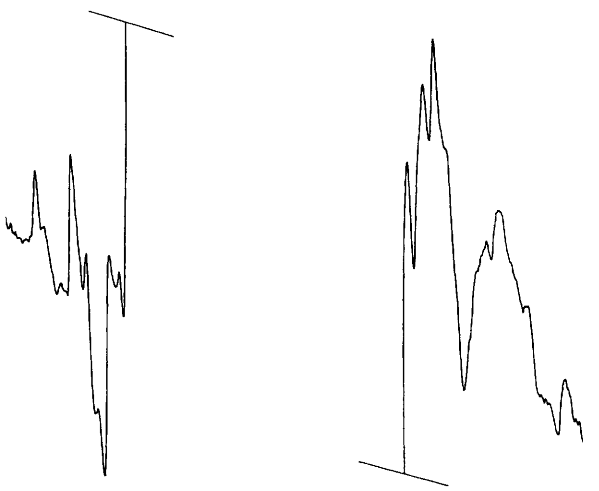


Fig. 2 EPR spectrum of $(C_6D_5)_2Hg^{\cdot+}$ radical cations isolated in a CCl_4 matrix at 77 K

believe to be the ^{201}Hg $|-\frac{3}{2}\rangle$ and ^{199}Hg $|+\frac{1}{2}\rangle$ components of the parallel spectrum; however, we cannot be sure of the location of the $g_{\parallel}$ feature which complicates the derivation of the $A_{\parallel}$ couplings. While there is a four-line pattern in the central region of the spectrum (α) which is a potential contender for this, the corresponding g-value is 2.031 which seems rather high, as we would have expected it to be closer to free-spin; however, taking this as the true $g_{\parallel}$ feature leads to $A_{\parallel}(^{199}\text{Hg}) = 409$ G. Alternatively, if we assume that the true value is at 2.002, we obtain a coupling of 514 G. In either case, one essential fact is unchanged: in contrast to the dibenzylmercury radical cations, where $|A_{\parallel}| < |A_{\perp}|$, the normal $|A_{\parallel}| > |A_{\perp}|$ condition now appears to prevail, and this deserves some comment.

We recall that, as discussed in ref. 2, the former inequality is characteristic of np^1 radicals in which the isotropic coupling is negative in sign and stems from spin polarisation of the s-electrons on mercury because of the nodal form of the σ_u SOMO. In previous work[4] on Tl^0 centres in ionic crystals, it was shown that the $|A_{\parallel}| < |A_{\perp}|$ condition held so long as crystal field forces did not mix the Hg 6s level directly into the SOMO: in the present case, the bonding with the chlorine atom would be expected to mix the 6s level into the SOMO as a consequence of the introduction of greater bonding character into the Hg–(Cl) unit. The conclusion is, therefore, that the isotropic ^{199}Hg coupling is now positive, the negative contribution from spin polarisation of the 5s and lower s-electrons on Hg being more than offset by the direct 6s occupancy. If, accordingly, we take $A_{\parallel}$ and $A_{\perp}$ as both positive, and use $A_{\parallel} = 514$ G, we estimate a value for the anisotropic coupling of 76 G, and a 6p occupancy of 17% using the Morton and Preston value[5] calculated for unit occupancy of an Hg 6p orbital. The alternative, mentioned earlier, of 409 G assuming that $g_{\parallel} = 2.031$, would lead to a negligible 6p population which does not accord with the substantial g-shifts observed. (All other value and sign combinations lead to huge 6p populations vastly in excess of 100% which is obviously inconsistent.)

Using the theory developed by Adrian *et al.*[6] as described by Williams and co-workers[7] for the CH_2HgCl radical, we are able to reconstruct the observed line positions and derive an estimate for the ^{201}Hg nuclear–electric quadrupolar coupling (e^2Qq). The value obtained is -1000 ± 40 MHz, which is in excellent agreement with the value (-1000 MHz) predicted for a single p-electron in the valence shell of mercury.[8] The negative sign arises because the ^{201}Hg quadrupole moment (eQ) is positive,[9] and the electric field gradient eq_z is negative if it is due to a single p-electron.[10] The ratio of the ^{199}Hg:^{201}Hg perpendicular couplings is 2.74, which is in the ratio found for other mercury-containing radicals[2,10] and in agreement with the ratio of the nuclear g-factors (2.70).[9]

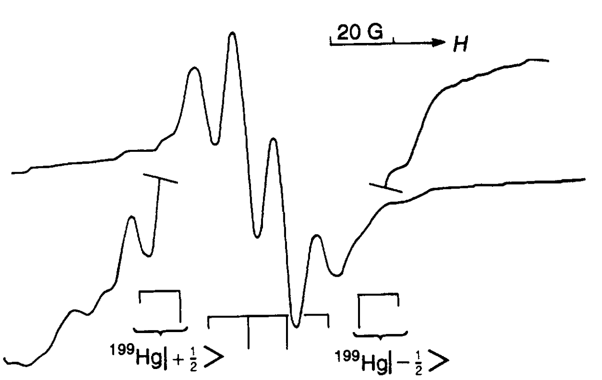
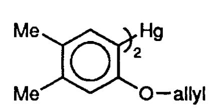


Fig. 3 EPR spectrum of $III^{\cdot+}$ radical cations isolated in a $CFCl_3$ matrix at 77 K

It is extremely curious that dibenzylmercury and diphenylmercury radical cations should form quite different complexes with a single $CFCl_3$ molecule. All we can suggest is that, in the dibenzylmercury series, bonding with a fluorine 2p orbital is possible in the linear (F–C–Hg–C) fashion discussed previously.[1,2] However, this is not possible in the diphenylmercury series because the required bonding site is blocked by the phenyl rings, one of which would need to distort impossibly to accommodate the solvent molecule in this way. Therefore, the bonding is switched to the Hg atom directly where the use of the chlorine atom is evidently favoured over fluorine.

Allyloxyphenylmercury Radical Cations.—The spectra shown in Figs. 3 and 4 are in complete contrast with those discussed above. These are clearly from π-radical cations in which most of the spin density is carried by a single aromatic ring. This shows that the two rings are electronically insulated by the Hg atom, and is a most significant observation: so much so, that we now discuss in detail our structural assignments and reasons for reaching this conclusion.

The compound **III** gives the most revealing spectrum (Fig. 3) since the central feature shows a 13 G coupling to only one of the methyl groups. This immediately eliminates any possibility of a SOMO which encompasses both rings, and so, despite the possibility of a π-interaction between the rings, mediated by the mercury atom, the SOMO is actually localised. The central quartet is flanked by satellite features from which we are able to measure an isotropic ^{199}Hg coupling of 43 G. We assign the SOMO to the symmetric orbital **V**, in which the oxygen atom is located at a position of high spin/charge density, and we believe that, as in our previous study of the *p*-methoxy and *p*-chloro derivatives, in which π-radical cations were formed, it is the π-electron releasing effect of the allyloxy substituent that has caused the switch-over from the σ- to the π-state. Given the substitution pattern in **III**, the strongly coupled methyl group is



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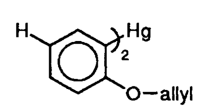

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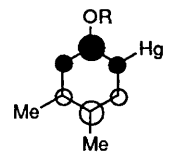

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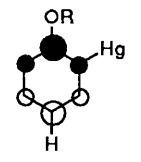

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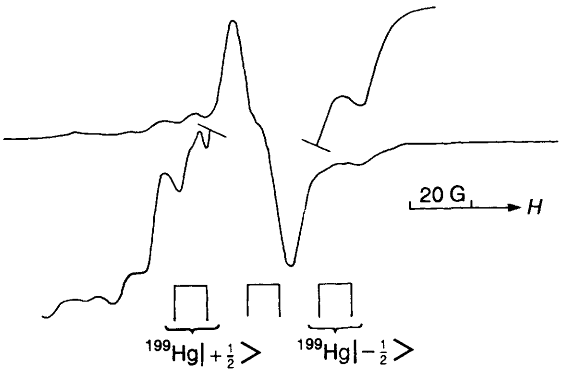

Fig. 4 EPR spectrum of IV$^{\cdot+}$ radical cations isolated in a CCl$_3$ matrix at 77 K

located at the other position of high spin (V) and the second methyl group and the mercury atom are at positions of reduced spin density, as in the Jahn–Teller distorted form of the benzene radical cation.[12] By means of the correlation found by Courtneidge *et al.*[13] that the substitution of a hydrogen atom by a mercury substituent at the periphery of an aromatic ring gives an isotropic ^{199}Hg coupling that is 21.5 times that of the original proton coupling, we obtain an 'effective' proton coupling of 2.0 G, which explains why the other proton couplings are within the linewidths: the other methyl group would not be expected, on this basis, to have a coupling of more than *ca.* 3 G which is, similarly, not resolved.

Given the above analysis, the spectrum in Fig. 4 is seen to reflect a similar electronic structure for the radical cation of **IV**. We assign a symmetric SOMO as in **VI** which explains why there is only a detectable coupling to a single proton (10 G). Again, the mercury substituent shows an isotropic ^{199}Hg splitting of 47 G, which is equivalent to a proton coupling of 2.2 G. This is now identical with that found for the weakly coupled protons in the benzene radical cation,[12] and the greater value than that deduced for the cation of **III** suggests that the methyl group in the latter case delocalises more spin density from the system. The idea, which is still surprising to us, that the SOMO is localised to a single ring is partly predicted by our AM1 calculations[2] for Ph$_2$Hg$^{\cdot+}$ from which a π-state was predicted as the most stable. However, there is no doubt that the σ-structure is formed in both CFCl$_3$ and CCl$_4$ matrices under our conditions. Since the mercury coupling is, apparently, isotropic, the spin density on the mercury atom arising *via* the π-system is extremely low, also as predicted by AM1 calculations for the π-state of the diphenylmercury radical cation.

Relationship to Reactivity Studies.—Product studies have been made by Shine and co-workers, concerning reactions of organomercury compounds with the thianthrene radical cation (Th$^{\cdot+}$). In the case of diethylmercury, evidence was obtained that the Et$_2$Hg$^{\cdot+}$ radical cation was formed and underwent rapid fragmentation,[14] to form free ethyl radicals; similar behaviour was found for dibenzylmercury,[15] which is consistent with EPR measurements on its radical cation[2] which was observed to decompose to free benzyl radicals even at 150 K. In contrast, diphenylmercury was found to react only very slowly with Th$^{\cdot+}$ and no evidence was obtained that suggested the intermediacy of free phenyl radicals.[14] The allyloxy mercurials (**III** and **IV**) reacted readily with Th$^{\cdot+}$, but again no evidence whatsoever was obtained for the formation of free aryl radicals. That is, reactions of diphenylmercury and of **III** and **IV** with Th$^{\cdot+}$ gave quantitative yields of 5-arylthianthreniumyl perchlorates, and, in the cases of **III** and **IV**, without the cyclisation that would have followed rapidly had free σ-allyloxyaryl radicals been formed. It was concluded that in these reactions the 5-arylthianthreniumyl perchlorate was formed through a complex of the Th$^{\cdot+}$ radical cation and diarylmercurial, rather than by formation and trapping of Ar$^{\cdot}$ from Ar$_2$Hg$^{\cdot+}$.

As mentioned in the text, and discussed previously,[2] EPR results for Et$_2$Hg$^{\cdot+}$ show that there is a substantial spin density in the C–Hg–C σ_u orbital on mercury,[16] and so it was concluded[2] that there is a substantial weakening of the C–Hg bonds in the radical cation which would encourage fragmentation: a similar argument predicted that dibenzylmercury radical cations should fragment easily, given that the C–Hg–C region is similarly depleted of electron density, according to EPR data,[1,2] as was observed.[15] The data for diphenylmercury radical cations are more complex, since the choice of substituent was found to influence whether the σ_u- or π-state was formed: as in the present work, oxygen or chlorine were found to stabilise the latter, at least in the solid freon matrix. Nonetheless, for such a subtle choice, we cannot eliminate the possibility that the alternative π-state is formed in solution for Ph$_2$Hg$^{\cdot+}$, at the behest of solvation effects. Since the EPR data for both σ- and π-radical cations of diphenylmercury derivatives show a markedly reduced spin population in the C–Hg–C region, we would predict a greater stability, and, indeed, we have not observed any organic radical products of fragmentation up to the melting point of the CFCl$_3$ matrix (160 K) for either σ- or π-states. In his studies of the allyloxy derivatives, Shine did not obtain any evidence for cyclisation of intermediate allyloxyphenyl radicals, which argued against their formation under solution conditions.[17] There is, therefore, reasonable accord with the EPR measurements.

Experimental

Diphenylmercury was prepared previously; the perdeuteriated derivative was made by the reaction between C$_6$D$_5$MgBr in THF (Aldrich) and HgCl$_2$, also in THF. The allyloxy derivatives were prepared as detailed in ref. 17. For the EPR measurements, dilute solutions (1.0 wt.%) of the mercurials were prepared in CFCl$_3$ (or CCl$_4$) and were frozen in liquid nitrogen prior to exposure to a nominal dose of 3 Mrad using a ^{60}Co source. The spectra were recorded† using Bruker ER 200D or Varian E9 spectrometers, generally with the sample contained in an insert Dewar filled with liquid nitrogen; samples were annealed above 77 K by decanting the liquid-nitrogen coolant from the insert Dewar and allowing the sample to warm, while continuously monitoring the EPR spectrum for any changes, then recooling to 77 K for final measurement.

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† *g*-Values were calibrated against DPPH (diphenylpicrylhydrazyl), the microwave power level was 1.0 mW, and the radicals are stable over several weeks if the temperature of the freon matrix is maintained at 77 K. The radical concentration is *ca.* 10^{-4} mol%.

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