Model Calculations on Spiro-compounds with Silicon and Phosphorus as Central Atoms

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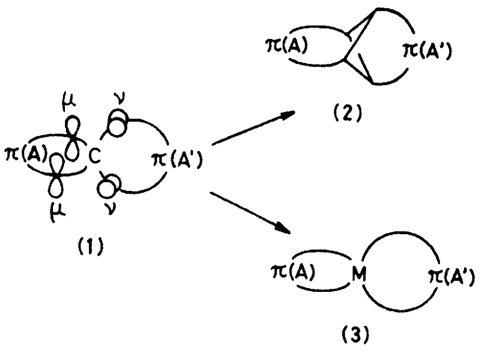
Spiro-compounds with silicon and phosphorus as central atoms have been studied using semiempirical molecular orbital calculations. The inclusion of 3*d* orbitals causes a considerable increase of the split between the antibonding b_1 and a_2 orbitals.

THE special interaction (spiro-conjugation) of two mutually perpendicular π systems which are connected by a central carbon atom [*e.g.* in (1) of Scheme 1] is a topic of wide current interest.[1-3] Using perturbation theory it can be shown that this spiro-conjugation is most important in those systems in which the π fragments (A) and (A′) of (1) are identical (*i.e.* D_{2d} symmetry). Within these conditions the total representation of π orbitals factorizes into three sets of A_2, B_1, and E symmetry. Those π orbitals with an even † number of nodal planes split into two symmetry adapted linear combinations of the irreducible representations A_2 and B_1. The π orbitals with an uneven † number of nodes remain degenerate and belong to the irreducible representation E. The energy difference of the orbitals a_2 and b_1 is due to the spatial interaction between the centres μ and ν in (1) (Scheme 1). The b_1 linear combination is bonding (in phase), the a_2 linear combination antibonding (out of phase).

Recently we have pointed out that the interaction of the two perpendicular π systems, π(A) and π(A′), can be influenced considerably on replacement of the central carbon atom in (1) by a four-membered ring as in the tricyclic system (2).[4] The four-membered ring acts like a relay and replaces the spiro-interaction present in (1) by a through bond interaction in (2).[4] Crucial for the relay effect[4] is the interaction of the a_2 and b_1 Walsh orbitals[5] of the four-membered ring with the corresponding linear combinations of the π units (see also Table 1).

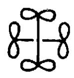
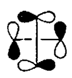
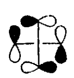
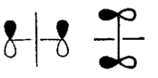
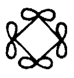
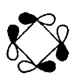
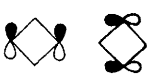
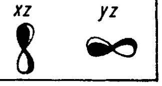


SCHEME 1

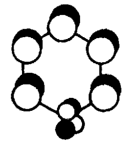
In this paper we discuss another relay system, which is provided by a central atom M with low lying empty 3*d* orbitals as indicated in (3; M = Si or P$^+$) of Scheme 1. In Table 1 a comparison is made of the irreducible representations of the two mutually perpendicular π systems of (1), the Walsh orbitals of the four-membered ring[5] in (2), and of the five 3*d* orbitals assuming the point group D_{2d}. It is evident from Table 1 that the split between a_2 and b_1 can be influenced by replacing the central carbon atom in (1) by a centre possessing empty or filled 3*d* orbitals.[6]

TABLE 1

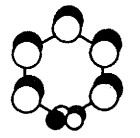
Comparison between the irreducible representations of two mutually perpendicular π systems, cyclobutane, and 3*d* orbitals in the point group D_{2d}

	A_1	A_2	B_1	B_2	E
					
					
3*d*	z^2 		*xy* 	x^2-y^2 	*xz* *yz* 

Embedding a centre with available 3*d* orbitals into a p_π system allows two possibilities for p_π–d_π conjugation, leading to a Hückel-type[7] and a Möbius-type[7,8] system. It is interesting to note that in a spiro-arrangement of type (3) the b_1 linear combination interacts with $3d_{xy}$ to form a Möbius type π-system. On the other hand the interaction between the *e* linear combination and the $3d_{xz}$ or $3d_{yz}$ (see Table 1) orbital creates a Hückel type π-system. This is indicated schematically.



Hückel system



Möbius system

Calculations.—As a measure of the interaction between the two π-systems in (1) or (3) the energy difference between the a_2 and b_1 orbitals is used. To derive the molecular orbital energies we carried out semiempirical calculations on some model compounds derived from (4).

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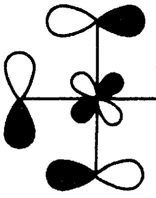
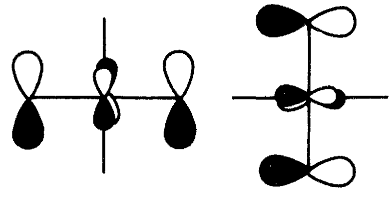
† It should be noted that π-orbitals possess a nodal plane to begin with.

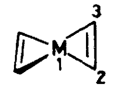
These model compounds are for n even in (4), systems (5) and (6), and for n odd in (4), systems (8) and (9). System (7) represents an isomer of (6) insofar as the endocyclic *double* bonds are replaced by *exo*-methylene groups.


b_1

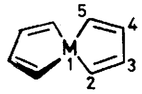

e

In the case of M = P^+ or M = P^- there already exists a qualitative discussion of the influence of $3d$ orbital participation for the systems (5c), (6c), (8c), and (9c).[9] In the derived stabilization schemes, however, there exists no consideration of the strong destabilizing π–σ through-bond interaction within the degenerate E representation. Therefore the results of our model calculations on (5) and (9) will put these findings on a more quantitative basis and lead to some new insight.

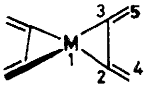
(4)



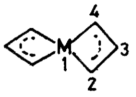
(5) a; M = C
b; M = Si
c; M = P^+



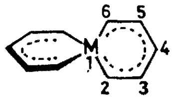
(6) a; M = C
b; M = Si
c M = P^+



(7) a; M = C
b; M = Si
c; M = P^+



(8) a; M = C
b; M = Si
c; M = P^+
d; M = P^-



(9) a; M = C
b; M = Si
c; M = P^+

For the model compounds listed in Table 2 we minimized the total energy of the system with respect to the geometrical variables using the MINDO/3 method.[10] The resulting structures together with the heat of formation are shown in Table 2. To probe the influence of $3d$ participation we first develop the bonding scheme without $3d$ orbitals on the Si or P atom. Then the calculations are repeated including $3d$ orbitals with a $3d$ exponent and an ionization potential which allows moderate interaction. The calculation procedure used for such a comparison was the extended Hückel (EH)[11] method. The geometrical parameters used are those listed in Table 2.

TABLE 2

Calculated heats of formation and molecular geometries of (5)—(8)

Molecule	H_f/kJ mol^{-1}	Geometry (bond lengths in pm; bond angles in degrees)
(5b)	266.0	SiC 180.7; C(2)C(3) 134.1; C(2)SiC(3) 43.6; SiC(2)C(3) 68.3
(5c)	249.43	PC 179.4; C(2)C(3) 132.8; C(2)PC(3) 43.5; PC(2)C(3) 68.25
(6b)	141.4	SiC 188.0; C(2)C(3) 135.4; C(3)C(4) 148.7; C(2)SiC(5) 90.6; SiC(2)C(3) 108.7; C(2)C(3)C(4) 116.0
(6c)	228.43	PC 184.5; C(2)C(3) 136.3; C(3)C(4) 148.7; C(2)PC(5) 89.1; PC(2)C(3) 111.84; C(2)C(3)C(4) 113.6
(7b)	306.3	SiC(2) 182.7; C(2)C(3) 149.6; C(2)C(4) 132.4; C(2)SiC(3) 48.3; SiC(2)C(3) 65.8; C(4)C(2)C(3) 140.8
(8d)	123.13 [a]	PC(2) 182.1; C(2)C(3) 141.0; C(2)PC(4) 74.5; PC(2)C(3) 91.3; C(2)C(3)C(4) 102.9
(9c)	219.1 [b]	PC(2) 183.3; C(2)C(3) 139.3; C(3)C(4) 142.9; C(2)PC(6) 100.0; PC(2)C(3) 124.0; C(2)C(3)C(4) 124.5; C(3)C(4)-C(5) 123.1

[a] Minimization was carried out for (8d) since no convergence could be obtained for (8b and c). [b] Optimized geometry and ΔH_f correspond to a triplet ground state.

Results for (5)—(7).—The most simple but unknown examples are the spiropentadiene derivatives (5). In Figure 1 we have shown the π molecular orbitals of (5b) as a representative example without (left) and with (right) $3d$ participation on the central atom. As in its carbon analogue spiro[2.2]pentadiene (5a) the degenerate

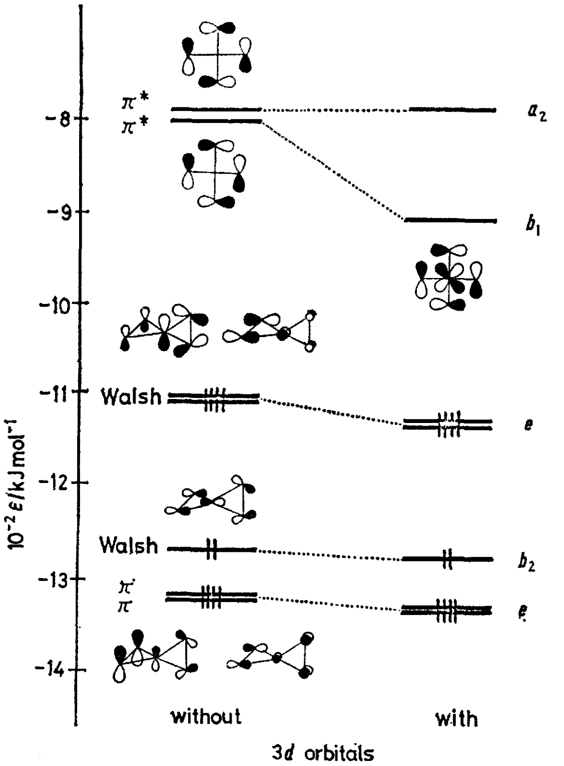


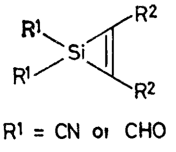
FIGURE 1 Highest occupied and lowest unoccupied molecular orbitals of silaspiro[2.2]pentadiene (5b) without (left) and with (right) $3d$ orbitals on the silicon centre according to an EH calculation

highest occupied molecular orbital of (5b and c) is a linear combination of the e (π) and e (Walsh) orbitals of the two moieties. However, in contrast to (5a), the σ component dominates in (5b and c).

As anticipated spiro-conjugation yields only a minor split between $1b_1$ and $1a_2$ for (5b and c) (see Table 3). The reduced split, calculated for (5b and c) compared with (5a) is due to the large, predicted M–C bond length in (5b) (1.81 Å) and (5c) (1.79 Å) compared with 1.49 Å computed for (5a).[4]

To date neither derivatives of (5b or c) nor derivatives of phosphacyclopropene are known. Only recently derivatives of silacyclopropene [12] and silacyclopropane [13] have been isolated. Based on semiempirical calculations it was suggested [14] that d-hyperconjugation in these three-membered ring systems contributes significantly to the strengthening of the Si–C bonds in the silacyclopropane system.

Another point which might contribute to the instability of the unknown systems just mentioned is the low energy of its highest occupied molecular orbitals (HOMOs), and to demonstrate this we have compared the orbital energies and the coefficients of the corresponding wave functions of cyclopropane and cyclopropene on one side and silacyclopropane and silacyclopropene on the other (Figure 2). These results reveal a destabilization of the two highest occupied molecular orbitals when compared with the corresponding carbon analogues. Additionally the wave function is changed in such a way that the coefficients of the atomic orbital at the Si centres is increased and the overlap population between the Si–C bonds decreased (Figure 2). The high-lying HOMOs suggest an increased reactivity towards electrophiles. To stabilize the system it is necessary to stabilize the HOMO and to increase the Si–C bond order, and a possible way in which to achieve the latter has been proposed elsewhere.[13] A decrease in the HOMO can be obtained by attaching electron-accepting groups [CN, CHO, $Si(CH_3)_3$] at the silicon or carbon centres as indicated. This, however, leads to a decrease of the Si–C bond order.[14] Another possibility will be demonstrated later in case of (13).



R^1 = CN or CHO
R^2 = $Si(CH_3)_3$

The results obtained with the EH and MINDO/3 method by calculating (6) and (7) are very similar to those discussed for (5). The spiro-conjugation due to the spacial overlap of the butadiene fragments is much smaller than for the corresponding hydrocarbons (see Table 3). The inclusion of 3d orbitals [11] on the Si and P centre in (6b and c) and (7b and c) leads to a considerable stabilization of the $b_1(\pi)$ orbitals. The interaction between $b_1(d_{xy})$ and $b_1(\pi^*)$ is much stronger than between $b_1(d_{xy})$ and $b_1(\pi)$ for energetic reasons. In all cases, a stabilization of the b_1 levels results, and the energy difference $|b_1 - a_1|$ is increased. In Table 3 the calculated energy differences between the a_2 and b_1 orbitals of (5)—(7) are compared with the corresponding values derived for the carbocyclic spiro-compounds.[4]

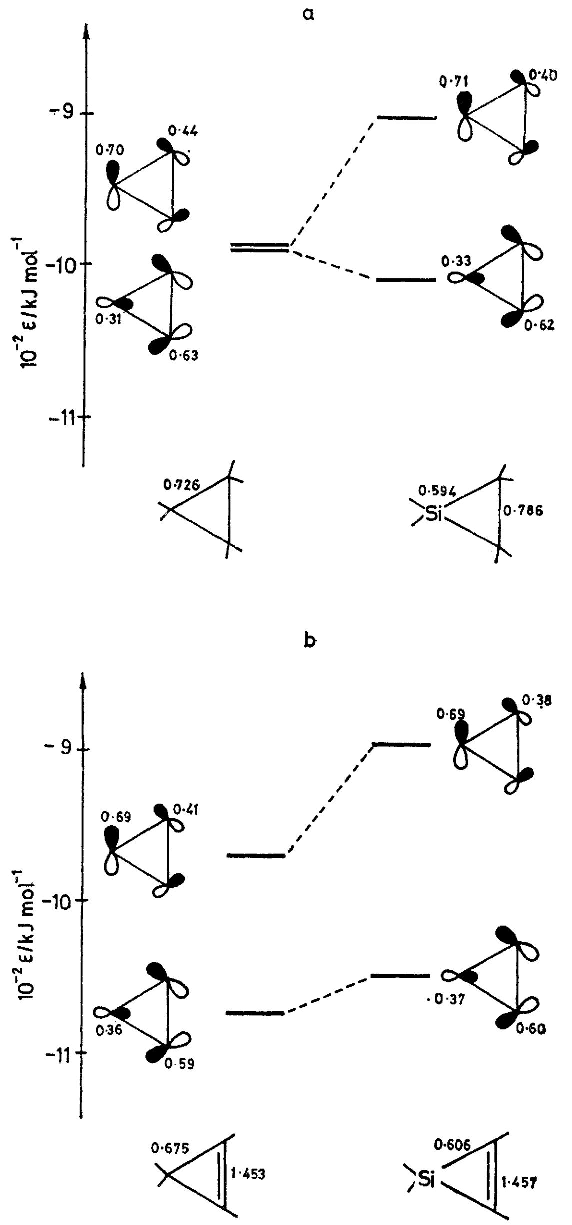


FIGURE 2 a, Orbital energies and wave functions (MINDO/3) of the highest occupied molecular orbitals and reduced overlap populations (EH) of cyclopropane and silacyclopropane. b, Orbital energies and wave functions (MINDO/3) of the highest occupied molecular orbitals and reduced overlap populations (EH) of cyclopropene and silacyclopropene

The predicted influence on the molecular orbitals by invoking d orbitals as a relay can be traced back to differences in the charge distribution and overlap population. As an example we will compare the calculated net charges and reduced overlap populations for

TABLE 3

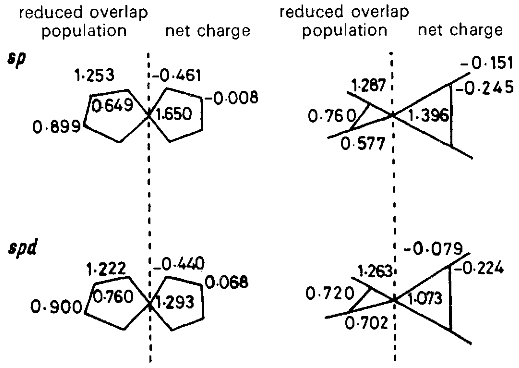
Comparison between the calculated orbital differences of (5)—(7) for the MINDO/3 and EH models. The energy differences are given in kJ mol^{-1}

Compound	Energy difference of orbitals	EH (*sp*)	EH (*spd*)	MINDO/3
(5a)	$1b_1 - 1a_2$	31		14
(5b)		6	104	3
(5c)		6	381	3
(6a)	$1b_2 - 1a_2$	53		61
	$2b_1 - 2a_2$	58		24
(6b)	$1b_1 - 1a_2$	14	26	14
	$2b_1 - 2a_2$	15	77	6
(6c)	$1b_1 - 1a_2$	46	109	15
	$2b_1 - 2a_2$	75	333	6
(7a)	$1b_1 - 1a_2$	8		8
	$2b_1 - 2a_2$	30		10
(7b)	$1b_1 - 1a_2$	1	14	2
	$2b_1 - 2a_2$	5	81	2
(7c)	$1b_1 - 1b_2$	1	21	*a*
	$2b_1 - 2a_2$	6	157	*a*

[a] No SFC convergence could be achieved.

(6b) and (7b) obtained without and with $3d$ participation. The results are shown in Scheme 2. The inclusion of $3d$ orbitals on the central atom yields a flow of negative charge from the π-system to the heteroatom, and to a less pronounced bond alternation. In the model system (7b) with the exocyclic π-fragments, there is also a considerable drift of charge from the high lying Walsh orbital to the $3d$-acceptor levels of the central atom.

These results can be analysed by applying simple Rayleigh–Schrödinger perturbation theory for the non-degenerate case within the EH formalism.[15] We consider in our example the interaction of levels of two systems, the π-system and the $3d$ levels, each with its characteristic set of orbitals. The unperturbed wave functions, ψ_i^0, and energy levels, ε_i^0, are known from an EH calculation without inclusion of $3d$ orbitals at the linking centre. The perturbation is defined by the matrix element $\langle b_1(\pi)/3d_{xy}\rangle$ between the b_1 linear combination of the perpendicular π systems and the $3d$ orbital of the central atom. The perturbed wave function is given by equation (1), in which the mixing



SCHEME 2

$$\psi_i = \psi_i^0 + \sum_{\neq i} C_{ji}\,\psi_j^0 \qquad (1)$$

coefficients C_{ji} can be expanded into a sum of first- and second-order contributions [equation (2)]. The higher

$$C_{ki} = C_{ki}' + C_{ki}'' \qquad (2)$$

order contributions are neglected. Analogously the energy of a perturbed level is given by equation (3).

$$\varepsilon_i = \varepsilon_i^0 + \varepsilon_i' + \varepsilon_i'' \qquad (3)$$

The explicit expressions for the first- and second-order corrections of the energy levels and coefficients including the group overlap integral are given in the literature.[15]

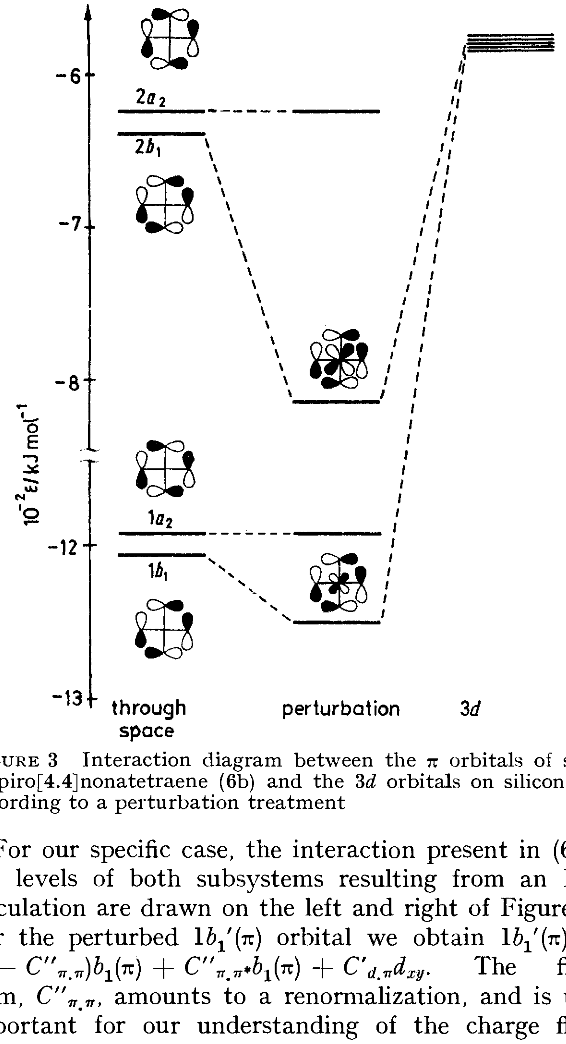
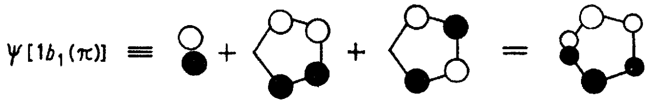


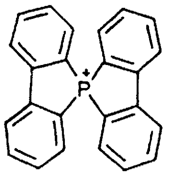
FIGURE 3 Interaction diagram between the π orbitals of silaspiro[4.4]nonatetraene (6b) and the $3d$ orbitals on silicon according to a perturbation treatment

For our specific case, the interaction present in (6b), the levels of both subsystems resulting from an EH calculation are drawn on the left and right of Figure 3. For the perturbed $1b_1'(\pi)$ orbital we obtain $1b_1'(\pi) = (1 - C''_{\pi,\pi})b_1(\pi) + C''_{\pi,\pi^*}b_1(\pi) + C'_{d,\pi}d_{xy}$. The first term, $C''_{\pi,\pi}$, amounts to a renormalization, and is unimportant for our understanding of the charge flow obtained. The second term, C''_{π,π^*}, is crucial, and describes the mixture between $1b_1(\pi)$ and $2b_1(\pi)$ under the influence of the perturbation ($3d_{xy}$). The third term, $C'_{\pi,\pi}$, is the first order correction term, and corresponds to the through-bond interaction between π and d. By adopting the following values for the group overlap integrals: $\langle 1b_1|3d\rangle$ 0.470 and $\langle 2b_1|3d\rangle$ 0.238, and the basis orbital energies given in Figure 3, we obtain the following values for the mixing coefficients: $C'_{d,\pi}$ 0.268, $C''_{\pi,\pi}$ −0.162, and C''_{π,π^*} 0.016. Although the last term has no great magnitude on an absolute scale, there is considerable influence on the bonding $b_1(\pi)$ combination by this second-order mixing. To obtain the resulting wave function of $1b_1'(\pi)$ the wave functions of $3d_{xy}$ and $2b_1(\pi^*)$ must be mixed with $1b_1(\pi)$ in a bonding fashion. The result is shown in Scheme 3. The coefficient at the central atom and at the adjacent carbon atom is enlarged while the coefficients at positions 3 and 4 have been reduced. This establishes that the negative charge transferred to the central atom stems mainly from positions 3 and 4. This polarization of the $b_1(\pi)$ combination also explains the decrease of the bond alternation under the influence of the $3d$ orbitals.



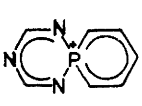
SCHEME 3

We have given a more detailed discussion to our results on (6b and c) since a derivative of (6c), the cation (10), has been prepared.[16]



(10)

Results for (8) *and* (9).—Both model systems formally represent biradicals. In (8) two allyl fragments and in (9) two pentadienyl fragments are held together perpendicularly by a central atom M. Of special interest are those systems [*e.g.* (8)] in which the HOMO and LUMO belong to a_1 or b_2. For these systems a stabilization of the singlet ground state by spiro-conjugation is predicted.[2] As a representative example we show the MO scheme for (8c) in Figure 4. In this case the inclusion of $3d$ basis functions on the central atom cause a considerable increase in the splitting between $1b_1$ and $1a_2$.[*] In case of (9b and c) the splitting of $2b_1$ and $2a_2$ is also considerable.[†] However, the highest occupied MO $7e$ remains only half filled. Attempts to remove the degeneracy by perturbing one ring system as exemplified in (11) and (12) leads to a split of *ca.* 1 eV without, and of *ca.* 0.5 eV with the inclusion of $3d$ orbitals on the central atom.



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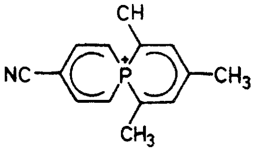
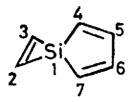


(12)

Examples of Lower Symmetry.—From the possible examples of compounds belonging to point group C_{2v} we will discuss silaspiro[2.4]heptatriene (13) and 1,1-butadienyl-λ^5-phosphorin (14). Our research on spiro[2.4]heptatriene[17] revealed that there is no essential interaction between $a_2(\pi)$ of the five-membered ring and between $a_2(\pi^*)$ of the three-membered ring. This raised the question whether or not the interaction between the two subsystems could be made possible under the influence of $3d$ orbital participation at the central atom. The inclusion of $3d$ orbitals on the Si centre in (13) causes a reduction of positive charge at the heteroatom, but the effect is relatively small (see below). No increase of charge flow in (13) could be achieved by attaching electron-donating groups at the five-membered ring and electron-attractive groups at the three-membered ring.



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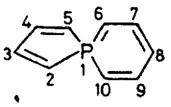
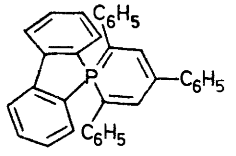


(14)



(15)

Compound (14) was chosen since a derivative, (15), has been prepared recently;[18] our calculations on (14) predict that the pentadienyl unit has a partial negative net charge (see below) while in the butadiene part of the charge is computed to be balanced. In contrast to (13), (14) shows a considerable response upon the inclusion of $3d$ orbitals on the central atom. A transfer of 0.58 and 0.33 e of the pentadienyl and butadienyl unit respectively to the centre is predicted. In Table 4 the predicted geometrical parameters of (13) and (14) are listed.

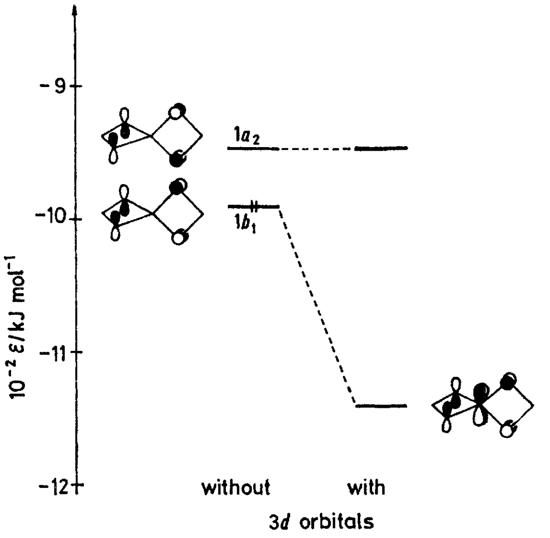


FIGURE 4 Highest occupied and lowest unoccupied molecular orbitals of (8c) without (left) and with (right) $3d$ orbitals on phosphorus according to an EH calculation

Experimental Evidence for Interactions via Si *or* P *Atoms in Spiro-compounds.*—Photoelectron spectroscopic investigations[19] on 9,9′-spirobi-9-silafluorene (16) have shown that the energy difference between the relevant π levels is *ca.* 60% smaller than in the corresponding

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[*] The split $|1b_1–1a_2|$ calculated (EH) for (8b) amounts to 55 without and 118 kJ mol^{-1} with $3d$ participation. The corresponding results for (8c) are 47 and 198 kJ mol^{-1}.

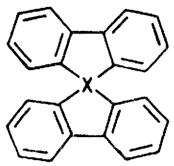
[†] The calculated split for (9c) without $3d$ participation is 40 ($1b_2 - 1a_2$) and 113 kJ mol^{-1} ($2b_1 - 2a_2$) respectively. The $3d$ orbitals increase these differences to 77 and 296 kJ mol^{-1}.

TABLE 4

Calculated heats of formation and molecular geometries of (13) and (14)

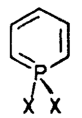
Molecule	H_f/kJ mol^{-1}	Geometry (bond lengths in pm, bond angles in degrees)
(13)	44.06	SiC(2) 183.4; C(2)C(3) 132.2; SiC(4) 186.0; C(5)C(6) 148.6; C(2)SiC(3) 92.2; SiC(2)C(3) 68.9; C(4)SiC(7) 92.2; SiC(4)C(5) 107.4; C(4)C(5)-C(6) 116.1
(14)	94.95	PC(2) 186.9; C(2)C(3) 135.6; C(3)-C(4) 148.4; PC(6) 179.2; C(6)C(7) 139.7; C(7)C(8) 141.3; P(2)PC(5) 87.0; PC(2)C(3) 112.9; C(2)C(3)-C(4) 113.6; C(6)PC(10) 101.8; PC(6)C(7) 122.5; C(6)C(7)C(8) 126.1; C(7)C(8)C(9) 121.0

carbon compound (17). This result is in accord with the assumption that 'interaction through space' (spiro-conjugation) is dominant, and, that any $3d$ participation is negligible. E.s.r. spectroscopic investigations on (16) and (17) of the lowest triplet state [20] are considered to give contradictory results. In the case of (17) there is a strong temperature dependence of the e.s.r. spectrum in contrast to (16). The observed spectra for (17) are compatible with the assumption that the triplet exciton is localized in one of the biphenylene moieties at 18 K. At 77 K the exciton, however, transfers rapidly between the two parts. In the case of (16) the triplet exciton remains localized in the whole temperature range measured. This difference has been attributed to the $3d$ orbitals on the spiro centre, but this is an unsatisfactory explanation.

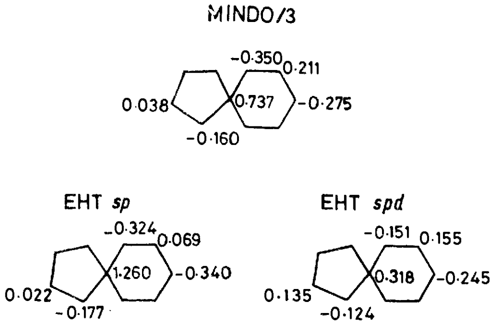


(16) X = Si

(17) X = C



(18) X = Cl, F, OCH_3, $N(C_2H_5)_2$



SCHEME 4

Photoelectron spectroscopic investigations on λ^5-phosphorins (18) have been rationalized [21] on the basis of CNDO/S calculations with a $3d$ orbital basis on the P atom. No interaction between the π system of the ring and the lone pairs on X has been reported indicating spiro-conjugation with strong $3d$ participation.

The experiments specified so far provide no clear evidence for $3d$ participation in systems related to (4). Judging from our calculations, the study of higher excited states seems to be the most promising, since the influence of $3d$ participation on the ground state is found to be small.

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