Theoret. chim. Acta (Berl.) 12, 427—430 (1968)

Calculation of the U.V. Spectrum of *p*-Disilylbenzene

P. G. PERKINS

Department of Inorganic Chemistry, University of Strathclyde, Glasgow

Received October 22, 1968

The electronic spectrum of *p*-disilylbenzene has been calculated by the Pariser-Parr-Pople method in order to test theoretical methods of including the d_π type orbitals of silicon.

Das Elektronenspektrum des *p*-Disilylbenzols wurde nach der Pariser-Parr-Pople-Methode berechnet, um theoretische Methoden zu prüfen, die die d_π-Orbitale des Siliziums berücksichtigen.

Le spectre électronique du *p*-disilylbenzène a été calculé par la méthode de Pariser-Parr-Pople afin d'éprouver l'inclusion dans la méthode des orbitales de type d_π du silicium.

The chemical behaviour of silicon compounds is frequently explained by invoking interaction between the empty 3*d* orbitals of silicon and adjacent atoms having excess electrons (e.g. nitrogen). These electrons are thought to delocalise *via* the medium of a $d_\pi - p_\pi$ bond [1]. The classic example of this phenomenon is trisilylamine and recent calculations have supported the existence of $d_\pi - p_\pi$ bonding in this compound [2].

However we cannot readily measure the $d_\pi - p_\pi$ bond energy so this calculation alone does not provide an adequate test of the method of including the silicon d_π orbitals in calculations.

A more convenient compound for study is *p*-disilylbenzene and, for this system, we have calculated the energies of the ground and lowest excited electronic states by the Pariser-Parr-Pople method [3].

Calculational Method and Results

The application of the Pariser-Parr-Pople method to organic and organometallic systems is well established. For silyl compounds it is reasonable to assume that the 3*p* orbitals of silicon are fully involved in σ-bonding with the adjacent carbon and hydrogen atoms. In silyl benzene there are two silicon d_π-orbitals (d_{xz} and d_{yz}) which can interact with the π-molecular orbitals of the phenyl ring. Actually only one of these is important in the present instance and interacts with the π-system of benzene *via* the p_π-orbital of the nearest carbon atom. The second *d*-orbital cannot bond with the latter because of its antisymmetry with respect to reflection across the C_2 axis. It can, however, interact with the linear combinations of carbon orbitals sited on more distant atoms but this effect can reasonably be neglected.

The Si–C bond length was taken as 1.843 Å [4]. The core integral appropriate to a silicon $3d_\pi$ orbital has been calculated [5] and is 0.95 eV, whilst the one-centre $d-d$ electron repulsion integral was given the value 3.59 eV [2, 6]. Unfortunately an experimental spectrum for the simple disilyl-compound is lacking but Bock *et al.* [7] have published details of the electronic spectrum of the closely related *p*-di(trimethylsilyl)benzene. Methyl groups in these positions are well-known to be spectroscopically inert and so it is reasonable to compare directly the present calculations with the experimental spectrum. The calculated and experimental band energies are given in Table 1.

The experimental data first merit some comment. The first band in the spectrum consists of a vibrational progression with a frequency separation of 800–850 cm^{-1}. The most intense transition is the second vibronic band which occurs at 4.592 eV. The second electronic band has two vibrational components with a separation of 1,100 cm^{-1}; of these the second is the more intense.

Table 1. *Calculated and experimental energies of p-di(trimethylsilyl) benzene*

State	Energy (eV)	Symmetry	f	Experimental Spectrum	
				E (eV)	ε max.
$^1\Psi_1$	4.564	$^1B_1$	0.029	4.493	390
				4.592	480
				4.697	460
				4.802	340
$^3\Psi_1$	2.785	$^3B_1$	—	—	—
$^1\Psi_2$	5.408	$^1A_1$	0.263	5.391	14,700 (sh)
				5.485	16,850
$^3\Psi_2$	3.758	$^3A_1$	—	—	—
$^1\Psi_3$	6.302	$^1A_1$	1.010	—	—
$^3\Psi_3$	3.948	$^3A_1$	—	—	—
$^1\Psi_4$	6.405	$^1B_1$	0.926	—	—
$^3\Psi_4$	4.793	$^3B_1$	—	—	—

Now in benzene itself a transition to the $^1B_{2u}$ state is formally forbidden and appears only by virtue of vibronic coupling. It is believed [8] that the pure $^1B_{2u}$ electronic state is coupled with a single excitation of an E_{2g} vibration of the molecule. This is a bending mode which appears at 606 cm^{-1} in the vibrational spectrum, but whose coupled frequency is 520 cm^{-1}. Further coupling with multiple excitations of the A_{1g} ring breathing frequency (923 cm^{-1}) are also manifest.

The set of one-electron levels for disilylbenzene are shown in Fig. 1 and the principal configurations composing the excited states are given in Table 2. The energy levels most affected by the inclusion of the silicon *d* orbitals are the three antibonding orbitals, ψ_{-1}, ψ_{-3}, and ψ_{-4}. Hence states incorporating configurations involving these three orbitals will be shifted with respect to the corresponding benzene states and will be of charge-transfer type. The *bonding* orbitals of benzene, on the other hand, are almost unaffected by the silicon atoms.

The agreement between the observed and calculated electronic spectrum is very good. The calculations show that the first excited state of *p*-disilylbenzene has $^1B_1$ symmetry and hence a transition to it is polarised perpendicular to the long axis of the molecule. It correlates with the $^1B_{2u}$ band in benzene and with the first band in the polarised absorption spectrum of the related compound *p*-dimethoxybenzene [9]. Because this state includes a large proportion of the configuration ψ_1^{-1} (Table 2) it will be red-shifted with respect to the benzene $^1B_{2u}$ band. The ψ_1^{-1} configuration brings about charge-transfer from the ring to *both* silicon atoms and hence the change in dipole moment and the overall low configurational transition moment is due only to the admixed configuration ψ_2^{-2}.

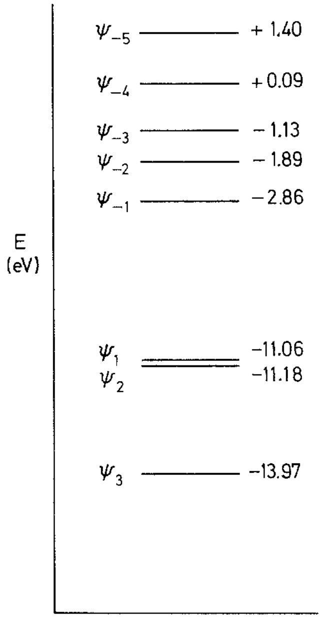

Fig. 1. Orbital energy levels for *p*-disilylbenzene

The 0→0 transition to the first excited state is allowed but in the experimental spectrum coupling with a vibration of frequency 800–850 cm^{-1} is observed. This is almost certainly essentially the same vibration as the totally symmetric species which couples with the $^1B_{2u}$ state in benzene and involves changes in the C–C bond lengths. Its lowered frequency is readily accountable because four of the π bond orders of benzene (0.667) are decreased by $2\frac{1}{2}$ % whilst the remaining two are increased by only 1 % on substitution of the ring by silyl groups.

Table 2. *Structure of the lowest four excited states of p-di(trimethylsilyl) benzene*

State	Mixing coefficients	
$^1\Psi_1$	$0.80\,\psi_1^{-1}$	$0.56\,\psi_2^{-2}$
$^1\Psi_2$	$0.38\,\psi_1^{-2}$	$0.92\,\psi_2^{-1}$
$^1\Psi_3$	$0.92\,\psi_1^{-2}$	$0.38\,\psi_2^{-1}$
$^1\Psi_4$	$0.58\,\psi_1^{-1}$	$0.82\,\psi_2^{-2}$

Although the second vibrational component has the greatest intensity it is unlikely to be the 0→0 transition, because this would mean that the first is a "hot" band. The frequency of 800 cm^{-1} is rather too large for this possibility and it may reasonably be assumed that the first vibrational component is the $0 \rightarrow 0$ band.

The second state, ${}^1\Psi_2(A_1)$, has only weak correspondence with the ${}^1B_{1u}$ state of benzene and the preponderant configuration in this state has charge-transfer character. The intensity is calculated to be some ten times greater than that of the first ${}^1B_1$ state and this is borne out by experiment. There are only two observed sub-bands which are separated by 750 cm^{-1}. The vibrational separation in this case does not correspond to the same vibration which characterises the ${}^1B_{1u}$ band of benzene. There is no mode involving the C–C links in benzene near to this value and it seems likely to be a C–H frequency. This could be of any symmetry since the $0 \rightarrow 0$ transition is already allowed.

The third and fourth excited states of *p*-disilylbenzene correspond fairly closely to the two components of the doubly degenerate ${}^1E_{1u}$ band of benzene. These states have apparently not yet been observed.

In conclusion it seems that a satisfactory account of the experimental electronic spectrum of this compound is produced by including the $3d_\pi$ orbitals of the two silicon atoms in the manner previously suggested [2].

In the ground state, the charge accumulating in each of the silicon d_π orbitals amounts to only 0.02 electrons. This is drawn from the positions in the ring *ortho* to each silicon atom. Thus it seems that the limited perturbation imposed by two silicon atoms on benzene can have dramatic effects on its U.V. spectrum.

References

1. Eaborn, C.: Organosilicon compounds. London: Butterworth 1960; Ebsworth, E. A. V.: Volatile silicon compounds. London: Oxford University Press 1963.
2. Perkins, P. G.: Chem. Comm. **1967**, 268
3. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466 (1953); Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
4. Interatomic distances in molecules and ions. Chem. Soc. (London) Special Publication No. **11** (1958).
5. Armstrong, D. R., and P. G. Perkins: Theoret. chim. Acta (Berl.) **5**, 69 (1966).
6. Zauli, C.: Boll. Sci. Fac. Chim. Ind. Bologna **17**, 74 (1957).
7. Alt, H., H. Bock, F. Gerson, and J. Heinzer: Angew. Chem. **6**, 941 (1967).
8. Murrell, J. N.: The theory of the electronic spectra of organic molecules, p. 129. London: Methuen 1963.
9. Albrecht, A. C., and W. T. Simpson: J. chem. Physics **23**, 1480 (1955).

Professor P. G. Perkins
Department of Inorganic Chemistry
University of Strathclyde
Glasgow, C. 1./Scotland