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Extended Hückel Calculations on Benzylmercuric Bromide. Evidence for σ-π Conjugation

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Abstract: Extended Hückel molecular orbital calculations suggest that benzylmercuric bromide exists in a conformation where the polarizable carbon-mercury bond can interact with the π system of the aromatic ring. Theoretical evidence for significant σ-π stabilization of the ortho and para Wheland intermediates involved in proton exchange of this mercurial is presented.

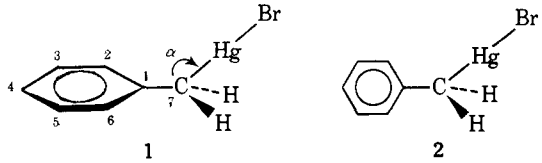
It has been established for some time that the R_3MCH_2 group (M = Si, Ge, Sn, Pb) has a greater electron-releasing capacity than the R_3M moiety.[1] On the basis of charge-transfer frequencies of phenyl-substituted organometallic compounds, it has been suggested that the $-CH_2-Sn(C_6H_5)_3$ group is as activating as a methoxy group, and the $-CH_2SnMe_3$ group is almost as effective as an amino substituent.[2] The $-CH_2Fe(CO)_2-\pi-C_5H_5$ group is also more highly activating toward aromatic electrophilic substitution than is the methoxy group.[3] Both chemical[4] and spectroscopic[5] evidence indicates that this enhanced reactivity is derived from σ-π conjugation of the carbon-metal bond with the neighboring cationic center. Moreover, recent theoretical evidence supports carbon-metal hyperconjugation in group IV allyl organometallic compounds[6a-c] and allylmercuric halides.[6d] On the basis of CNDO/2 calculations, Jones[6e] has suggested that d orbitals are more important than hyperconjugative p-pπ interaction in the ground state with *m*-trimethylsilyl-*N,N*-dimethylaniline. Extended Hückel (EH) calculations on Si, Ge, and Pb allyl derivatives give essentially identical results regardless of whether inner d orbitals and/or outer d orbitals are included.[6c] Our molecular orbital calculations on the acid cleavage of allylmercuric bromide strongly suggested that the degree of σ-π stabilization in the transition state for this acid cleavage was dependent upon the conformation of the allymercuric halide. These data were in excellent agreement with experimental evidence of Traylor[2,5c] and Pitt[4e] who established the necessity for the coplanarity of the C-M bond and the axis of the electron-deficient π orbital. In these calculations, the d-orbital participation in the ground state and in the transition state for protolysis was also found to be minimal. In a study of the deuteriodemetalation of benzylmercuric chloride with DCl in dioxane, Reutov[4c] reported almost exclusive incorporation of deuterium in the ortho position of the aromatic ring. This was attributed to σ-π conjugation and a favored six-member cyclic transition state. Traylor[7] has also reported incorporation of deuterium in the aromatic ring when dibenzylmercury was treated with trifluoroacetic acid-*d* in chloroform. The ortho to para rate ratio for exchange, however, was 0.84, and a σ-π conjugation mechanism was again invoked. We now report extended Hückel molecular orbital calculations which support the σ-π conjugation mechanism for the protonation-deprotonation of benzylmercury compounds.

Experimental Section

Extended Hückel molecular orbital calculations, as developed by Hoffmann,[8] were carried out as previously described.[6d,9] The aromatic ring was located in the *xy* plane. Bond angles for sp^2 and sp^3 carbon atoms were taken as 120 and 109.5°, respectively. Carbon-carbon bond distances were taken as 1.395 (aromatic) and 1.52 Å, while the C-Br, C-Hg, and Hg-Br bond distances were 2.00, 2.074, and 2.406 Å, respectively. Carbon-hydrogen bond distances were taken as 1.084 (ring) and 1.09 Å (benzylic), except for a carbon-proton bond distance of 1.2 Å in the transition states for proton addition to the benzene ring. The H-C-H bond angle in the Wheland intermediates was 109.5° with a C-H bond distance of 1.084 Å. The H-Cl bond distance in the HCl complex (**8**) with benzylmercuric chloride was 1.2 Å, and the Cl-Hg bond distance was taken as 2.22 Å. The hydrogen was 1.2 Å above the ortho carbon with a C_2-H-Cl bond angle of 120°. The Hg-O bond distance in the aquocomplex **9** was 2.13 Å, and the C_7-Hg-Cl bond angle was 120°. The H-O-H bond angle was 104.5°, and the O-H bond distances were 0.96 and 1.27 Å with the latter hydrogen being 1.08 Å above the ortho carbon with a C_2-H-O bond angle of 120°.

Results and Discussion

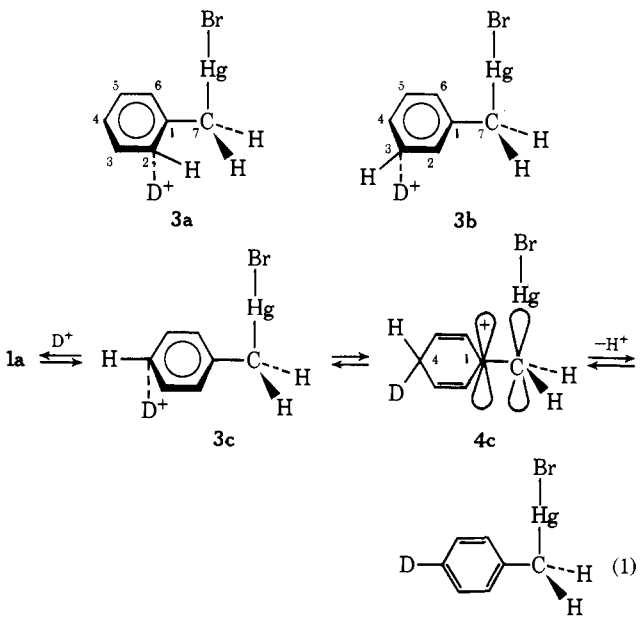
We first directed our attention toward calculating the preferred conformation of benzylmercuric bromide in order to compare these results with those obtained in allymercuric bromide.[6d] Extended Hückel molecular orbital calculations suggest that in the ground state benzylmercuric bromide is more stable in conformation **1** (β = 90°), where the polari-



1 **2**

zable carbon–mercury bond can interact with the π system of the aromatic ring, than in the planar conformation **2** (β = 0°), where the HgBr moiety is in the nodal plane of the aromatic ring. These results are in good accord with vibrational spectral data which suggest that benzylmercuric halides have a nonplanar configuration.[10a] However, when the hybridization at C_7 was varied from sp^3 in **1** (α = 109.5°) to sp^2 affording **1a** (α = 90°), a slight decrease in total energy was observed (Table I). Similar results were obtained with EH calculations[6d] on allymercuric bromide and reflect an exaggeration of the degree of σ–π interaction in the ground-state conformation. An X-ray analysis[11] has shown the C_6H_5–C–Hg bond angle in benzyltriphenylmethylthiomercury to be 112°. However, the crystal structures[10b] of a series of tetrabenzyl derivatives of Zr, Hf, and Ti have established a novel distortion of the C–C–M bond angle from a tetrahedral value of 109.5°. The average angles were 92, 94, and 103°, respectively, while the angle at the methylene carbon in tetrabenzyltin was shown to be 111°. The calculations are in excellent agreement with the observed conformation for the above benzylmercury derivative since the dihedral angle between the plane formed by the Hg, the methylene carbon, and C_1 of the phenyl group was found to be 87°[11] (i.e. the conformation depicted in **1**).

We next examined the relative merits of σ–π conjugation in the ortho and para vs. meta transition states and Wheland intermediates involved in protonation–deprotonation of benzylmercuric bromide. In an effort to approximate the transition states for hydrogen–deuterium exchange in benzylmercuric bromide, we added a proton (D^+) at a 90° angle to the plane of the aromatic ring in **1a** (α = 90°) at a distance of 1.2 Å above the ortho, meta, and para carbon atoms affording **3a, 3b,** and **3c,** respectively. Rehybridization at the site of proton attack from sp^2 to sp^3 affords the Wheland intermediates **4a, 4b,** and **4c.** For example, attack of D^+ in the para position of **1a** affords **4c** (eq 1). Extended



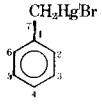
Hückel calculations indicated that addition of a proton to **1** and **1a** was slightly favored from the side opposite the HgBr moiety. The data in Table I further suggest that the transition states for protonation of **1a** at the ortho position (**3a**) and the para position (**3c**) are approximately equal in energy. However, the para Wheland intermediate (**4c**) is more stable than the ortho intermediate **4a.** The decrease in total energy on conversion of the ortho and para transition states **3a** and **3c** to the corresponding Wheland intermediates was 20.8 and 28.8 kcal/mol. However, the meta Wheland intermediate was only 4.8 kcal/mol lower in energy than the meta transition state. The pronounced stabilization of the ortho and para Wheland structures suggests that they are discrete intermediates on the reaction coordinate for proton exchange.

Despite the fact that the extended Hückel method sometimes gives unreliable total energies, the above conclusions based upon total energy considerations are in good agreement with the experimental observations that deuterium exchange occurs at the ortho and para positions. Calculations of the bond orders, based on Mulliken overlap populations,[12] between the carbon–mercury σ bond and the π orbital at C_1 also are consistent with previous findings based upon experimental data.[7] Thus, with ortho and para substitution, the transition states **3a** and **4a** and the Wheland intermediates **3c** and **4c** exhibit an increase in $\rho_{C_1-C_7}$ and a concomitant decrease in carbon–mercury bonding, ρ_{C_7-Hg}, due to the σ–π delocalization. Of particular relevance, however, is the significant increase in the π contribution to the total C_1–C_7 bonding (i.e., the σ–π interaction component of $\rho_{C_1-C_7}$) in both the ortho and para intermediates. For example, the σ–π contribution to $\rho_{C_1-C_7}$ is 0.060 in **1a,** 0.130 in **3a,** and 0.165 in the ortho Wheland intermediate **4a.** It should be noted that d orbitals are not extensively involved in the carbon–mercury bond. The bonding in the C_7–Hg bond in **1a, 3a,** and **4a** was comprised of approximately 63% s-, 36% p-, and only 1% d-orbital contribution from mercury. Thus, the calculations adequately reflect the increase in $\rho_{\sigma-\pi}$ in the transition state, which bears a full positive charge, relative to the ground state. In both meta addition products **3b** and **4b,** the C_1–C_7 bonding interaction ($\rho_{C_1-C_7}$) and the σ–π component of that interaction ($\rho_{\sigma-\pi}$ = 0.064 and 0.063) are essentially the same as in the unprotonated species **1a.** A significant increase in σ–π interaction is only noted for deuterium exchange at the ortho and para positions. Since the calculated energy minimum for benzylmercuric bromide occurs at a 90° angle at the methylene carbon (C_7), we chose this as our ground-state geometry. However, similar conclusions were reached when calculations on reaction intermediates were carried out with sp^3 geometry at C_7 as in **1.**

Further support for the very strong ortho,para directing, electronic effect of the mercurimethyl group ($-CH_2HgX$) comes from the charge distributions in Table I. With the ortho and para intermediates, the positive charge on the ring is more heavily concentrated at C_1 where it can be stabilized through carbon–metal hyperconjugation. In **3a** and **4a,** the C_3–C_4 double-bond order ($\rho_{C_3-C_4}$) and the π contribution to that bond are also noticeably increased as is the positive charge at C_1. Similarly, in **3c** and **4c** with para attack, the double-bond character at C_2–C_3 is enhanced with a greater portion of positive charge localized at C_1. With meta attack, where σ–π interaction in insignificant, the charge distribution and the bond orders are more evenly spread over the aromatic sextet. The increase in negative charge at C_7 and the lower positive charge on mercury in the meta intermediates are also consistent with a reduced σ–π interaction.

The present study also corroborates earlier suggestions based upon experimental evidence[7] that the stabilization of the adjacent carbonium ion at C_1 by σ–π conjugation ($\rho_{\sigma-\pi}$) is considerably greater than that by neighboring group participation (ρ_{C_1-Hg}). In an effort to assess the importance of neighboring group participation in these reactions, we centered the HgBr moiety between C_1 and C_7 (**5**) while adding a proton to the ortho position. As shown in Table I, the total energy of **5** is higher than the comparable transition state

Table I. EH Calculations on Benzylmercuric Bromide



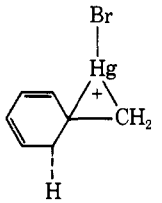
	E_T, kcal/mol	ρ_{C_7Hg}[b]	ρ_{C_1Hg}	$\rho_{C_1C_2}$	$\rho_{C_2C_3}$	$\rho_{C_3C_4}$	$\rho_{C_1C_6}$	$\rho_{C_1C_7}$	ρ_{CH^+}	Q_{C_1}[c]	Q_{C_2}	Q_{C_3}	Q_{C_4}	Q_{C_5}	Q_{C_6}	Q_{C_7}	Q_{Hg}	Q_{Br}
1 (α, 109.5; β, 90)[a]	−20584.3	0.601	−0.054	1.132[d]	1.124	1.120	1.132	0.786[d]		0.080	−0.023	−0.001	−0.023	−0.001	−0.023	−0.189	0.649	−0.372
				0.290[e]	0.299	0.293	0.290	0.034[e]										
1a (α, 90; β, 90)	−20587.0	0.496	0.003	1.123	1.132	1.114	1.123	0.825		0.103	−0.044	−0.008	−0.049	−0.008	−0.044	−0.220	0.720	−0.356
				0.270	0.306	0.287	0.270	0.060										
2 (α, 109.5; β, 0)	−20542.1	0.274	−0.098	1.118	1.134	1.110	1.118	0.845		0.049	−0.035	−0.006	−0.044	−0.006	−0.035	−0.428	0.820	−0.342
				0.269	0.307	0.285	0.269	0.088										
3a (ortho H^+)	−20894.5	0.455	0.033	0.923	0.907	1.195	1.098	0.901	0.831[f]	0.253	0.151	0.145	−0.011	0.073	0.001	−0.164	0.757	−0.342
				0.108	0.106	0.362	0.249	0.130	0.600[g]									
3b (meta H^+)	−20865.2	0.493	0.002	1.138	0.933	0.928	1.099	0.827	0.825	0.135	0.139	0.171	0.127	0.028	0.059	−0.213	0.725	−0.354
				0.287	0.138	0.132	0.255	0.064	0.558									
3c (para H^+)	−20893.9	0.456	0.026	1.065	1.203	0.903	1.065	0.885	0.826	0.184	−0.008	0.141	0.148	0.141	−0.008	−0.166	0.760	−0.339
				0.222	0.372	0.103	0.222	0.120	0.597									
4a (ortho Wheland)	−20915.3	0.427	0.047	0.878	0.863	1.232	1.094	0.940	0.785	0.252	0.089	0.114	0.002	0.104	0.006	−0.129	0.784	−0.327
				0.056	0.053	0.401	0.246	0.165										
4b (meta Wheland)	−20869.9	0.495	0.001	1.158	0.899	0.899	1.084	0.825	0.750	0.140	0.136	0.105	0.138	0.039	0.129	−0.215	0.725	−0.354
				0.310	0.089	0.087	0.236	0.063										
4c (para Wheland)	−20922.7	0.421	0.043	1.032	1.239	0.867	1.032	0.925	0.777	0.222	0.008	0.113	0.089	0.113	0.008	−0.115	0.791	−0.324
				0.183	0.409	0.055	0.185	0.159										
5 (Hg bridging)	−20893.5	0.318	0.114	0.900	0.894	1.204	1.063	0.924	0.826	0.255	0.115	0.135	0.028	0.054	0.001	−0.169	0.775	−0.291
				0.093	0.102	0.370	0.213	0.156	0.659									

[a] α is the C_1–C_7–Hg bond angle in degrees, and β is the C_2–C_1–C_7–Hg dihedral angle in degrees. [b] ρ_{ij} is the Mulliken overlap population between atoms i and j. [c] Q_i is the charge on atom i. [d] Total overlap population. [e] Contribution of the π bond to the overlap population. [f] Aromatic ring hydrogen. [g] Attacking proton.

Table II. EH Calculations on Benzylmethyl Mercury

	E_T, kcal/mol	$\rho_{C_1C_2}$	$\rho_{C_2C_3}$	$\rho_{C_3C_4}$	$\rho_{C_1C_7}$	$\rho_{C_7H_9}$	ρ_{C_1Hg}	$\rho_{C_2H^+}$	Q_1	Q_2	Q_3	Q_4	Q_7	Q_{Hg}	Q_C of Me	IP, eV
6 (α, 109.5; β, 90)[a]	−20859.8	1.131[b]	1.125	1.120	0.789	0.598	0.053		0.077	0.024	−0.002	−0.024	−0.211	0.619	−0.264	−10.7
		0.288	0.299	0.292	0.037											
6a (α, 90; β, 90)[a]	−20862.0	1.111[c]	1.132	1.113	0.832	0.488	0.003		0.097	0.045	−0.008	−0.050	−0.246	0.692	−0.253	−10.3
		0.268	0.306	0.286	0.068											
6b (ortho H^+)	21169.2	0.921	0.907	1.200	0.910	0.446	0.031	0.831[d]	0.246	0.149	0.144	−0.012	0.186	0.733	0.246	−10.7
		0.106	0.105	0.363	0.139			0.601[e]								
6c (ortho Wheland)	21189.5	0.876	0.862	1.233	0.952	0.415	0.045	0.786	0.242	0.087	0.111	0.001	−0.145	0.761	−0.236	−10.8
		0.054	0.052	0.402	0.177			0.786								

[a] See footnote a, Table I. [b] Total overlap population. [c] π-Overlap population. [d] Aromatic ring hydrogen. [e] Attacking proton.



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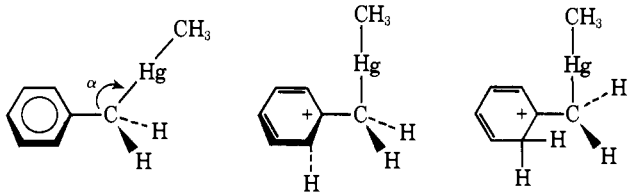
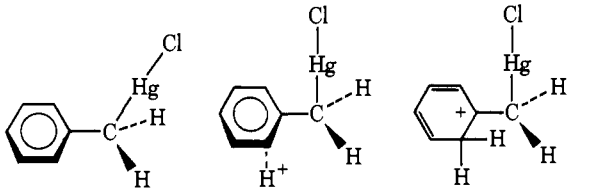
3a, suggesting that σ–π conjugation is more important than neighboring group participation involving extensive heavy-atom motion in stabilizing the developing positive charge on protonation of the aromatic ring. Moreover, the present work is consistent with our previous calculations,[6d,f] which show that the charge at carbon in mercurinium ion intermediates formed in oxymercuration reactions is stabilized principally by σ–π conjugation and not by electron density on mercury, i.e., neighboring group participation.

In an effort to ascertain the effect of the substituent X on the activating moiety CH_2HgX, we also carried out EH calculations on benzylmethylmercury (**6**) and benzylmercuric

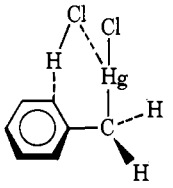


6 **6b** **6c** (β = 90°)

chloride (**7**). Our results suggest that the preferred confor-



7a **7b** **7c** (β = 90°)



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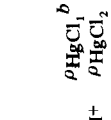
mation for **6** has the C–Hg bond perpendicular to the aromatic ring as noted above for **1**. Again a C_1–C_7–Hg bond angle (α) of 90° (**6a**) was slightly preferred over the tetrahedral bond angle of 109.5°. Our calculations suggested that replacement of the bromine ligand with a methyl group affording **6** results in a slight increase in $\rho_{C_1-C_7}$ and in the σ–π contribution to that bonding interaction (Table II). Protonation of **6a** in the ortho position (**6b**) and formation of the ortho Wheland intermediate **6c** also result in an increased σ–π conjugation relative to protonation of **1a**.

Our calculations are thus in good accord with experimental data where a very strong ortho,para directing, electron-donating effect of the metallomethyl group has been observed. The ortho to para relative rate factor of 0.84 for deuterium exchange in dibenzylmercury with CF_3COOD[7] is also consistent with our calculations on **1** which suggest that the ortho and para positions are stabilized to about the same extent by σ–π conjugation.

The high ortho selectivity of hydrogen-deuterium exchange in benzylmercuric chloride has been ascribed to a

Table III. EH Calculations on Benzylmercuric Chloride



	E_T, kcal/mol	$\rho_{C_1C_2}$	$\rho_{C_2C_3}$	$\rho_{C_3C_4}$	$\rho_{C_1C_7}$	ρ_{C_7Hg}	ρ_{C_1Hg}	$\rho_{C_2H^+}$	ρ_{HgCl_1}[b] ρ_{HgCl_2}	Q_{C_1}	Q_{C_2}	Q_{C_3}	Q_{C_4}	Q_{C_7}	Q_{Hg}	Q_{Cl}	IP, eV
7 (α, 109.5, β, 90)[a]	−20821.2	1.133[c]	1.124	1.121	0.782	0.615	−0.054		0.517	0.082	−0.021	−0.001	−0.021	−0.170	0.719	−0.471	−10.95
		0.291[d]	0.298	0.293	0.030												
7a (α, 90, β, 90)[a]	−20821.5	1.114	1.131	1.114	0.817	0.514	0.005		0.517	0.107	−0.042	−0.007	−0.046	−0.203	0.786	−0.458	−10.47
		0.271	0.305	0.287	0.054												
7b (ortho H^+)	−21128.7	0.908	1.194	1.060	0.925	0.474	0.035	0.598[e]	0.526	0.259	0.152	0.146	−0.009	0.149	0.825	−0.446	−10.92
		0.0	0.107	0.361	0.126			0.831[f]									
7c (ortho Wheland)	21148.3	0.865	1.230	1.025	0.929	0.448	0.050	0.784	0.532	0.261	0.090	0.118	0.004	−0.119	0.852	−0.435	−11.03
		0.058	0.054	0.399	0.155			0.783									
8 (HCl complex)	−23581.1	0.988	0.989	1.095	0.843	0.428	−0.056	0.241	0.431	0.058	0.269	−0.171	−0.089	−0.264	0.646	−0.542	8.67
		0.128	0.179	0.270	0.055			0.868	0.374							0.122	

[a] See footnote *a*, Table I. [b] Cl_1 is the chlorine of the $C_6H_5CH_2HgCl$, and Cl_2 is the Cl of HCl. [c] Total Mulliken overlap population. [d] π-Overlap population. [e] Proton attacking ring. [f] Proton in plane of benzene ring.

Table IV. EH Calculations on Benzyl Bromide

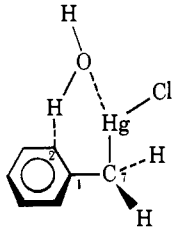
	E_T, kcal/mol	ρ_{C_7Br}	ρ_{C_1Br}	ρ_{12}	ρ_{23}	ρ_{34}	ρ_{17}	Q_{Br}	Q_{C_1}	Q_{C_2}	Q_{C_3}	Q_{C_4}	Q_{C_5}	IP, eV
$\alpha = 109.9, \beta = 0°$	−16177.4	0.555	−0.130	1.155[a]	1.114	1.125	0.769[a]	−0.160	0.093	−0.019	−0.003	−0.011	0.111	−10.77
				0.300[b]	0.292	0.300	0.001[b]							
$\alpha = 109.5, \beta = 90°$	−16207.7	0.526	−0.095	1.135	1.123	1.121	0.773	−0.128	0.099	−0.012	0.00	−0.014	0.114	−10.78
				0.293	0.297	0.294	0.012							
Ortho H^+	−16493.4	0.519	−0.067	0.941	0.922	1.173	0.798	−0.098	0.275	0.172	0.167	0.022	0.130	−10.95
				0.133	0.123	0.339	0.029							
Ortho Wheland	−16500.5	0.516	−0.060	0.905	0.887	1.200	0.709	−0.081	0.284	0.107	0.160	0.031	0.132	−10.94
				0.084	0.076	0.369	0.038							
Meta H^+	−16484.0	0.527	−0.094	1.167	0.928	0.932	0.770	−0.124	0.135	0.166	0.176	0.165	0.119	−10.88
				0.319	0.134	0.135	0.011							
Meta Wheland	−16488.9	0.528	−0.093	1.188	0.896	0.901	0.769	−0.120	0.141	0.165	0.110	0.171	0.119	−10.80
				0.343	0.087	0.088	0.011							
Para H^+	−16492.3	0.521	−0.073	1.105	1.172	0.923	0.786	−0.099	0.201	0.024	0.169	0.169	0.126	−10.93
				0.265	0.339	0.125	0.023							
Para Wheland	−16505.1	0.515	−0.056	1.078	1.201	0.890	0.798	−0.070	0.260	0.035	0.162	0.106	0.135	−10.88
				0.233	0.371	0.077	0.035							

[a] Total overlap population. [b] π-Overlap population.

cyclic transition state **8** involving DCl.[4c] Inclusion of ligands that bond well to mercury should facilitate ortho exchange if the bonding interaction is appreciable. However, addition of chloride ion does not increase the solubility of alkylmercury halides. In contrast, chloride ion has been observed to increase the rate of acid cleavage of the C–Hg bond through salt effects rather than ligand effects.[13] To ascertain the role of the DCl in this exchange reaction, we carried out calculations with benzylmercuric chloride in the presence (**8**) and absence of a molecule of HCl in the transition state. Benzylmercuric chloride exhibited a trend similar to that noted above for the conformation of benzylmercuric bromide (**1**) and benzylmethylmercury (Table III). Again a C_1–C_7–Hg bond angle of 90° (**7a**) was slightly preferred over one of 109.5°. Replacement of the bromide of **1** with a chloride ligand results in a slight decrease in $\rho_{C_1-C_7}$ and in the σ–π contribution to that bonding interaction. Protonation of the ortho position of **7a** results in a decrease in the σ–π conjugation of the approximated transition state **7b** and the Wheland intermediate **7c** relative to the corresponding activating moiety $-CH_2HgBr$. This minor difference probably reflects the increased electronegativity of Cl relative to Br. The charge on mercury (Q_{Hg}) for **1, 6,** and **7** also reflects the inductive effects of these ligands. However, the ortho transition states and the Wheland intermediates for all three benzylmercury derivatives show comparable σ–π stabilization of these intermediates which lie along the reaction pathway for hydrogen exchange.

When HCl was included in the transition state, affording complex **8,** the attacking chlorine exhibits a substantial bonding interaction with the mercury atom (ρ_{Hg-Cl} = 0.374). Although the σ–π interaction ($\rho_{\sigma-\pi}$ = 0.099) and C_2–H^+ overlap population ($\rho_{C_2-H^+}$ = 0.241) are less than in the corresponding ortho transition state **7b** where they are 0.126 and 0.598, respectively, this intermediate still provides the most plausible explanation for the observed ortho/para ratio of deuterium exchange.

In an effort to test the effect of solvation on these reactions, we also included a water molecule in the transition state for proton exchange affording **9.** The calculations suggest that some rehybridization at mercury should occur since **9,** which has sp^2 hybridization at Hg, is 12 kcal/mol lower in energy than a linear sp mercury complex. As anticipated, the bonding between mercury and and oxygen is moderate (ρ_{Hg-O} = 0.184), resulting in a stronger C_2–H^+ bond ($\rho_{C_2-H^+}$ = 0.427) than in **7b.** However, the σ–π interaction is greater than that observed in the HCl complex **8** ($\rho_{\sigma-\pi}$ = 0.112).



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To further test the validity of this method of calculation to qualitatively measure the degree of σ–π conjugation with heavy metals, we have also briefly examined benzyl bromide as a model compound. It has been suggested[14] on the basis of NQR data that in benzyl chloride the π electrons of the phenyl group interact with the C–Cl σ bond in a hyperconjugative manner. NMR data also suggest that CH_2Br acts predominantly by a hyperconjugative mechanism as an electron-withdrawing group.[4h] Photoelectron spectroscopy experiments have also provided convincing evidence for carbon-halogen hyperconjugation in benzyl[15] and allyl[16] halides. EH calculations suggest that benzyl bromide prefers the same conformation as **1** (β = 90°), where the C–Br σ MO and the ring π MO's can maximize their interaction, except that it exhibited sp^3 geometry (α = 109.5) at the methylene group. Examination of the data in Table IV further suggests that the σ–π interaction is considerably weaker than in **1.** In particular, however, $\rho_{C_1-C_7}$ and the σ–π interaction did not exhibit a marked change on protonation at the ortho, meta, or para positions. These results suggest that the above conclusions with the CH_2HgX moiety are not an artifact of the method of calculation.

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Chemical and Physical Consequences of 2p–3d Overlap in *o*-Anisylphosphines and *o*-Anisylphosphonium Salts

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Abstract: Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride are presented. There are two particularly striking effects. (1) The presence of an *o*-methoxy group in the phosphine causes a marked acceleration of the reaction. (2) The difference in the rates of reaction of a given triarylphosphine with benzyl chloride and *n*-butyl chloride is less than 20, probably the smallest difference ever found in SN2 reactions of these halides. An explanation of these effects is offered based partly on the concept of overlap of a pair of 2p electrons of an *o*-anisyl group with a 3d orbital (or hybrid orbital) of phosphorus in the transition state and partly on the concept that the transition state for each of the benzyl halide reactions lies much closer to the reagents than to the products along the reaction coordinate of the energy profile diagram. Additional evidence for the postulated 2p–3d overlap is found in the uv and NMR spectra of the phosphines and corresponding phosphonium salts. Finally, it has been found that *o*-anisyldiphenylphosphine exhibits mass spectral reactions not evidenced by the meta and para isomers. The eliminations of H_2O, $CH_3O\cdot$, and $C_7H_7\cdot$ from the molecular ion of the ortho isomer, involving skeletal and specific hydrogen rearrangements, have been studied by means of deuterium labeling.

Data which demonstrate that the presence of an *o*-anisyl group causes a marked acceleration of the SN2 reaction of a triarylarsine with benzyl bromide to give the quaternary arsonium bromide and of a triarylphosphine with benzyl chloride to give the quaternary phosphonium chloride have been presented in previous communications.[2] The major rationalization for these results consisted of the suggestion that overlap of a pair of 2p electrons of an *o*-methoxy group with a 4d orbital of arsenic or with a 3d orbital of phosphorus, respectively, lowers the energy of the transition state for each of these SN2 reactions. We now wish to present new data and to discuss the probable mechanism of reaction in greater detail.

Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride are given in Table I. The activation parameters for some of these reactions are presented in Table II. Some of the highlights of the data are the following. (1) The relative rates of reaction of tris(*o*-anisyl)phosphine, bis(*o*-anisyl)phenylphosphine, *o*-anisyldiphenylphosphine, and triphenylphosphine with benzyl chloride in benzene–methanol (3:2 v/v) at 31.0° are 27.0, 20.2, 7.42, and 1.00, respectively. (2) The relative rates of reaction of *o*-anisyldiphenylphosphine and triphenylphosphine with benzyl chloride in chloroform at 31.0° are 5.07 and 1.00, and the reactions in this solvent are approximately 0.75–1.09 times as fast as those in benzene–methanol (3:2 v/v). (3) The relative rates of reaction of bis-*o*-anisylphenylphosphine, *o*-anisyldiphenylphosphine, tris-*o*-anisylphosphine, triphenylphosphine, and *m*-anisyldiphenylphosphine with benzyl bromide in chloroform at 31.0° are 6.45, 5.15, 1.59, 1.00, and 0.95, respectively; the benzyl bromide reactions are approximately 102–104 times more rapid than the corresponding benzyl chloride reactions. (4) The relative rates of reaction of bis(*o*-anisyl)phenylphosphine, *o*-anisyldiphenylphosphine, tris-*o*-anisylphosphine, and triphenylphosphine with *n*-butyl chloride in chloroform at 31.0° are 13.5, 4.68, 3.89, and 1.00, respectively; the benzyl chloride reactions are approximately 18.8–20.4 times faster than the corresponding *n*-butyl chloride reactions. (5) The k_o/k_p ratios for the trisanisyl, bisanisylphenyl, and anisyldiphenylphosphine reactions with benzyl chloride in benzene–methanol (3:2 v.v) at 31.0° are 4.1, 6.0, and 3.7, respectively; the k_o/k_p ratio for the anisyldiphenylphosphine reactions with benzyl bromide in chloroform at 31.0° is 4.0. (6) *m*-Anisyldiphenylphosphine reacts at a slower rate with benzyl bromide in chloroform than the *o*-anisyl or the *p*-anisyl isomers and even at a slower rate than triphenylphosphine. (7)