Ultraviolet Spectra of Biphenyl Derivatives of Group IVb

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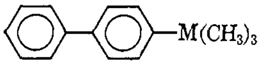
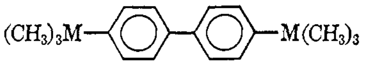
Abstract: The ultraviolet spectra of the compounds 4-$(CH_3)_3MC_6H_4C_6H_5$ and 4, 4′-$(CH_3)_3MC_6H_4C_6H_4M(CH_3)_3$ (M = C, Si, Ge, Sn) are presented and discussed in terms of a heteroatom model for M = C, Si, Ge. The spectra are characterized by a broad band at approximately 250 mμ (p band) and a strong band at approximately 200 mμ (β band). The heteroatom parameters previously used in the interpretation of the esr spectra of the silicon- and germanium-substituted biphenyl anion radicals are found to correctly predict the ordering of the energies of the 250-mμ transition. A heteroatom model for the *t*-butyl-substituted biphenyls also gives transition energies in good agreement with experiment, and the results are also consistent with the observed polarographic reduction potentials and esr spectra.

The experiments of Goodman, *et al.*,[1] and of Bedford, *et al.*,[2] provide new evidence that both silicon and germanium withdraw π-electron density and thus utilize their d orbitals in bonding to unsaturated carbon. Curtis and Allred[3] investigated the electron spin resonance (esr) spectra of the anion radicals of I and II and interpreted the spectra in terms of a heteroatom model for the $(CH_3)_3Si$ and $(CH_3)_3Ge$ groups. Using such a model, π-bond orders of 0.18 and 0.13 were calculated for the C–Si and C–Ge bonds, respectively, whereas no conjugative interaction was allowed in the model for the *t*-butyl group (*i.e.*, an inductive model was employed). In this work it is shown that the heteroatom model,[4] *i.e.*, setting $\alpha_M = \alpha_0 + h_M\beta_0$ and $\beta_{CM} = k_{CM}\beta_0$ (M = C, Si, Ge), correctly predicts the trends observed in the ultraviolet spectra of I and II, and that a heteroatom model for the *t*-butyl group (M = C) also gives results consistent with the previous esr work.[3]



I



II

a, M = C c, M = Ge
b, M = Si d, M = Sn

Results and Discussion

Dewar and Longuet-Higgins[5] have discussed the origin of the three bands usually observed in the ultraviolet spectra of aromatic hydrocarbons. The p band arises from the transition $\pi_m \rightarrow \pi_{m+1}$ (Figure 1), while the transitions $\pi_{m-1}' \rightarrow \pi_{m+1}$ and $\pi_m \rightarrow \pi_{m+2}$ interact to give a strong band at low wavelengths (β band) and a weak band at longer wavelengths (α band). For the biphenyl derivatives reported here, the β band occurs near 200 mμ, while the α band is not observed and perhaps is under the p band[6] (Figure 2).

Since the transition associated with the 250-mμ band is nondegenerate and of different symmetry from the other transitions, it is expected that configuration interaction may be neglected in a first-order approximation[7] with the result that the simple Hückel treatment may describe the behavior of the 250-mμ band caused by perturbations of the energies, ϵ_{m+1} and ϵ_m.[8] Conversely, the simple theory cannot be expected to account for shifts in the 200-mμ band caused by a series of substituents, since configuration interaction plays a large part in determining the energy of this transition.

The observed ultraviolet spectra of the substituted biphenyls (I and II) are very similar to the spectrum of biphenyl and are listed in Table I along with the calculated transition energies (see below) where $\Delta\epsilon = \epsilon_{m+1} - \epsilon_m$. In the case of the silicon- and germanium-substituted biphenyls, the energies were obtained from calculations originally performed to interpret the esr spectra of the radical anions of Ib and c and IIb and c.[3] The *h* and *k* values for silicon and germanium were found to be $h_{Si} = -1.20$, $k_{CSi} = 0.450$, $h_{Ge} = -1.05$, $k_{CGe} = 0.300$ (inductive parameter = 0.1).[3,4] Thus, the $(CH_3)_3M$– (M = Si, Ge) group furnishes a high-energy, vacant orbital which withdraws π-electron density from the aromatic system and lowers the energies of both π_m and π_{m+1}. However, the energy of π_{m+1} is depressed to a greater degree so that the p band occurs at longer wavelengths than in biphenyl itself.

The esr spectra[3] of the *t*-butyl-substituted anion radicals have been interpreted in terms of an inductive model in which the electrons in the $C–CH_3$ bonds did not interact with the conjugated π system. This model cannot be used to interpret the ultraviolet spectra of Ia and IIa, however, since a purely inductive perturbation of the π system raises both ϵ_{m+1} and ϵ_m to the same degree so that no change is predicted in λ_{max} upon substitution of $(CH_3)_3C$– for hydrogen.[9] Hence, a hyperconjugation model must be chosen for the *t*-butyl group. There are several models for methyl hyperconjugation. Two of the most widely used are the H_3 pseudo-atom approach in which the methyl group behaves as a "triple" bond, $—C{\equiv}H_3$, and the heteroatom approach in which the methyl group simply donates a filled, low-energy orbital

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[1] L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Am. Chem. Soc.*, **87**, 1012 (1965).

[2] J. A. Bedford, J. R. Bolton, A. Carrington, and R. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).

[3] M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965).

[4] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

[5] M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.* (London), **A67**, 795 (1954).

[6] I. B. Berlman and O. J. Steingraber, *J. Chem. Phys.*, **43**, 2140 (1965).

[7] W. Moffitt, *ibid.*, **22**, 1820 (1954).

[8] This is especially true in the case of small perturbations in which the second-order configuration terms are nearly constant in the series.

[9] R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry, Methods and Applications," Interscience Publishers, Inc., New York, N. Y., 1959.

Table I. Ultraviolet Spectra and Calculated Transition Energies of 4- and 4,4′-Substituted Biphenyls

$R–C_6H_4C_6H_4–R'$		P band[a]			β band[a]	
R	R′	λ_{max}, mμ	Molar absorptivity (× 10^{-3})	$-\Delta\epsilon\ (\beta)$	λ_{max}, mμ	Molar absorptivity (× 10^{-3})
H	H	247.1 ± 0.1	16.8	1.409	202.0[b]	38.8
H	$C(CH_3)_3$	252.4	20.8	1.378	202.0	46.1
H	$Si(CH_3)_3$	255.0	23.4	1.364	202.0	45.4
H	$Ge(CH_3)_3$	253.6	22.9	1.378	202.0	45.4
H	$Sn(CH_3)_3$	254.5	25.1	...	202.5	49.9
$(CH_3)_3C$	$C(CH_3)_3$	256.8	24.0	1.356	203.0	38.1
$(CH_3)_3Si$	$Si(CH_3)_3$	262.2	30.3	1.331	202.5	47.5
$(CH_3)_3Ge$	$Ge(CH_3)_3$	260.0	29.5	1.352	203.5	38.9
$(CH_3)_3Sn$	$Sn(CH_3)_3$	262.4	32.7	...	...	51.6

[a] Nomenclature of E. Clar; see p 215 ff of ref 4. [b] Due to baseline uncertainty, the error is ±1.0 mμ for the high-energy absorption.

to the π system.[10] It has been shown that the pseudoatom approach gives an incorrect ordering of the lowest unoccupied MO's in the toluene anion radical unless an inductive parameter is also used.[11] The value of the inductive parameter necessary to bring about a correct ordering of these energy levels appears rather arbitrary, especially in view of recent indications that, in comparison to hydrogen, the methyl group is electron withdrawing in the σ framework.[12,13]

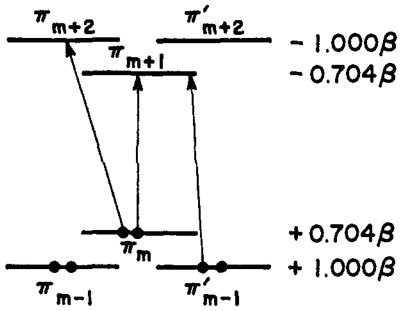

Figure 1. Lowest antibonding and highest bonding molecular orbitals of biphenyl.

It was found that a heteroatom model, in which a methyl (or *t*-butyl) group supplies a low-energy, filled orbital, gives the correct ordering of energy levels in the toluene (or *t*-butylbenzene) anion radical without the necessity of including an inductive parameter. The *h* and *k* values chosen for the *t*-butyl group are those used for the methyl group by Bolton, *et al.*,[14] in their interpretation of the esr spectra of some methyl-substituted aromatic ions, namely, $h_{t\text{-Bu}} = 1.5$ and $k_{C-t\text{-Bu}} = 0.5$. Thus, the *t*-butyl group furnishes a low-energy, filled orbital to the system which raises the energies of both π_m and π_{m+1}. Since the energy rise of π_m is greater, π_m and π_{m+1} are crowded closer together, and the p band again lies at a longer wavelength than that of the parent biphenyl.

The least-squares plot of the calculated energies *vs.* the observed frequencies (Figure 3) shows that an excellent correlation is obtained. The slope of the line gives a value of 91 kcal/mole for β, which is in the range normally found from spectroscopic measurements when overlap is neglected.[15]

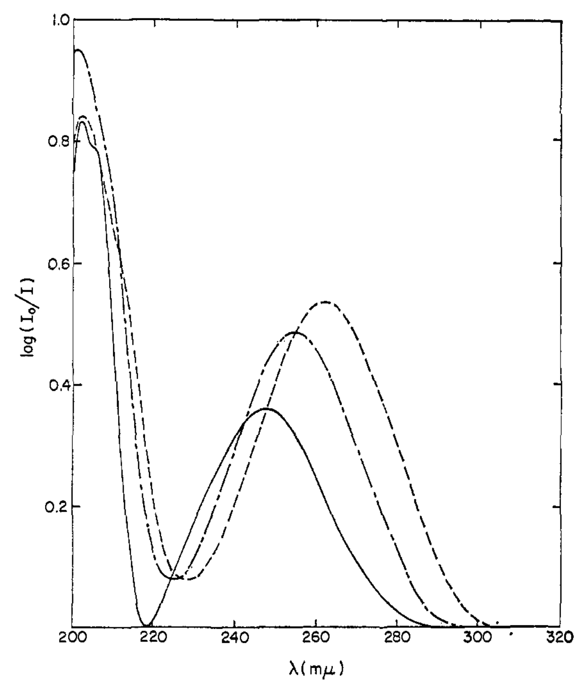

Figure 2. Ultraviolet spectra of biphenyl (———), 2.14 × 10^{-5} *M*; trimethylsilylbiphenyl (— · —), 2.09 × 10^{-5} *M*; bistrimethylsilylbiphenyl (- - - -), 1.77 × 10^{-5} *M*.

As stated above, the parameters necessary for the energy calculations for the silicon- and germanium-substituted biphenyls were originally derived from esr spectra, whereas the heteroatom model for the *t*-butyl group was introduced here solely to explain the ultraviolet spectra of the *t*-butylbiphenyls. It would therefore be instructive to compare the results derived from the heteroatom model of *t*-butyl with those obtained earlier using the inductive model. Table II lists the ob-

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(10) See ref 4, p. 131 ff, for a discussion of hyperconjugation.

(11) D. Lazdins and M. Karplus, *J. Am. Chem. Soc.*, 87, 920 (1965).

(12) H. J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, 85, 148 (1963).

(13) V. W. Laurie and J. S. Muenter, *ibid.*, 88, 2883 (1966), and references therein for supporting kinetic data.

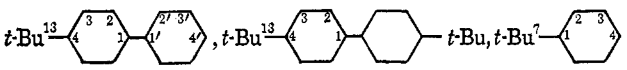
(14) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, 5, 31 (1962).

(15) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 370 ff.

Table II. Calculated and Observed Spin Densities and Energies of *t*-Butylbiphenylides and *t*-Butylbenzenides

Anion	Atom[a]	ρ_i (obsd)[b]	ρ_i (calcd) Inductive[b]	ρ_i (calcd) Heteroatom	$\epsilon_{m+1}(E_{1/2})$[b]	ϵ_{m+1} (calcd) Inductive[b]	ϵ_{m+1} (calcd) Heteroatom
4-*t*-Butylbiphenylide	2	0.10	0.109	0.112	−0.716 ± 0.035	−0.712	−0.722
	3	0.0	−0.030	−0.033			
	2′	0.09_1	0.106	0.104			
	3′	0.02_3	−0.026	−0.025			
	4′	0.20_0	0.217	0.220			
	13	0.00_4	...	0.006			
4,4′-Di-*t*-butylbiphenylide	2	0.094	0.109	0.111	−0.745 ± 0.035	−0.720	−0.740
	3	0.018	−0.030	−0.032			
	13	~0.004	...	0.007			
t-Butylbenzenide[c]	2	0.166	0.294	0.295	...	−1.000	−1.000
	3	0.166	0.294	0.294			
	4	0.062	−0.089	−0.088			
	7	<0.004	...	−0.005			

[a] Numbering system



[b] From ref 3. The spin densities for the *t*-butylbiphenyls have been refined with the aid of a computer program since the original report. The reduction potentials were measured by dc polarography with respect to a silver–silver nitrate reference electrode and then referred to a mercury pool electrode by adding 1.03 v. The $E_{1/2}$ values were confirmed in this work by ac polarography. [c] Esr coupling constants taken from ref 2.

served spin densities of the *t*-butylbiphenylides and *t*-butylbenzenide radicals and the calculated values using the inductive and heteroatom models. Also listed in Table II are the energies, $\epsilon_{m+1}(E_{1/2})$, of the lowest vacant orbital derived from polarographic data and the corresponding calculated values, ϵ_{m+1} (calcd). (See ref 3 for details.)

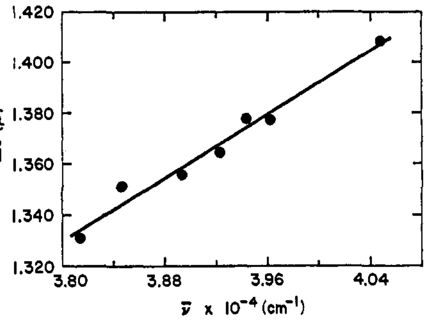


Figure 3. Calculated energy of the $\pi_m \rightarrow \pi_{m+1}$ transition *vs.* the observed frequency.

As can be seen from Table II, all results calculated with the heteroatom model are within experimental error. A better fit is obtained for the *t*-butylbenzenide spin densities by mixing in a Boltzmann population of the ϵ_{m+2} level ($\epsilon_{m+2} - \epsilon_{m+1} = -0.033\beta$).[16] At room temperature, the population of ϵ_{m+2} may amount to a few per cent depending on what value is assumed of β. A Boltzmann distribution has the effect of decreasing ρ_2 and ρ_3 while increasing ρ_4. Possibly of greater importance than the Boltzmann population, vibronic coupling of these nearly degenerate levels also increases ρ_4 at the expense of ρ_2 and ρ_3.[17]

No attempt was made to interpret the spectra of the tin compounds, since supporting esr data are lacking.

Experimental Section

The preparation of the biphenyl derivatives is described in ref 3. Ultraviolet spectra of solutions containing approximately 2 × 10^{-5} *M* solute in spectrograde heptane (Matheson Coleman and Bell) were obtained using 1-cm quartz cells and a Cary 14 spectrometer.

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(16) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, 5, 43 (1962).

(17) Reference 15, p 257.