# Coupled electron pair calculations for $R-C\equiv E$ molecules (E = N, P, As or Sb)

H. M. Schmidt[a], H. Stoll[a], H. Preuss[a], G. Becker[b] and O. Mundt[b]

[a]*Institut für Theoretische Chemie der Universität Stuttgart, Pfaffenwaldring 55, W-7000 Stuttgart 80 (Germany)*
[b]*Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55, W-7000 Stuttgart 80 (Germany)*

(Received 9 December 1991)

## Abstract

The effect of substituents R (R = H, $H_3C$, F or $H_5C_6$) on $C\equiv E$ groups in alkylidyne compounds $R-C\equiv E$ (E = N, P, As or Sb) has been studied at the level of valence electron CEPA (coupled electron pair approximation) calculations. Although the reactivities of $R-C\equiv E$ compounds differ widely (depending on E), the isolated molecules all have surprisingly similar electronic structures. For the H, $H_3C$ and F species, our calculated bond lengths $r_e(R-C)$ and $r_e(C\equiv E)$ agree well with experimental values where such are known. Along with the force constants, some trends for the changes in bond strength emerge. A plausible dependence of the dipole moments on E is observed.

For benzonitrile ($H_5C_6-C\equiv N$), published experimental values of the $C-C(\equiv N)$ bond length differ. The problem is explored using several basis sets and methods to obtain a value of 1.436(10) Å. The $C-C(\equiv P)$ bond length in benzylidynephosphane ($H_5C_6-C\equiv P$) is calculated to be 1.435(10) Å. Possible uncertainties of some of the experimental values are discussed.

## INTRODUCTION

The existence of molecules containing a double or triple bond between carbon and trivalent phosphorus shows that the customary rule, according to which thermally stable compounds with multiple bonds would occur only for elements of the second period, must be loosened. Over the last fifteen years, phospha-alkenes ($RR'C=P \sim R''$) and phospha-alkynes ($R-C\equiv P$) have received considerable attention. Weakly stable methylidyne-phosphane ($H-C\equiv P$), which later turned out to be the first member of a whole family of $R-C\equiv P$ molecules, was detected by Gier [1] in 1961. Kroto,

Nixon and co-workers [2] reported the pyrolytic preparation and the identification of C=P-containing species. At the same time experiments were successful in attaining stability at room temperature for compounds with C=P [3] and (some years later) C≡P bonds [4, 5]. Experimental methods and perspectives in the field have recently been reviewed by Nixon [6], Appel and Knoll [7], Markovski and Romanenko [8], Regitz and Binger [9] and Regitz [10]; a comprehensive treatise has been provided by Regitz and Scherer [11].

Quantum-chemical calculations show that R−C≡P as an isolated molecule has a stable ground state for many substituents R. Early Hartree–Fock calculations on H−C≡P were made by Botschwina et al. [12]. Botschwina and Sebald [13] obtained accurate spectroscopic data for H−C≡P using extensive *ab initio* calculations in conjunction with empirical corrections. Nguyen [14] and Bachrach [15] have reported Hartree–Fock results for numerous species like $H_3C-C\equiv P$, $H_2N-C\equiv P$, $HO-C\equiv P$ and $F-C\equiv P$. Very recently, Pyykkö and Zhao [16] have treated various triatomic phosphorus-containing species using the second order Møller–Plesset method (MP2). Some of those species containing arsenic or antimony, respectively, in place of phosphorus have been studied in all-electron Hartree–Fock calculations by Lohr and Scheiner [17] and by Dobbs et al. [18]. The latter paper discusses the reactivities of R−C≡E molecules in terms of HOMO and LUMO energies.

The objective of the present work is to achieve a more precise structure determination for several R−C≡E molecules (E = N, P, As or Sb) using valence-correlated wave functions. Substituents R of different electronegativities, (namely H, $H_3C$, F and $H_5C_6$) are to be considered. The valence electrons are treated at the level of Meyer's [19] coupled electron pair approximation (CEPA). The atomic cores are described using the pseudo-potentials of Igel–Mann et al. [20]. The pseudopotential method offers the advantage of requiring a lower computational effort compared with an equally accurate all-electron calculation, provided normal (not extreme) accuracy is to be reached. A concise review of the method has been given by Krauss and Stevens [21]. When heavier atoms occur, like arsenic and antimony in this paper, pseudopotentials are furthermore able to implicitly cover the scalar relativistic effects of the atomic core. For very heavy elements, however, a more complete theory would become necessary, taking explicit account of spin–orbit coupling (see, for example, Durand [22] and Dolg et al. [23]). For the latter reason, we have excluded molecules containing bismuth from this investigation although a possible C≡Bi group would be as interesting as its lighter congeners.

Computational details and results for the H, $H_3C$ and F ligands are described in the next two sections. The phenyl compounds, with a broader

discussion of basis set questions, are presented separately. The final section is a short conclusion.

DETAILS OF THE METHOD

All calculations reported in this paper have been performed using the 1990 version of the MOLPRO program written by Werner and Knowles [24]. After application of pseudopotentials [20], four valence electrons remain for carbon, five for each of the elements E (N, P, As or Sb) and seven for fluorine; they are treated at the Hartree–Fock and CEPA levels. The CEPA method accounts for that part of electron correlation arising from single and double substitutions, and covers higher substitutions in part. It is "size consistent", i.e. the CEPA energy for a system of non-interacting sub-systems is additive [25].

The pseudopotentials [20] have been adjusted in a "single-electron fit" (SEFIT) procedure employing *experimental* energies of different states of the atomic ion made up by the core plus one electron. In the case of antimony the adjustment is based on all-electron Dirac–Fock calculations. The valence basis sets to be used below include optimised four-s and four-p Gaussian sets [26] for each atom. The respective innermost two functions have been contracted. One set of d functions is added for C($\alpha$ = 0.75), F($\alpha$ = 1.496), N($\alpha$ = 0.80), P($\alpha$ = 0.34), As($\alpha$ = 0.293), Sb($\alpha$ = 0.211), and one set of p functions for H($\alpha$ = 1.0). This basis set will be denoted "A". A few of the calculations use a basis set "B", in which carbon and each of the atoms E carry two sets of d functions using exponents from ref. 27. For each of the molecules R–C≡E, the bond lengths $r_e$ and the force constants $k_e$ of the stretching vibration are determined for the two bonds R–C and C≡E. Cubic interpolation is used.

Table 1 gives the results for the H–C≡E series. The SEFIT pseudopotentials can be judged by comparing their results at the Hartree–Fock level ("VE-SCF/A") with those of all-electron calculations ("SCF"). Accurate all-electron calculations are available only for hydrogen cyanide (H–C≡N) and methylidynephosphane (H–C≡P). The agreement is seen to be satisfactory, although SEFIT shows a slight tendency to produce smaller $r_e$ and larger $k_e$ values; it can be improved by employing "multi-electron fit" (MEFIT) pseudopotentials [36]. These use the same numbers $n_c$ of core electrons and the same analytical shape as before, but are adjusted to energy levels of the ($n_c$ + $n_v$) electron atomic ion where ($n_v \geq 1$). These potentials with the appropriate (four-s, four-p) basis sets [36] and the same polarisation functions as previously yield the following Hartree–Fock values for H–C≡P: $r_e$(H–C) = 1.062 Å; $k_e$(H–C) = 0.425 a.u.; $r_e$(C≡P) = 1.518 Å; $k_e$(C≡P) = 0.734 a.u.

The CEPA results demonstrate the significance of valence electron cor-

TABLE 1

Properties of H–C≡E molecules (E = N, P, As or Sb)

| E | Method[a] | $r_e$(H–C) (Å) | $k_e$(H–C) (a.u.) | $r_e$(C≡E) (Å) | $k_e$(C≡E) (a.u.) | $\mu$[b] (D) | Ref. |
|---|---|---|---|---|---|---|---|
| N | VE-SCF/A | 1.053 | 0.445 | 1.119 | 1.582 | 3.21 | – |
| | **VE-CEPA/A** | 1.061 | 0.414 | 1.152 | 1.237 | 2.87 | – |
| | VE-CEPA/B | 1.064 | 0.403 | 1.147 | 1.228 | 2.86 | – |
| | SCF[c] | 1.058 | 0.440 | 1.127 | 1.560 | – | [28] |
| | CI[c] | 1.065 | 0.420 | 1.149 | 1.328 | – | [28] |
| | CEPA[d] | 1.0665 | 0.4027 | 1.1534 | 1.2330 | – | [29] |
| | Experiment | 1.06549 | 0.4015 | 1.15321 | 1.20130 | 2.940 | [30,31] |
| P | VE-SCF/A | 1.058 | 0.433 | 1.505 | 0.766 | 0.27 | – |
| | **VE-CEPA/A** | 1.068 | 0.400 | 1.543 | 0.592 | 0.71 | – |
| | VE-CEPA/B | 1.069 | 0.393 | 1.537 | 0.608 | 0.58 | – |
| | SCF[e] | 1.059 | – | 1.513 | – | – | [18] |
| | SCF[f] | 1.065 | 0.423 | 1.517 | 0.755 | – | – |
| | CEPA[g] | 1.082 | 0.3874 | 1.554 | 0.5979 | – | [13] |
| | Experiment | 1.0692(8) | 0.4014 | 1.5398(2) | 0.5845 | 0.39 | [32,33] |
| | Experiment | 1.0660(1) | – | 1.54045(2) | – | – | [34] |
| As | VE-SCF/A | 1.061 | 0.428 | 1.605 | 0.645 | 0.12 | – |
| | **VE-CEPA/A** | 1.071 | 0.393 | 1.649 | 0.485 | 0.18 | – |
| | VE-CEPA/B | 1.071 | 0.388 | 1.651 | 0.481 | 0.07 | – |
| | SCF[e] | 1.062 | – | 1.629 | – | – | [18] |
| | SCF[h] | 1.046 | – | 1.615 | – | – | [17] |
| | Experiment[i] | – | – | 1.651(5) | – | – | [35] |
| Sb | VE-SCF/A | 1.604 | 0.421 | 1.803 | 0.490 | – 0.75 | – |
| | **VE-CEPA/A** | 1.074 | 0.384 | 1.857 | 0.348 | – 0.49 | – |
| | VE-CEPA/B | 1.074 | 0.380 | 1.862 | 0.344 | – 0.70 | – |
| | SCF[e] | 1.066 | – | 1.853 | – | – | [18] |

[a] VE denotes valence electron calculations using SEFIT pseudopotentials [20] with basis sets A or B, respectively.
[b] Dipole moment.
[c] Basis set after contraction: 6s, 3p, 1d.
[d] Basis set after contraction: 8s, 4p, 2d on C and N; 4s, 2p on H. The original values have been slightly rounded.
[e] Basis set: DZP on E; DZ on C.
[f] This work, basis set after contraction: 9s, 6p, 1d on P; 7s, 4p, 1d on C; 4s, 1p on H.
[g] Basis set after contraction: 9s, 6p, 1d on P; 6s, 3p, 1d on C; 3s, 1p on H.
[h] Basis set: double zeta.
[i] From an X-ray crystal structure determination of the compound 2,4,6-[(H$_3$C)$_3$C]$_3$ H$_2$C$_6$–C≡As.

TABLE 2

Properties of $H_3C-C\equiv E$ molecules (E = N, P, As or Sb)

| E | Method[a] | $r_e$(C–C) (Å) | $k_e$(C–C) (a.u.) | $r_e$(C≡E) (Å) | $k_e$(C≡E) (a.u.) | $\mu^b$ (D) | Ref. |
|---|---|---|---|---|---|---|---|
| N | VE-SCF/A | 1.451 | 0.374 | 1.121 | 1.548 | 4.06 | – |
|   | **VE-CEPA/A** | 1.456 | 0.350 | 1.154 | 1.223 | 3.65 | – |
|   | SCF[c] | 1.468 | – | 1.135 | – | – | [40] |
|   | MP2[d] | 1.461 | – | 1.178 | – | – | [40] |
|   | Experiment | 1.458(3) | – | 1.157(3) | – | 3.913(2) | [37,38,41] |
| P | VE-SCF/A | 1.455 | 0.366 | 1.512 | 0.738 | 1.78 | – |
|   | **VE-CEPA/A** | 1.462 | 0.341 | 1.549 | 0.577 | 1.67 | – |
|   | SCF[c] | 1.468 | – | 1.521 | – | – | [15] |
|   | Experiment | 1.465(3) | – | 1.544(4) | – | 1.499(1) | [39] |
| As | VE-SCF/A | 1.457 | 0.360 | 1.613 | 0.616 | 1.30 | – |
|   | **VE-CEPA/A** | 1.464 | 0.336 | 1.656 | 0.468 | 1.15 | – |
| Sb | VE-SCF/A | 1.456 | 0.356 | 1.816 | 0.467 | 0.64 | – |
|   | **VE-CEPA/A** | 1.466 | 0.330 | 1.866 | 0.340 | 0.52 | – |

[a,b]See footnotes to Table 1.
[c]Basis set 6-31G*.
[d]Second-order Møller–Plesset calculation with basis set 6-31G*.

relation, particularly for the C≡E triple bond. In comparison with Hartree–Fock values, the CEPA results move considerably closer to experiment. The difference between VE-CEPA/A and VE-CEPA/B results is a rough measure of the basis set error remaining in the VE-CEPA/A approximation. Altogether, this approximation appears to be an acceptable compromise between computational effort and resulting accuracy, and this method is adopted in the next section. For the phenyl substituted molecules $H_5C_6-C\equiv E$ both SEFIT and MEFIT pseudopotentials are compared and several basis sets tested in a further section.

## THE SUBSTITUENTS H, $H_3$C AND F

The symmetry is assumed to be $C_{\infty v}$ for the hydrogen and fluorine, and $C_{3v}$ for the methyl species. The inner geometry of the $H_3C$ group has been fixed at the experimental structure of acetonitrile ($H_3C-C\equiv N$): C–H = 1.103 Å; H–C–C = 109.5° [37,38]. This simplification is suggested by the insignificant difference between the experimental $H_3C$ geometries of $H_3C-C\equiv N$ and ethylidynephosphane ($H_3C-C\equiv P$), for which the following parameters have been determined: C–H = 1.107Å; H–C–C = 110.3° [39].

For the substituents H, $H_3$C and F (Tables 1–3), we observe the following from our results:

TABLE 3

Properties of F–C≡E molecules (E = N, P, As or Sb)

| E | Method[a] | $r_e$(F–C) (Å) | $k_e$(F–C) (a.u.) | $r_e$(C≡E) (Å) | $k_e$(C≡E) (a.u.) | $\mu$[b] (D) | Ref. |
|---|---|---|---|---|---|---|---|
| N | VE-SCF/A | 1.237 | 0.695 | 1.118 | 1.551 | 2.33 | – |
| | **VE-CEPA/A** | 1.264 | 0.579 | 1.155 | 1.183 | 2.13 | – |
| | SCF | 1.249 | – | 1.132 | – | – | [42] |
| | Experiment | 1.262 | 0.5933 | 1.159 | 1.089 | 1.68(5) | [43,44] |
| P | VE-SCF/A | 1.249 | 0.623 | 1.507 | 0.721 | − 0.02 | – |
| | **VE-CEPA/A** | 1.276 | 0.530 | 1.550 | 0.553 | 0.16 | – |
| | **VE-CEPA/B** | 1.280 | 0.500 | 1.544 | 0.566 | 0.07 | – |
| | SCF[c] | 1.265 | – | 1.517 | – | – | [16] |
| | MP2[d] | 1.294 | – | 1.568 | – | – | [16] |
| | Experiment[e] | 1.285(5) | 0.5358 | 1.541(5) | 0.5183 | 0.279(1) | [45,46] |
| As | VE-SCF/A | 1.250 | 0.607 | 1.612 | 0.588 | − 0.54 | – |
| | **VE-CEPA/A** | 1.280 | 0.511 | 1.660 | 0.442 | − 0.42 | – |
| Sb | VE-SCF/A | 1.251 | 0.590 | 1.819 | 0.432 | − 1.21 | – |
| | **VE-CEPA/A** | 1.284 | 0.496 | 1.872 | 0.318 | − 1.08 | – |

[a,b]See footnotes to Table 1.
[c]Basis set 6-31G*.
[d]MP2 calculation with basis set 6-31G*.
[e]For the sign of $\mu$ see section entitled The substituents H, $H_3$C and F.

(i) Considering the R–C bond for some fixed substituent R in the sequence {E = N, P, As, Sb} there is a slight monotonic increase in $r_e$(R–C), together with a noticeable decrease of the corresponding force constant $k_e$. This decrease in bond strength is slightly more pronounced for fluorine than for the other two substituents (Fig. 1).

(ii) The second observation refers to the change in the C≡E bond caused by different substituents. On the CEPA level there is a slight increase of $r_e$(C≡E), together with a more pronounced decrease of $k_e$, in the order H, $H_3$C, F for any choice of E (Fig. 2). Of these three substituents, hydrogen is therefore the one to yield the strongest C≡E bond.

The agreement of the CEPA results with experiment is very satisfactory. The force constants of the theory are, as usual, relatively inaccurate. For (fluoromethylidyne)phosphane (F–C≡P), the experimental C≡P bond length has been given [45] as $r_e$ = (1.541 ± 0.005) Å, which is practically identical to the corresponding value of 1.540 Å in the parent compound H–C≡P [32,34]. VE-CEPA calculations with both basis sets A and B provide an increase of this bond length by 0.007 Å when going from the H–C≡P to the F–C≡P molecule. We therefore expect a true value for
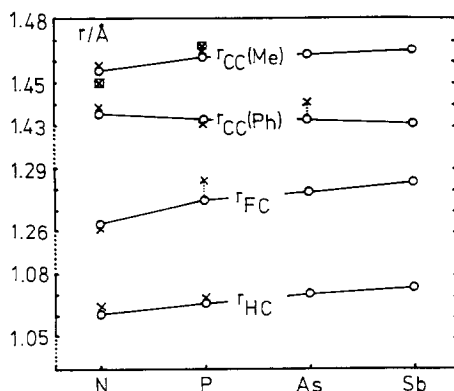
Fig. 1. R–C bond lengths in R–C≡E molecules {E = N, P, As or Sb; R = H, F, $H_5C_6$ (Ph) or $H_3C$ (Me)}. VE-CEPA/A or, for the phenyl species, VE-CEPA/$A_0$ results from Tables 1–3 or Table 4, respectively, are denoted O. References for experimental values (x) are given in Tables 1–4. The two experimental points ⊠ belong to the phenyl sequence; see discussion in the section entitled The phenyl substituent.

F–C≡P close to $r_e$ = 1.547 Å, i.e. at the upper end of the interval given in ref. 45.

Dipole moments $\mu$ (Tables 1–3) are plotted in Fig. 3. A positive sign ($\mu > 0$) corresponds to a positive charge on the R side of the R–C≡E molecule. The $\mu$ values show the expected shift downward along the sequence {E = N, P, As, Sb}. In addition, the calculations yield a monotonic decrease in $\mu$, from the $H_3C$ via H to the F substituent. Calculated dipole
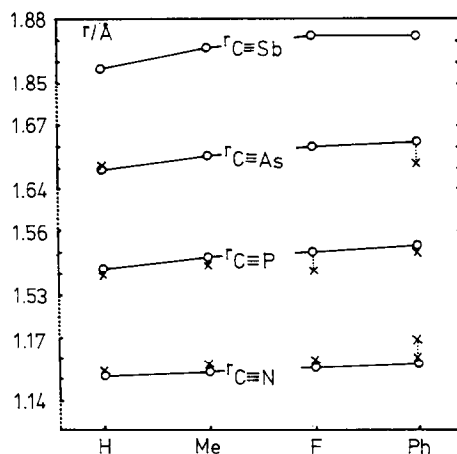


Fig. 2. C≡E bond lengths in R–C≡E molecules {R = H, $H_3C$ (Me), F or $H_5C_6$ (Ph); E = N, P, As or Sb}. O denote VE-CEPA/A and VE-CEPA/$A_0$ results from Tables 1–3 or Table 4, respectively. Experimental values (see Tables 1–4) are denoted x.
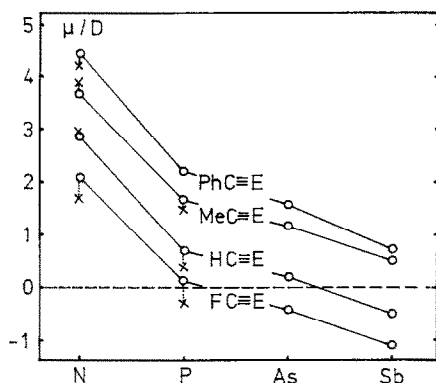
Fig. 3. Dipole moments $\mu$ (in debye units) for the four R–C≡E sequences. Positive sign of $\mu$ corresponds to a charge distribution $R^{\delta+}$–C≡$E^{\delta-}$. VE-CEPA/A results (O) and experimental values (x). For F–C≡P see remark in the section entitled The substituents H, $H_3C$ and F.

moments are known to be very sensitive towards defects of the wave function; accordingly Fig. 3 shows considerable deviations from the experimental values $\mu_{exp}$. Unfortunately, the experiment does not provide the sign of $\mu$. For the H–C≡P species, Kroto et al. [45] have deduced a dipole moment pointing toward the phosphorus atom; this means ($\mu_{exp} < 0$) in our convention. According to Fig. 3, the opposite sign is much more probable for this quantity, however. For (fluoromethylidyne)phosphane (F–C≡P), with its very low value of ($|\mu_{exp}| = 0.279\,D$), the question of sign is particularly difficult to decide. Tentatively, $\mu_{exp} = -0.279\,D$) has been assumed in Fig. 3.

THE PHENYL SUBSTITUENT

The $H_5C_6$–C≡E molecules are taken to be planar with $C_{2v}$ symmetry (Fig. 4). We make the simplification of fixing the inner geometry of the phenyl substituent at the experimentally determined structure of ben-
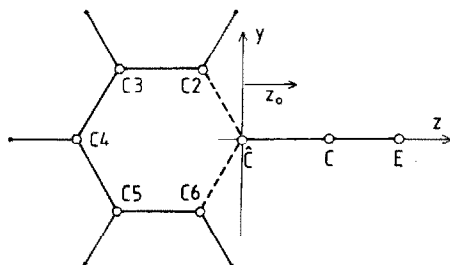


Fig. 4. Notation for $H_5C_6$–C≡E. The fragment Č–C≡E is displaced by $z_0$ in order to obtain a simplified geometry optimisation of the ring.

zonitrile [47]. It is plausible that the electronic structure and the geometric parameters of the $\hat{C}-C\equiv E$ fragment ($\hat{C}$ = *ipso* carbon atom) are only weakly influenced by the accurate ring geometry. Alterations of the ring (compared with benzene) affect mainly the angle $\varepsilon$ (C2–$\hat{C}$–C6) and the bond length $a$ ($\hat{C}$–C2; $\hat{C}$–C6), and are relatively small:

(i) The measured ring geometries of benzonitrile ($H_5C_6-C\equiv N$) [47,48] and of ethynylbenzene ($H_5C_6-C\equiv C-H$) [49] deviate from those of benzene by less than 0.01 Å or 2°.

(ii) The ring geometries of numerous monosubstituted benzene derivatives have been thoroughly studied at the Hartree–Fock level [50]. Even though they are not entirely in agreement with the available experimental values, the differences compared with benzene are 0.01 Å and 3° at most.

Each of the $H_5C_6-C\equiv E$ molecules contains 38 valence electrons. In the main part of our calculations SEFIT pseudopotentials [20] have again been used. The previous basis set A (see the section entitled Details of the method) has been reduced to a set "$A_0$". $A_0$ is identical to A on the atoms $\hat{C}$, C($\equiv$E) and E, whereas on the remaining carbon and hydrogen atoms of the ring polarisation functions are omitted and the tighter contraction 31 is used. $A_0$ contains 101 contracted Gaussians. Besides the complete CEPA wherein all of the valence orbitals are "correlated", a restricted CEPA has also been evaluated in which the lowest three SCF orbitals of $a_1$ symmetry remain unsubstituted. These orbitals have fairly strong contributions from s orbitals on the atoms $\hat{C}$, C($\equiv$E) and E, and non-substitution of them will influence the description of electron correlation around these atoms.

The results are collected in Table 4. It is of interest to compare the methyl derivatives $H_3C-C\equiv E$ (Table 2) with the phenyl compounds. In the whole sequence {E = N, P, As or Sb}, going from the methyl to the phenyl substituted molecule one observes a slight weakening of the C$\equiv$E bond: its length $r_e$(C$\equiv$E) is slightly longer and the force constant $k_e$(C$\equiv$E) is noticeably smaller. At the same time, the neighbouring C–C bond is strengthened, detectable by shorter $r_e$ lengths and higher $k_e$ values. The conjugation between the $\pi$ electrons of the C$\equiv$E moiety and the phenyl ring (which is thought to be present in benzonitrile) is therefore maintained in its homologues (see Fig. 1). The smaller bond length $r_e$($\hat{C}$–C($\equiv$E)) in these systems, however, reflects at least in part the well-known reduction of covalent radii when going from $sp^3$ to $sp^2$ carbon atoms. The $\hat{C}$–C($\equiv$E) bond is influenced by electron correlation in a complicated way. Comparison of SCF, restricted CEPA and full CEPA results (Table 4) indicates a sensitive balance between correlation effects in the $\hat{C}$–C($\equiv$E) and C$\equiv$E bonds.

Some ambiguity exists about the $\hat{C}$–C($\equiv$N) bond length in benzonitrile. Using microwave spectroscopy and isotopic substitution, Casado et al. [47] (cf. ref. 48) obtained an $r_s$ value of 1.4509(6) Å, well above the equilibrium distance ($r_e$ = 1.436 Å) resulting from our VE-CEPA/$A_0$ calculation (Table 4).

TABLE 4

Properties of $H_5C_6-C{\equiv}E$ molecules (E = N, P, As or Sb)

| E | Method[a] | $r_e(\hat{C}-C({\equiv}E))$[b] (Å) | $k_e(\hat{C}-C({\equiv}E))$[b] (a.u.) | $r_e(C{\equiv}E)$ (Å) | $k_e(C{\equiv}E)$ (a.u.) | $\mu$[c] (D) | Ref. |
|---|---|---|---|---|---|---|---|
| N | VE-SCF/$A_0$ | 1.435 | 0.399 | 1.123 | 1.533 | 4.69 | – |
|   | VE-CEPA (restr)[d] | 1.450 | 0.355 | 1.148 | 1.257 | 4.61 | – |
|   | **VE-CEPA/$A_0$** | 1.436 | 0.396 | 1.157 | 1.193 | 4.40 | – |
|   | SCF[e] | 1.445 | – | 1.137 | – | 4.85 | [50,51] |
|   | Experiment[f,g] | 1.4509(6) | – | 1.1581(2) | – | 4.18(8) | [47,52] |
|   | Experiment[g,h] | 1.444 | – | 1.156 | – | – | [47] |
|   | Experiment[i] | 1.438(5) | – | 1.168(3) | – | – | [53] |
|   | Experiment[j] | 1.434(3) | – | 1.166(6) | – | – | [54] |
|   | Experiment[k] | 1.401(14) | – | 1.137(14) | – | – | [55] |
| P | VE-SCF/$A_0$ | 1.431 | 0.395 | 1.514 | 0.724 | 2.00 | – |
|   | VE-CEPA (restr)[d] | 1.439 | 0.344 | 1.540 | 0.599 | 2.16 | – |
|   | **VE-CEPA/$A_0$** | 1.435 | 0.366 | 1.553 | 0.564 | 2.18 | – |
|   | Experiment | 1.467[g] | – | 1.544 | – | – | [56] |
|   | Experiment[k,l] | 1.432(4) | – | 1.550(3) | – | – | [35] |
| As | VE-SCF/$A_0$ | 1.430 | 0.392 | 1.616 | 0.603 | 1.43 | – |
|   | VE-CEPA (restr)[d] | 1.438 | 0.335 | 1.646 | 0.480 | 1.53 | – |
|   | **VE-CEPA/$A_0$** | 1.434 | 0.358 | 1.661 | 0.455 | 1.54 | – |
|   | Experiment[k,l] | 1.441(7) | – | 1.651(5) | – | – | [35] |
| Sb | VE-SCF/$A_0$ | 1.426 | 0.392 | 1.819 | 0.455 | 0.69 | – |
|   | VE-CEPA (restr)[d] | 1.423 | 0.359 | 1.867 | 0.328 | 0.75 | – |
|   | **VE-CEPA/$A_0$** | 1.431 | 0.355 | 1.872 | 0.325 | 0.71 | – |

[a] See footnote to Table 1.
[b] $\hat{C}$ is the ipso carbon atom of the phenyl substituent.
[c] Dipole moment.
[d] Restricted CEPA calculations with basis set $A_0$ in which some orbitals remain unsubstituted.
[e] Basis set 6-31G**.
[f] Microwave spectroscopy "substitution structure".
[g] Compare comment in section entitled The phenyl substituent.
[h] Microwave spectroscopy "average structure".
[i] Electron diffraction.
[j] NMR measurement.
[k] X-ray structure determination.
[l] Values refer to $2,4,6-[(H_3C)_3C]_3H_2C_6-C{\equiv}E$.

Casado et al. [47] claim the $r_s$ structure to be "still the best estimate of the equilibrium structure of benzonitrile". However, the paper also determines an average structure with $r_z = 1.444$ Å for the C–C bond in question. The average structure is a corrected substitution structure that takes into account shortening of bonds induced by substitution. The sensitive depen-

TABLE 5

Bond lengths of the molecules $H_5C_6-C\equiv N$ and $H_5C_6-C\equiv P$ from calculations using MEFIT pseudopotentials [36]

| E | Method | Basis set | $r_e(\hat{C}-C(\equiv E))$ (Å) | $r_e(C\equiv E)$ (Å) |
|---|--------|-----------|------------------|-----------|
| N | VE-SCF | 31(d) | 1.447 | 1.135 |
| | VE-CEPA | 31(d) | 1.458 | 1.172 |
| | VE-SCF | 211(d) | 1.440 | 1.128 |
| | VE-CEPA | 211(d) | 1.441 | 1.162 |
| | VE-SCF | 211(dd) | 1.439 | 1.123 |
| | VE-CEPA | 211(dd) | 1.442 | 1.156 |
| | SCF[a] | 6-31(d) | 1.451 | 1.138 |
| | CEPA[a] | 6-31(d) | 1.460 | 1.174 |
| | SCF[a,b] | 6-31G* | 1.445 | 1.136 |
| P | VE-SCF | 211(d) | 1.437 | 1.527 |
| | VE-CEPA | 211(d) | 1.441 | 1.567 |
| | VE-SCF | 211(dd) | 1.434 | 1.522 |
| | VE-CEPA | 211(dd) | 1.437 | 1.561 |

[a] All-electron calculation for comparison.
[b] Ref. 50.

dence of the resulting substitution structure upon these corrections has been stressed by Kuchitsu et al. [57]. In fact, there is a recent electron diffraction study of benzonitrile by Hargittai and co-workers [53] yielding an $r_g$ value of 1.438(5) Å for the $\hat{C}-C(\equiv N)$ bond. This agrees well with the $r_\alpha$ value of 1.434(3) Å, determined by Diehl et al. [54] by an NMR investigation of the oriented molecule. Furthermore, there is an X-ray crystal structure determination [55] measured at a temperature of 198 K which, however, is of little help, because $\hat{C}-C(\equiv N)$ and $C\equiv N$ distances of 1.401(14) and 1.137(14) Å, respectively, indicate severe shortening by thermal motion.

We have investigated the situation by means of the following calculations:

(i) The choice of the pseudopotential is of minor influence: MEFIT pseudopotentials [36] (cf. section entitled Details of the method) which enlarge the atomic cores slightly, yield an increase in $r_e(\hat{C}-C(\equiv N))$ of about 0.005 Å.

(ii) All-electron calculations comparable with the pseudopotential calculations with respect to basis sets, produce a result very close to the MEFIT data (see Table 5).

(iii) We also have examined the following extensions of the basis set: providing all ring carbon atoms with s-p sets of 211 contraction has almost no influence on $r_e(\hat{C}-C(\equiv N))$. Similarly, employing two d sets or diffuse s

and p functions on the atoms of the fragment $\hat{C}-C\equiv N$ has only little effect on $r_e(\hat{C}-C(\equiv N))$.

(iv) In opposition to this, a contraction of the initial $A_0$ basis set from 211 to 31 produces an artificial increase in $r_e(\hat{C}-C(\equiv N))$ to 1.458 Å (Table 5). Presumably the Hartree–Fock/6-31G** value of 1.445 Å [50] similarly raised by the 31 contraction of the basis set used.

In summary, the best calculated $\hat{C}-C(\equiv N)$ bond lengths of 1.436 Å (Table 4: SEFIT, VE-CEPA/$A_0$) and 1.442 Å (Table 5: MEFIT, VE-CEPA 211 dd) match the electron diffraction value of 1.438(5) Å well and the NMR value of 1.434(3) Å fairly well. In view of the good agreement between calculated and experimental distances in the previous sections, we therefore strongly suggest that the true $r_e$ parameter lies in this range, too, and consider the uncorrected $r_s$ value of ref. 47 to be markedly too high. We decide $r_e = 1.436(10)$ Å to be the final result of our calculations.

For benzylidynephosphane, Burckett-St. Laurent et al. [56] have determined (from measured rotational constants) the $\hat{C}-C(\equiv P)$ bond length to be 1.467 Å which is far above our VE-CEPA/$A_0$ value (Table 4) of 1.435 Å. There are, however, uncertainties with this experimental value due to the fact that the site of the ipso carbon atom $\hat{C}$ in the $H_5C_6-C\equiv P$ molecule is very close to the centre of gravity. Determining the $\hat{C}$ position from the rotational constants would thus require very accurate positions to be known for the remaining atoms in the structure. These atoms have been fixed in ref. 56 with the help of two assumptions, the uncertainty of which has been emphasised by the authors.

(a) The value of $r(C\equiv P)$ remains unchanged compared with ethylidyne-phosphane $H_3C-C\equiv P$.

(b) The ring geometry is the same as in benzonitrile.

Deviating from assumption (a), the VE-CEPA/A calculations (Tables 2 and 4) indicate a slight expansion of the $C\equiv P$ bond by $\delta r_e = 0.004$ Å between $H_3C-C\equiv P$ and $H_5C_6-C\equiv P$. A noticeable *widening* of the phenyl ring when going from $H_5C_6-C\equiv N$ to $H_5C_6-C\equiv P$ is also probable, as the following calculation shows. We make a simplified one-parameter geometry optimisation of the ring: The $\hat{C}-C\equiv E$ fragment with fixed inner geometry is shifted by $z_0$ along the symmetry axis of the molecule relative to a second block containing C2 through C6 and the adjacent hydrogen atoms at their previous positions (see Fig. 4). A positive sign of $z_0$ denotes a shift *away* from the ring. Minimal energy on the Hartree–Fock level (VE-SCF/$A_0$) is found at $z_0 = 0.004$ Å for benzonitrile and at $z_0 = 0.017$ Å for benzylidynephosphane. Within the model, this furnishes an outward movement of the ipso carbon atom $\hat{C}$ by $\delta z_0 = 0.013$ Å going from the nitrogen to the phosphorus compound. The modifications of assumptions (a) and (b), with the experimental moments of inertia being given [56], both result in a shortening of the emerging $\hat{C}-C(\equiv P)$ bond length compared to

the original 1.467Å [56]. Yet the model presented above is too rough to determine the bond shortening quantitatively.

Assuming the VE-CEPA/$A_0$ method to be as useful as in our previous calculations, we arrive at a $\hat{C}$–C($\equiv$P) bond length of 1.435(10) Å for benzylidynephosphane, which is practically the same value as in benzonitrile.

## CONCLUSION

The molecules investigated in this work have been studied on the level of pseudopotential CEPA calculations by uniformly employing atomic valence basis sets of the sizes A or $A_0$. The reduced $A_0$ size has been used to describe the non-ipsocarbon and the hydrogen atoms of the phenyl ring. The resulting values of bond lengths $r_e$ and force constants $k_e$ appear under "VE-CEPA/A" in Tables 1–3 and "VE-CEPA/$A_0$" in Table 4. The $r_e$ values are also plotted in Figs. 1 and 2. We estimate the uncertainty of the calculated $r_e$ to be not larger than ± 0.01 Å and to be around ± 0.005 Å for many of the species.

Our bond lengths are in good agreement with experiment for those species (R–C$\equiv$N and R–C$\equiv$P) for which unambiguous experimental values are available. Some clarification has been achieved for the $\hat{C}$–C($\equiv$E) bonds in the phenyl derivatives $H_5C_6$–C$\equiv$N and $H_5C_6$–C$\equiv$P. For the important case of benzonitrile (E = N) our calculation has provided an $r_e(\hat{C}$–C($\equiv$N)) bond length of 1.436 Å, close to the results of electron diffraction (1.438 Å) and NMR measurements (1.434 Å). The $r_s$ value of 1.451 Å determined by microwave spectroscopy appears to lie noticeably above $r_e$. For the phosphorus species $H_5C_6$–C$\equiv$P a bond length $r_e(\hat{C}$–C($\equiv$P)) of 1.435 Å has been calculated, a value considerably lower than the previous experimental estimate of 1.467 Å which had been determined under relatively uncertain assumptions.

Most of the alkylidynearsanes and all of the corresponding stibanes have not yet been prepared and the calculated data should be useful when these molecules become experimentally accessible.

## REFERENCES

1   T.E. Gier, J. Am. Chem. Soc., 83 (1961) 1769.
2   M.J. Hopkinson, H.W. Kroto, J.F. Nixon and N.P.C. Simmons, J. Chem. Soc., Chem. Commun., (1976) 513.

3   G. Becker, Z. Anorg. Allg. Chem., 423 (1976) 242.
4   G. Becker, G. Gresser and W. Uhl, Z. Naturforsch., Teil B, 36 (1981) 16.
5   G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Weeber and M. Westerhausen, Nova Acta Leopold., Neue Folge, No. 264, 59 (1985) 55.
6   J.F. Nixon, Chem. Rev., 88 (1988) 1327.
7   R. Appel and F. Knoll, Adv. Inorg. Chem., 33 (1989) 259.
8   L.N. Markovski and V.D. Romanenko, Tetrahedron, 45 (1989) 6019.
9   M. Regitz and P. Binger, Angew. Chem., 100 (1988) 1541.
10  M. Regitz, Chem. Rev., 90 (1990) 191.
11  M. Regitz and O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990.
12  P. Botschwina, K. Pecul and H. Preuss, Z. Naturforsch., Teil A, 30 (1975) 1015.
13  P. Botschwina and P. Sebald, J. Mol. Spectrosc., 100 (1983) 1.
14  M.T. Nguyen, Z. Naturforsch., Teil. A, 39 (1984) 169.
15  S.M. Bachrach, J. Comput. Chem., 10 (1989) 392.
16  P. Pyykkö and Y. Zhao, Mol. Phys., 70 (1990) 701.
17  L.L. Lohr and A.C. Scheiner, J. Mol. Struct. (Theochem), 109 (1984) 195.
18  K.D. Dobbs, J.E. Boggs and A.H. Cowley, Chem. Phys. Lett., 141 (1987) 372.
19  W. Meyer, Int. J. Quantum Chem., Suppl., 5 (1971) 341; J. Chem. Phys., 58 (1973) 1017.
20  G. Igel-Mann, H. Stoll and H. Preuss, Mol. Phys., 65 (1988) 1321.
21  M. Krauss and W.J. Stevens, Annu. Rev. Phys. Chem., 35 (1984) 357.
22  P. Durand, Int. J. Quantum Chem., 29 (1986) 915.
23  M. Dolg, H. Stoll and H. Preuss, J. Chem. Phys., 90 (1989) 1730.
24  H-J. Werner and P.J. Knowles, J. Chem. Phys., 89 (1988) 5803; P.J. Knowles and H-J. Werner, Chem. Phys. Lett., 145 (1988) 514.
25  W. Kutzelnigg, in H.F. Schaefer III (Ed.), Methods of Electronic Structure Theory, Plenum, New York, 1977.
26  H.J. Poppe and H. Stoll, unpublished work, 1988.
27  S. Huzinaga (Ed.), Gaussian Basis Sets for Molecular Calculations, Elsevier, Amsterdam, 1984.
28  U. Wahlgren, J. Pacansky and P.S. Bagus, J. Chem. Phys., 63 (1975) 2874.
29  P. Botschwina, J. Chem. Soc., Faraday Trans. 2, 84 (1988) 1263.
30  G. Winnewisser, A.G. Maki and D.R. Johnson, J. Mol. Spectrosc., 39 (1971) 149.
31  B.N. Battacharya and W. Gordy, Phys. Rev., 119 (1960) 144.
32  G. Strey and I.M. Mills, Mol. Phys., 26 (1973) 129.
33  J.K. Tyler, J. Chem. Phys., 40 (1964) 1170.
34  J. Lavigne, C. Pépin and A. Cabana, J. Mol. Spectrosc., 104 (1984) 49.
35  G. Becker, H. Schmidt, W. Schwarz, G. Märkl and H. Seijpka, to be published.
36  A. Bergner, W. Küchle and H. Stoll, unpublished work, 1990.
37  C.C. Costain, J. Chem. Phys., 29 (1958) 864.
38  J.L. Duncan, D.C. McKean, F. Tullini, G.D. Nivellini and J.P. Peña, J. Mol. Spectrosc., 69 (1978) 123.
39  H.W. Kroto, J.F. Nixon and N.P.C. Simmons, J. Mol. Spectrosc., 77 (1979) 270.
40  T-A. Chang, M.D. Harmony and S.W. Staley, J. Mol. Struct., 190 (1988) 17.
41  P.A. Steiner and W. Gordy, J. Mol. Spectrosc., 21 (1966) 291.
42  A.A. Hasanein and A. Hinchliffe, J. Mol. Struct. (Theochem), 149 (1987) 323.
43  J.K. Tyler and J. Sheridan, Trans. Faraday Soc., 59 (1963) 2661.
44  V.K. Wang and J. Overend, Spectrochim. Acta, Part A, 29 (1973) 1623.
45  H.W. Kroto, J.F. Nixon and N.P.C. Simmons, J. Mol. Spectrosc., 82 (1980) 185.
46  K. Ohno, H. Matsuura, H. Murata and H.W. Kroto, J. Mol. Spectrosc., 100 (1983) 403.
47  J. Casado, L. Nygaard and G.O. Sørensen, J. Mol. Struct., 8 (1971) 211.

48　B. Bak, D. Christensen, W.B. Dixon, L. Hansen-Nygaard and J. Rastrup-Andersen, J. Chem. Phys., 37 (1962) 2027.

49　A.P. Cox, I.C. Ewart and W.M. Stigliani, J. Chem. Soc., Faraday Trans. 2, 71 (1975) 504.

50　C.W. Bock, M. Trachtman and P. George, J. Mol. Struct. (Theochem), 122 (1985) 155; J. Comput. Chem., 6 (1985) 592.

51　S. Marriott, T. Silvestro, R.D. Topsom and C.W. Bock, J. Mol. Struct. (Theochem), 151 (1987) 15.

52　R.C. Weast (Ed.), Handbook of Chemistry and Physics, 68th edn., CRC Press, Boca Raton, 1987.

53　G. Portalone, A. Domenicano, G. Schultz and I. Hargittai, J. Mol. Struct., 160 (1987) 97.

54　P. Diehl, J. Amrein and C.A. Veracini, Org. Magn. Reson., 20 (1982) 276.

55　G. Fauvet, M. Massaux and R. Chevalier, Acta Crystallogr., Sect. B, 34 (1978) 1376.

56　J.C.T.R. Burckett-St.Laurent, H.W. Kroto, J.F. Nixon and K. Ohno, J. Mol. Spectrosc., 92 (1982) 158.

57　K. Kuchitsu, T. Fukuyama and Y. Morino, J. Mol. Struct., 4 (1969) 41.