Vapour-phase Conformation of Benzylmercuric chloride†

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Summary Photoelectron spectroscopy is used to show that benzylmercuric chloride exists in the vapour phase in a conformation where the carbon–mercury bond can interact with the π system of the aromatic ring.

IT has been shown recently that benzylmercury derivatives ($PhCH_2HgX$) adopt both in solution ($X = Cl$,[1,2] Br,[1,2] I,[1,2] C_6H_{11},[2] CH_2Ph[2,3]) and in the solid state[4] ($X = SCPh_3$) a conformation with the C_{Ph}=C_{Ph}–C–Hg dihedral angle ϕ approaching 90° (for $X = SCPh_3$ this angle is 87° [4]) in accord with the isolated molecule EH ($X = Br$) suggestion.[5] Here we present results showing that benzylmercuric chloride exists in a 90° or near 90° (*gauche*) conformation also in the gas-phase. Such conformational results which would otherwise be hard to obtain are easily accessible from a photoelectron (p.e.) spectroscopic approach[6] to the problem.

The basic principle of the p.e. method[6] is simple. Rotamers of $PhCH_2HgX$ with ϕ *ca.* 90° are expected to give rise to a first π ionization much lower than the corresponding π ionization in benzene (found at 9·25 eV[7]) as a consequence of C–Hg hyperconjugation.[2–5,8] Rotamers with ϕ *ca.* 0° cannot lead to such an ionization shift because hypercon-

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† For previous papers in the series: 'Theory and Application of Photoelectron Spectroscopy,' see: W. Schäfer and A. Schweig, *J. Amer. Chem. Soc.* submitted for publication.

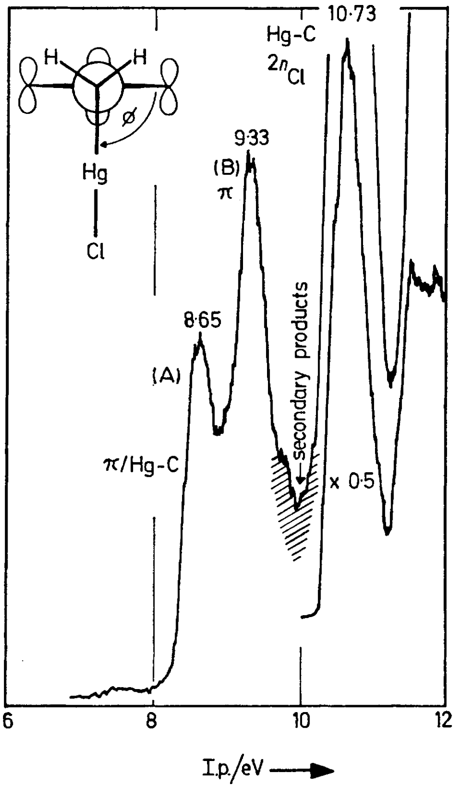

FIGURE. P.e. spectrum of benzylmercuric chloride. The numbers associated with each band are vertical ionization potentials. The shaded area indicates ionizations arising from secondary or byproducts.

jugation is not allowed in these conformations. Additionally, in favourable cases, the measured relative p.e. intensities (I_{90}/I_0) may serve to derive information about the relative rotameric concentrations (n_{90}/n_0) from equation (1), where

$$I_{90}/I_0 = (\sigma_{90}/\sigma_0) \times (n_{90}/n_0) \qquad (1)$$

σ_{90}/σ_0 denotes the relative differential photoionization cross sections.[9]

Comparison of the p.e. spectrum of benzylmercuric chloride (Figure) with those of benzene[7] and methylmercuric chloride[10] shows that the first two ionizations (A) and (B) correspond to the π (e_{1g}) benzene ionizations whilst the intense third band is connected with the two Cl lone pair (n_{Cl}) ionizations and the σ (C–Hg) ionization of the $-CH_2-HgCl$ group (all occurring in MeHgCl at *ca.* 10·8 eV[10]). The shifted first band (A) unambiguously shows that the 90° form is predominantly present in the gas phase under the conditions of the p.e. experiment (86 °C). The magnitude of the shift obtained (0·60 eV) relative to the π (e_{1g}) benzene ionization leads, after correction for the C–H hyperconjugative destabilization (0·12 eV),[11] to the destabilization δE (0·48 eV), exclusively‡ caused by Hg–C hyperconjugation. Together with the difference in energy, ΔE (1·55 eV), between the π (9·25 eV) and the σ (Hg–C) basis orbitals, equation (2)[12] yields the interaction integral $H_{\pi\pi} = 0·99$ eV.

$$H_{\pi\pi} = [\delta E(\delta E + \Delta E)]^{\frac{1}{2}} \qquad (2)$$

The corresponding $H_{\pi\pi}$ (0·98 eV)§ in allylmercuric chloride[8] is in close agreement suggesting that the dihedral angles ϕ may be rather similar in both cases. Owing to the overlapping band structure in the spectral π region and the observation that secondary or byproduct ionizations¶ occur around 10 eV (shaded area in the Figure) and extend below band (B) we cannot use equation (1) in the present instance to decide whether benzylmercuric chloride exclusively exists in the 90° rotameric form or whether any noticeable amount of the 0° isomer is also present.

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‡ The inductive effect of the mercurimethyl chloride group on the benzene π ionization is negligible compared with the hyperconjugative effect. This follows from the small shift of the second π ionization of benzylmercuric chloride and the π ionizations of phenylmercuric chloride.

§ Calculated from equation (2) using the experimental data of ref. 8.

¶ Such secondary or byproduct ionizations seem to be difficult to avoid owing to the instability of benzylmercury compounds to light. See ref. 4.

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