Theoret. Chim. Acta (Berl.) 34, 31—38 (1974)

The UHF-CNDO/2 Study of Tetra-Atomic Radicals Containing Silicon and Phosphorus

Yuri I. Gorlov and Ivan I. Ukrainsky
Institute for Theoretical Physics, Academy of Sciences of the Ukrainian SSR, Kiev, USSR

Vladimir V. Penkovsky
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, USSR

Received October 13, 1973/January 14, 1974

The UHF-CNDO/2 calculations have been performed for several radicals containing C, Si or P. The equilibrium geometries found by the minimization of the total energies and calculated spin densities are compared with results from ESR experiments and INDO calculations. The electronic structure of the radicals is discussed for their equilibrium geometries.

Key words: Radicals containing silicon and phosphorus – Spin density – Equilibrium geometry of tetra-atomic radicals

Introduction

Silicon-centered and phosphorus-centered free radicals play important roles in various chemical reactions. For this reason, their reactivity is studied intensively. The main factor influencing it seems to be a high spin density on the central atom probably determined in turn by the hybridization of this atom. In recent years a number of unstable free radicals which contain silicon or phosphorus have been identified by ESR spectroscopy (see e.g. [1–5]), and the relation between the spin density distribution and the character of hybridization of silicon or phosphorus in radicals has been discussed at length [1, 3, 5]. To consider this problem more thoroughly, one should compare the ESR data with the geometries of radicals. However, for most silicon- and phosphorus-containing radicals the structure either is not quite precisely determined or is unknown at all. Therefore, a theoretical investigation of their equilibrium geometries is of interest.

In the present paper the geometries and the electronic structure of tetra-atomic inorganic radicals SiH_3, SiH_2F, $SiHF_2$, SiF_3 and PH_3^+ as well as carbon radicals CH_3 and CHF_2 have been studied by the CNDO method. The severe approximations of this method of course influence some results of calculations negatively. However, the CNDO method has shown its best side in the conformational analysis of some molecules [6, 7]. Therefore, one may believe that the principal regularities of changes in the electronic and spatial structure in the row of similar radicals are described by the CNDO method in a correct way.

Method

For the calculation of molecular integrals we have used the standard CNDO/2 approximation [8, 9]. The self-consistent solutions were obtained in the framework of the unrestricted Hartree-Fock (UHF) method [10]. Besides that, spin populations of orbitals have been calculated on the basis of the results obtained for the doublet component of the UHF wave function. In order to project the UHF wave function we used the projection operator method supposed by Löwdin [11].

To reach the minimum of the total energy, we varied the energy functional with respect to coordinates of atomic nuclei. To perform this variation of a nonlinear many-variable function, we have applied the minimization procedure called usually a direct search of extrema [12].

Variations of nuclei coordinates had been restricted by radical symmetry requirements. In the case the radicals of the AB_3 form symmetry of the C_{3v} group has been assumed due to the ESR data for SiH_3 [2] and SiF_3 [5] and the IR spectrum of SiF_3 [13]. As a consequence, the total energies of AB_3 radicals have been treated as functions of two variables: the AB bond length and the BAB valence bond angle. In the case ABC_2 radicals the C_{2v} symmetry has been assumed so that their total energies have been considered as functions of the following variables: the AB and AC bond lengths and the BAC and CAC valence bond angles.

To test our method we have calculated equilibrium geometries of CH_3 and CHF_2. The corresponding results can be found in Table 1.

Table 1. Total energy and geometrical structure of the MH_nF_{3-n} radicals

Radical	Energy (a.u.)	Calculated equilibrium geometries				Other data
		R_{MH}, Å	R_{MF}, Å	∠HMH (FMF)	∠HMF	∠HMH (FMF)
CH_3	− 9.1174	1.103	—	120°	—	119°42′[a]
CHF_2	−63.1372	1.112	1.322	111°	117°30′	109°[a]
SiH_3	− 6.2573	1.612	—	106°24′	—	112°50′[b]
SiH_2F	−33.1914	1.612	1.861	111°40′	105°	
$SiHF_2$	−60.1200	1.673	1.858	149°6′	104°20′	
SiF_3	−87.0399	—	1.865	108°	—	109° ± 2°[c]
PH_3^+	− 8.6994	1.523	—	109°27′	—	114°[b] 112–120°[d]

[a] INDO calculation, Ref. [16]; in CHF_2 ∠ HCF = 116°.

[b] Calculated from the hyperfine splitting constants, Ref. [3], using Eq. (1).

[c] IR spectroscopy data from Ref. [13].

[d] Values from Ref. [21]. See text.

Structure of Radicals

The theory of the dependence of the valence bond angles in the radicals of AB_3 form upon the electronegativities of A and B is considered in detail elsewhere [1]. According to Walsh's correlation diagram, the valence bond angle should increase with increasing electronegativity of A and decrease with increasing electronegativity of B. The relation between the valence bond angle φ and the hybridization parameter of the atom $\lambda = Cp/Cs$ is given by the Coulson equation:

$$\varphi = \arccos\left[\frac{1}{2}\left(\frac{3}{2\lambda^2+3} - 1\right)\right]. \tag{1}$$

Evidently $\lambda = (\varrho_p/\varrho_s)^{1/2}$ where $\varrho_{p,s}$ is the s or p orbital spin density on the atom A. Thus the λ value can be found empirically if the hyperfine splitting values in the ESR spectrum of an AB_3 radical are known.

These statements are shown to be valid for the methyl and trifluoromethyl radicals. The first one is planar ($\varphi = 120°$), the second one is pyramidal with $\varphi = 111.1°$ [14]. Quantum-chemical calculations of CH_3 and CF_3, both by the SCF MO LCAO *ab initio* method [15] and by the UHF–INDO method [16], give a far-reaching coincidence with the values cited above. Symons *et al.* [3] used Eq. (1) widely for evaluations of φ in radicals where A is a second row element. This manner is already doubtful because the above theory completely ignores a possible participation of the 3d orbitals in bonding.

Equation (1) may be applied only to the radicals with C_{3v} symmetry. However, qualitative conclusions about the dependence of geometry of an AB_3 radical on the electronegativity of B are also valid for CH_2F and CHF_2, which, according to the ESR data and the INDO calculation [16], become more non-planar with the increasing number of fluorine atoms, but the inversion barrier of CH_2F is very small – by 45 times less than that for CF_3 [15].

The problem of interatomic bond lengths R_{AB} in the AB_3 type radicals was not considered systematically. Quantum-mechanical optimization of the φ value [15, 16] has been made under the assumption that the R_{AB} values are the same as those in the parent neutral molecules.

The results of our calculation of total energies, equilibrium bond lengths and bond angles for tetra-atomic radicals are collected in Table 1. All the interatomic distances are larger than those in neutral molecules. In the case of the C–H bond this difference is small, but for the Si–F bond it is ca. 0.3 Å as compared with the values of 1.55 Å in SiF_4 and 1.565 Å in $SiHF_3$ [17]. This result seems to reflect the weakening of bonds in radicals as compared with the neutral molecules. The lengthening of the Si–H bond in $SiHF_2$ is especially noticeable. Consequently, our calculations predict weakening of this bond as compared with SiH_3 and SiH_2F. The experimental Si–H bonds lengths in the $SiHF_3$ and SiH_3F molecules are practically equal: 1.455 Å and 1.460 Å [17], respectively.

The optimized valence bond angle in SiH_3 quoted in Table 1 is much smaller than that obtained by Begum *et al.* [3] using Eq. (1). Moreover, our calculations have shown that this value is smaller than the tetrahedral angle, whereas according to [3] it should be larger than the tetrahedral angle. The optimization of the geometry of the CH_3 radical in the CNDO/2 approximation made by us for comparison gives a correct results, so the discrepancy of our data with those from [3] cannot be explained by the shortcomings of this method. The INDO optimization of the geometry of SiH_3 [18] gives the value of 110° for the HSiH angle which is somewhat closer to the results of Begum *et al.* [3]. However, by the analogy with the Gillespie-Nyholm rule [19], the equilibrium structure of SiH_3 obtained by us may be more probable. From the standpoint of the electronegativity difference factor, the increase of the valence bond angle in SiF_3 comparing with SiH_3 is alsolutely unexplainable. On the other hand, the numerical value of $\varphi = 108°$ (that is, less than the tetrahedral one), obtained by us, is in agreement with the ESR spectrum of SiF_3 [5], with the structure of SiF_3 obtained by a theoretical analysis of its IR spectrum [13], with the Gillespie-Nyholm rule (the SiF_4 molecule is a tetrahedron [17]) and even with the conception of the role of electronegativity of a central atom when compared with the CF_3 radical. Using the last argument Pauling [20] has predicted that the FMF angle in the trifluorides of silicon, germanium and tin should be somewhat less than the tetrahedral value. We believe the increase of the φ angle in SiF_3 as compared with SiH_3 may be explained by two reasons. The first one is the electrostatic repulsion of the fluorine atoms bearing comparatively large charges (see Table 2). The second one is the increase of the populations of the silicon $3d$ orbitals in SiF_3 as compared with SiH_3 and their more considerable donation into the Si–F bonding which corresponds to the $sp^m d^n$ hybridization of the silicon atom.

In SiH_2F and $SiHF_2$ the valence bond angles formed by the bonds of two similar atoms with the silicon atom are much above those in symmetric radicals. An overall tendency of the increase in the pyramidal shape of radicals with increasing electronegativity of substituents leads to a corresponding decrease of the HSiF angles. Both tendencies were pointed out earlier in the INDO-optimized structure of CH_2F [16]. However, our calculation of CHF_2 which agrees with the data of [16] (Table 1), leads to the conformation where the FCF angle is smaller than the HCF angle. This difference in the geometries of CHF_2 and $SiHF_2$ seems to be explained by a more considerable Coulomb repulsion of the fluorine atoms in the last one. Indeed, the charges on the fluorine atoms in $SiHF_2$ are more than twice higher than those in CHF_2 (see Table 2). The influence of hydrogen-fluorine interaction upon the structure of both radicals plays a secondary role as a result of longer interatomic distances and lower charges on hydrogen atoms.

The increase of electronegativity of the central atom in PH_3^+ as compared with SiH_3 results in the increase of the valence bond angle to the tetrahedral one. In this case the numerical value of φ is also lower than that obtained by Begum *et al.* [3]. Boyd and Whitehead have optimized [21] the geometry of PH_3^+ by the modified CNDO/2 in the sp basis set and have found that $\varphi = 112$–$120°$ depending on the choice of the numerical values of parameters. On the base of the spin density values on the phosphorus atom (see below) these values of φ seem to be less probable. Powell and Hall [22] stated the formation of racemic

Table 2. Atomic charges in the MH_nF_{3-n} radicals

Radical	Charge		
	M	H	F
SiH_3	0.4428	−0.1476	—
SiH_2F	0.6175	−0.1439	−0.3279
$SiHF_2$	0.7883	−0.1144	−0.3370
SiF_3	0.9427	—	−0.3142
PH_3^+	0.7138	0.0954	—

phosphine oxides in the reaction of an optically active phosphine with tetracyanoethylene and believed therefore that the arylphosphinium radical cation was planar or had a very low value of the inversion barrier. We estimated the inversion barrier for PH_3^+ to be ca. 15 kcal/mole. It seems to us that PH_3^+ must not be considered as a "model" of the arylphosphinium radical cation. The hybridization of the phosphorus atom in the latter should be different, possibly on account of the phosphorus 3*d* orbitals (in PH_3^+ their population is the lowest of all the radicals investigated here). This problem requires further investigations.

Spin Density

The isotropic components of hyperfine splittings A_{iso} observed in ESR spectra and caused by the Fermi contact term are known to be a linear function of the values of the *s* orbital spin populations (*s* spin densities):

$$A_{\text{iso}} = Q_s \varrho_s \tag{2}$$

where the Q_s value is constant for a given *s* orbital of a given atom. The Q_s values are listed in [1]. It should be noted however that they have been calculated for the second row atoms without considering the spin polarization of the inner 1*s* and 2*s* shells. By account of these effects the absolute values of Q_s will be diminished, so the values of ϱ_s in Eq. (2) should be increased correspondingly.

The calculated *s* orbital spin density distribution for the SiH_nF_{3-n} radicals and the PH_3^+ radical cation is shown and compared with the experimental one in Table 3. One can see that the projection of the UHF wave function on the pure spin state gives rise to the increase of the silicon (phosphorus) *s* orbital spin density and to the decrease of that for ligand atoms. The calculated fluorine *s* orbital spin densities are in good accordance with the experiment whereas the silicon *s* orbital spin densities are somewhat overestimated. Similar results have been obtained by the UHF-INDO calculations (with the annihilation of quartet) of SiH_3 [18] where $\varrho_s^{\text{Si}} = 0.259$. In SiF_3 both silicon and fluorine spin densities are positive. Thus, the Si^{29} and F^{19} hyperfine splitting constants should have opposite signs, $A_{\text{iso}}^{\text{Si}}$ being negative and $A_{\text{iso}}^{\text{F}}$ positive. This conclusion is completely supported by the results of the ESR investigation of SiF_3 [5]. Our calculations predict that the Si^{29} hyperfine splitting values in the ESR spectra of SiH_2F and $SiHF_2$ which were not measured experimentally will be closer to the $A_{\text{iso}}^{\text{Si}}$ value for SiH_3 increasing however systematically in the row SiH_3–SiF_3. Consequently, according to our data, *the increase of the s orbital spin density for the central atom of a tetra-atomic radical is not strictly connected with the decrease of the valence bond angle.* This conclusion was also drawn intuitively by Merritt and Fessenden [5]. However, from Table 3 one can see a clear correlation between the increase of the *s* orbital spin density on the central atom and the increase of its 3*d* orbital electron population. If a radical of the AB_3 form is planar then all the unpaired electron density will be in the $3p_z$ orbital of A and the 3*d* orbital population, as well as *s* orbital spin density will be equal to zero. This case corresponds to a trigonal hybridization of an atom A, and its *d* orbitals thus evidently do not participate in bonding. In cases where the radical is bent the hybridization of A changes: the share of polarizational *p* and *d* orbital increases. The

Table 3. $3d$ orbital populations and s orbital spin densities for the MH_nF_{3-n} radicals

Radical	$3d$ orbital population	Calculated s orbital spin density						Experiment[a]		
		M		F		H		M	F	H
		Unprojected	Projected	Unprojected	Projected	Unprojected	Projected			
1	2	3	4	5	6	7	8	9	10	11
PH_3^+	0.266	0.1044	0.1215	—	—	0.1405	0.0960	0.1420[b]	—	—
SiH_3	0.313	0.2480	0.2655	—	—	0.1271	0.0874	0.1557[c]	—	0.0157[e]
SiH_2F	0.572	0.2917	0.3115	0.0035	0.0032	0.1995	0.1441	—	0.0032[d]	0.0681[d]
$SiHF_2$	0.764	0.3795	0.3915	0.0058	0.0052	0.4050	0.3305	—	0.0045[d]	0.1770[d]
SiF_3	0.844	0.5382	0.5477	0.0059	0.0057	—	—	0.4082[d]	0.0079[d]	—

[a] Calculated from Eq. (2) using the Q_s values given in Ref. [1].
[b] Value from Ref. [3].
[c] Value from Ref. [23].
[d] Values from Ref. [5].
[e] Value from Ref. [2].

correlation of the s orbital density values with the d orbital electron population seems to point out that under these conditions the unpaired electron prefers to be in the spherically symmetrical s orbital. Simultaneously, the charge of the central atom A increases because of the growing electronegativity of ligands.

The orbital analysis of the wave function has also shown that in all studied radicals the unpaired electron is placed on a fully symmetrical orbital (A_1 symmetry). Both in radicals containing silicon and in PH_3^+ the orbital occupied by the unpaired electron is formed with the participation of $3d$ orbital of the central atom (the sum of squares of coefficients at $3d$ orbitals is ca. 0.1). Therefore, the empirical Eq. (1) is only approximately valid for these radicals.

Projecting the UHF wave function on the pure spin state (here on the doublet state) we have transformed self-consistent orbitals (say, $\varphi_{i\downarrow}$ and $\varphi_{i\uparrow}$) into so-called corresponding orbitals (say, X_i and Y_i). The corresponding orbitals [24] satisfy the relations

$$\langle X_i | Y_i \rangle = \eta_i \delta_{ij} \qquad (i, j = 1, 2, \dots, m \leqq n)$$

where m is the number of electrons with the $\downarrow$-spin, n is the number of electrons with the $\uparrow$-spin. The η_i values can serve as a measure of a declination of the UHF wave function from that of the restricted Hartree-Fock (HF) method: the larger is

$$\Lambda = \sum_{i=1}^{m} (1 - \eta_i)$$

the stronger is this declination. In the case of radicals considered here $\Lambda \leqq 0.01$. Thus, the difference between the UHF and HF self-consistent functions is very small.

All the hydrogen spin densities obtained in our calculations are above the experimental values though the spin projection somewhat diminishes them. Nevertheless, our calculations confirm that the proton hyperfine splitting constants for SiH_3, SiH_2F and $SiHF_2$ are positive [5]. The tendency in the change is given in a correct way and the ratio of their values for SiH_2F and $SiHF_2$ is in agreement with the experiments. We feel that the overestimation of absolute values of spin densities on hydrogen atoms in our calculations is not a consequence of an unsuitable parametrization, but rather follows from the CNDO method. Because of neglect of the differential overlapping the CNDO bond orders are different from accurate electron populations. In particular, the heteroatom-hydrogen bond orders are lowered. This fact leads to an overestimation of *s* electron density near the hydrogen atom [25]. The Si–H bond in the radicals studied here seems to show the same feature. The result is, in this case, that the hydrogen spin densities and, possibly, some bond lenghts are overestimated. It is noteworthy that this shortcoming can be eliminated even by partial account of the differential overlapping: the INDO calculations of SiH_3 [18] had the result $\varrho_s^H = 0.011$ in accordance with the experimental value.

The reason of the difference between isoelectronic carbon and silicon atoms is obviously a considerable participation of the silicon 3*d* orbitals in the chemical bonding. The role of 3*d* orbitals in the spin density redistribution is, however, almost negligible: the *d* orbital spin density is zero in SiH_3, 0.0125 for SiH_2F and 0.0278 for SiF_3.

The calculated phosphorus 3*s* orbital spin density in PH_3^+ is in good agreement with the experimental value. If the valence bond angle in PH_3^+ is assumed to be 114° [3] the phosphorus *s* orbital spin density value lowers to 0.099. Taking into consideration that the CNDO calculations can only overestimate the *s* orbital spin density on the central atom, one should conclude that the increase of the HPH valence bond angle up to 114° or more cannot lead to the value $A_{\text{iso}}^P = 517$ gauss found by Begum *et al.* [3] in the ESR spectrum of PH_3^+. Thus, once again evidence is presented against the application of Eq. (1) for radicals which contain silicon, phosphorus and other second row elements.

Our calculation shows that the hydrogen spin densities in PH_3^+ are comparable with those in SiH_3. From the ESR spectra of SiH_3, $A_H = 7.96$ gauss [2]. Therefore the proton hyperfine splittings in the ESR spectra of PH_3^+ might be detected experimentally (no such attempt was made by Begum *et al.* [3] either for SiH_3 or for PH_3^+). In both radicals A_H should be positive.

To summarize briefly some results given above, we may conclude that the CNDO method with the original parametrization [8, 9] is in general suitable at least for qualitative predictions of the geometries of radicals including those ones which contain silicon or phosphorus.

References

1. Atkins, P. W., Symons, M. C. R.: The structure of inorganic radicals. Amsterdam: Elsevier 1967
2. Krusič, P. J., Kochi, J. K.: J. Am. Chem. Soc. **91**, 3938 (1969)
3. Begum, A., Lyons, A. R., Symons, M. C. R.: J. Chem. Soc. (Lond.) (A) 2290, 2388 (1971)
4. Lyons, A. R., Symons, M. C. R.: J. C. S. Faraday II, **68**, 1589 (1972)
5. Merritt, M. V., Fessenden, R. W.: J. Chem. Phys. **56**, 2353 (1972)
6. Pullman, B.: Int. J. Quantum Chem. S **4**, 319 (1971)
7. Robinet, G., Leibovici, C., Labarre, J.-F.: Chem. Phys. Letters **15**, 90 (1972)
8. Pople, J. A., Segal, G. A.: J. Chem. Phys. **44**, 3289 (1966)
9. Santry, D. P., Segal, G. A.: J. Chem. Phys. **47**, 158 (1967)
10. Pople, J. A., Nesbet, R. K.: J. Chem. Phys. **22**, 571 (1954)

11. Löwdin, P.-O.: Rev. Mod. Phys. **36**, 966 (1964)
12. Hooke, R., Jeeves, T.-A.: J. Assoc. Comput. Machinery **8**, 212 (1961)
13. Milligan, D. E., Jacox, M. E., Guillory, W. A.: J. Chem. Phys. **49**, 5330 (1968)
14. Fessenden, R. W., Schuler, R. H.: J. Chem. Phys. **43**, 2704 (1965)
15. Morokuma, K., Pedersen, L., Karplus, M.: J. Chem. Phys. **48**, 4801 (1968)
16. Beveridge, D. L., Dobosh, P. A., Pople, J. A.: J. Chem. Phys. **48**, 4802 (1968)
17. Tables of interatomic distances and configurations in molecules and ions, Special Publication No. 11, London 1958
18. Benson, H. G., Hudson, A.: Theoret. Chim. Acta (Berl.) **23**, 259 (1971)
19. Gillespie, R. J., Nyholm, R. S.: Quart. Rev. (London) **11**, 339 (1957)
20. Pauling, L.: J. Chem. Phys. **51**, 2767 (1969)
21. Boyd, R. J., Whitehead, M. A.: J. C. S. Dalton (1972), 81
22. Powell, R. L., Hall, C. D.: J. Am. Chem. Soc. **91**, 5403 (1969)
23. Jackel, G. S., Gordy, W.: Phys. Rev. **176**, 443 (1968)
24. Amos, A. T., Hall, G. G.: Proc. Roy. Soc. (London) A **263**, 483 (1961)
25. Boyd, D.: J. Am. Chem. Soc. **94**, 64 (1972)

Dr. V. V. Penkovsky
Institute of Organic Chemistry
Academy of Sciences
of the Ukrainian SSR
Murmanskaya 5
Kiev 252660, USSR