Element−Element Bonds. IX.[1] Structures of Tetrakis(trifluoromethyl)diphosphane and -diarsane: Experimental and Theoretical Investigations[†]

Gerd Becker,*,[2] Winfried Golla,[3] Joseph Grobe,*,[3] Karl Wilhelm Klinkhammer,[2] Duc Le Van,[3] Andreas H. Maulitz,*,[4] Otto Mundt,[2] Heinz Oberhammer,*,[5] and Martin Sachs[2]

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany, Anorganisch-Chemisches Institut, Westfälische Wilhelms-Universität,
Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany, Institut für Anorganische Chemie,
Martin-Luther-Universität Halle−Wittenberg, Kurt-Mothes-Strasse 2, D-06120 Halle, Germany, and
Institut für Physikalische und Theoretische Chemie, Eberhard-Karls-Universität,
Auf der Morgenstelle 8, D-72076 Tübingen, Germany

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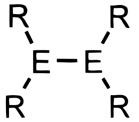
X-ray structure determinations of tetrakis(trifluoromethyl)diphosphane (**2c**, mp −82 °C, triclinic, $P\bar{1}$; $Z = 1$, $a = 529.7(3)$ pm, $b = 681.6(2)$ pm, $c = 802.8(3)$ pm, $\alpha = 108.58(1)°$, $\beta = 99.66(1)°$, $\gamma = 103.29(1)°$, wR2 = 0.204) and -diarsane (**3c**, mp −52 °C, monoclinic, $P2_1/c$; $Z = 2$, $a = 769.5(3)$ pm, $b = 750.0(3)$ pm, $c = 960.7(2)$ pm, $\beta = 105.26(1)°$, wR2 = 0.115), both at −100(3) °C, reveal the molecules to adopt the trans conformation in the solid. Compared with the tetramethyl derivatives, the E−E (224.6(2)/246.3(1) pm, E = P, As) and E−C (188.3(4)/201.3(7) pm) bonds are elongated by 4.5/4.8 pm and 3.4/3.4 pm, respectively. From gas electron diffraction studies of diphosphane **2c** a mixture of 85(10)% trans and 15(10)% gauche conformers can be deduced; diarsane **3c** shows the trans form exclusively. The molecular parameters (E−E, 224.8(11)/245.2(6); E−C, 189.6(4)/201.2(4) pm) agree excellently with those determined for the crystalline state. As a result of quantum chemical calculations at Hartree−Fock and hybrid density functional levels of theory using 6-311+G* basis sets, the gauche conformer of hydrazine derivative **1c** and the trans conformer of diarsane **3c** are clearly lowest in energy. However, for diphosphane **2c** the gauche and not the trans form is found to be slightly more stable. Variations of calculated E−E and E−C bond lengths are analyzed and compared with corresponding values of the parent compounds E_2H_4 (**1a** to **3a**) as well as the tetramethyl derivatives **1b** to **3b**.

Introduction

In recent studies the crystal structures of the congeneric compounds tetramethyldiphosphane (**2b**), -diarsane (**3b**),[6] -distibane,[7] and -dibismuthane[8] have been found to be characterized by extended, almost linear sequences of dipnicogen moieties with gradually decreasing intermolecular distances. Whereas the phosphorus derivative shows the ordinary van der Waals value, in the dibismuthane the lengths of the intermolecular contacts and the primary Bi−Bi bonds differ by about 15% only. As for the heavier members of the series these shortenings are accompanied by a drastic color change upon melting or dissolution. Even though this so-called thermochromic effect[9] is not yet completely understood,[10] it is indicative of significant intermolecular electronic interactions of the secondary bonding[11] type. Carrying on our investigations in this field, we now report on X-ray crystal structure determinations of tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**) (Chart 1).

Chart 1



E = N **1**, P **2**, As **3**

R = H **a**, CH_3 **b**, CF_3 **c**, F **d**

Additionally, a comparison of these structures with those of the methyl derivatives **2b** and **3b** should provide further insight into a phenomenon called *altruistic covalent interaction* by Marsden and Bartell[12] more than twenty years ago: As is well documented in the literature, the E−C bond lengths in the $E(CF_3)_n$ and $E(CH_3)_n$ compounds of halogens ($n = 1$), chalcogens ($n = 2$), or pnicogens ($n = 3$) may differ considerably depending on the electronegativity χ of element E.[13] For each main group a linear relationship has been found showing negative differences—i.e., shorter E−C bonds in the trifluoromethyl derivatives—for elements with $\chi > 2.5$, virtually no

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* Corresponding authors.

[†] Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday.

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Table 1. Summary of Crystal Data and Refinement Results for Compounds **2c** and **3c**

	$(F_3C)_2P{-}P(CF_3)_2$ (**2c**)	$(F_3C)_2As{-}As(CF_3)_2$ (**3c**)
empirical formula	$C_4F_{12}P_2$	$C_4As_2F_{12}$
CAS registry number	[2714−60−5]	[360−56−5]
formula mass (g mol^{-1})	337.98	425.88
melting point (°C)	−82	−52
space group	$P\bar{1}$ (triclinic, No. 2)	$P2_1/c$ (monoclinic, No. 14)
a (pm)	529.7(3)	769.5(3)
b (pm)	681.6(2)	750.0(3)
c (pm)	802.8(3)	960.7(2)
α (deg)	108.58(1)	90
β (deg)	99.66(1)	105.26(1)
γ (deg)	103.29(1)	90
V (10^{-30} m^3)	258	535
Z	1	2
T (°C)	−100(3)	−100(3)
ρ_{calcd} (10^3 kg m^{-3})	2.175	2.644
μ_{calcd} (10^2 m^{-1})	5.75	63.95
crystal length/diameter (mm)	0.1/0.3	0.3/0.1
weighing function	$e = 0.1469$	$e = 0.0704$
$w^{-1} = \sigma^2(F_o^2) + (eP)^2 + fP^a$	$f = 0.2302$	$f = 0.1086$
R1^b	0.072	0.042
wR2^c	0.204	0.115
GoF^c	1.08	1.23

[a] $P = (F_o^2 + 2F_c^2)/3$ with negative intensities (F_o^2) set to zero. [b] $R1 = \Sigma(|F_o - |F_c||)/\Sigma F_o$ (calculated for 1091/1102 reflections with $\{F_o \geq 1.41\sigma(F_o)\}$). [c] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$; $GoF = \{\Sigma w(F_o^2 - F_c^2)^2/(z - p)\}^{1/2}$ (calculated for $z = 1144/1288$ reflections and $p = 82/83$ refined parameters).

change for iodine ($\chi \approx 2.5$), and positive values—i.e., longer E−C bonds—for elements with $\chi < 2.5$; this correlation has been rationalized in terms of an electrostatic model.[14]

As far as trimethyl- and tris(trifluoromethyl)phosphane are concerned, Marsden and Bartell[12] suggested from extended Hückel molecular orbital calculations that the observed weakening of the P−C bonds can be rationalized by phosphorus 3d orbital contributions and may be called altruistic as it is associated with a *strengthening* of the adjacent C−F bonds. In contrast to these statements, however, the C−F bond lengths of $E(CF_3)_n$ compounds rather tend to *increase* with decreasing electronegativity of element E.[13] Furthermore, from subsequent ab initio calculations some controversy[15,16] arose about the early interpretation and especially the role of d orbitals. Only about 10 years ago, a correct description of this phenomenon has been achieved with pseudopotential SCF calculations;[17] additionally, the substitution effects turned out to be simulated very well by an external electrostatic field—a result confirming the simple model[14] mentioned above.

Keeping this model in mind, the bond between two positively polarized phosphorus atoms in a compound like tetrakis(trifluoromethyl)diphosphane (**2c**) is expected to exceed the standard of 221 pm[18] definitely. More than twenty years ago, however, Bartell and co-workers published an unreasonably short P−P distance of 218.2(16) pm only, as obtained from a gas electron diffraction (GED) study.[19] Despite the well-known fact that a mixture of conformers may impose severe problems in a GED study, the authors took the presence of small amounts of gauche conformer into consideration but ultimately based their determination on the presence of the trans conformer only. Contradictory to these results but as anticipated above, the crystal structure determination reported below revealed an elongated P−P distance of 224.6(2) pm. This discrepancy prompted us to reexamine the gas-phase structure of **2c,** to support the study by an ab initio approach and to include tetrakis(trifluoromethyl)diarsane (**3c**) as well.

To shed further light upon the so-called gauche effect,[20] the conformations of tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**) have been investigated by various spectroscopic methods (for a review see ref 21). From vibrational spectra it has been deduced that **2c** exists as trans[22] conformer in the solid and as a mixture of about 70% trans and 30% gauche in the liquid and gaseous states.[23] Photoelectron-spectroscopic studies resulted in a trans-to-gauche ratio of 90:10.[24] Only the trans conformer of tetrakis(trifluoromethyl)diarsane (**3c**) has been observed in all phases.[24,25]

Experimental Section

Preparation. The starting compound trifluoroiodomethane (cf. ref 26) was prepared from commercially available trifluoroacetic acid, silver carbonate and iodine, and reacted with either red phosphorus and iodine[27] or with lumps of arsenic[28] in sealed tubes. For safety reasons this procedure has to be carried out in an autoclave under external pressure. Iodobis(trifluoromethyl)phosphane and -arsane formed were separated from the corresponding tris(trifluoromethyl) and diiodo-

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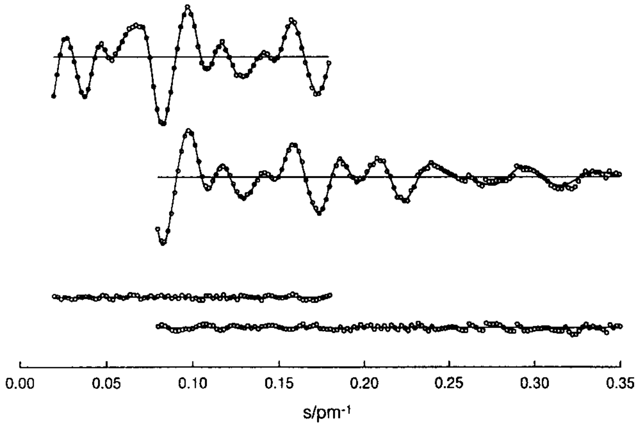

Figure 1. Experimental (dots) as well as calculated molecular intensities (full lines) and differences for **3c**. The upper curve corresponds to the long and the lower curve to the short nozzle-to-plate distance, respectively.

Table 2. Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (10^{-23} m^2) for the Atoms of the Asymmetric Units

	x	*y*	*z*	U_{eq}
(a) Tetrakis(trifluoromethyl)diphosphane (**2c**)				
P	3392(1)	5452(1)	9238(1)	28.7(4)
C1	2054(9)	2825(6)	7193(5)	48.2(9)
C2	5623(8)	6998(7)	8193(6)	47.8(9)
F11	3770(8)	1797(6)	6738(5)	96(1)
F12	920(7)	3165(5)	5751(4)	70(1)
F13	105(8)	1487(5)	7502(5)	96(1)
F21	7275(8)	6047(8)	7458(6)	98(1)
F22	4188(6)	7417(5)	6924(5)	72(1)
F23	7122(8)	8884(6)	9475(5)	98(2)
(b) Tetrakis(trifluoromethyl)diarsane (**3c**)				
As	3635.9(8)	−10.5(6)	441.6(6)	47.1(4)
C1	2065(8)	−1136(9)	−1361(7)	62(2)
C2	3019(9)	2501(9)	−232(7)	58(1)
F11	2627(7)	−985(8)	−2538(5)	87(2)
F12	414(7)	−478(9)	−1630(7)	86(1)
F13	1926(7)	−2869(6)	−1129(6)	84(1)
F21	3106(7)	2857(6)	−1566(5)	81(1)
F22	1373(6)	2940(7)	−171(6)	79(1)
F23	4147(7)	3596(5)	639(5)	76(1)

Table 3. Selected Bond Lengths (pm), Angles, and Torsional Angles (deg) from the Crystal Structures

	2c (E = P)	**3c** (E = As)
E−E′ [a]	224.6(2)	246.3(1)
E−C1	188.6(4)	201.8(6)
E−C2	188.0(4)	200.8(7)
C−F (mean[b])	131.7(4)	132.4(2)
C1−E−C2	96.3(2)	94.5(3)
E′−E−C1[a]	97.1(1)	94.6(2)
E′−E−C2[a]	96.6(1)	91.9(2)
E−C1−F11	116.7(3)	116.3(4)
E−C2−F21	115.8(3)	115.6(4)
E−C1−F12	110.1(3)	109.8(5)
E−C2−F22	110.8(3)	111.5(5)
E−C1−F13	108.5(3)	108.8(5)
E−C2−F23	108.6(3)	108.6(5)
F−C−F (mean[c])	107.1(3)	107.0(3)
C1−E−E′−C2′ [a]	−82.8(3)	−85.3(4)
E′−E−C1−F12[a]	−154.2(3)	−144.7(5)
E′−E−C2−F22[a]	+168.4(3)	+169.0(5)
C2−E−C1−F13	−172.1(3)	−168.4(5)
C1−E−C2−F23	−171.7(3)	−167.9(4)

[a] Symmetry operations for primed (′) atoms: $-x+1, -y+1, -z+2$ (**2c**); $-x+1, -y, -z$ (**3c**). [b] Individual values between 130.1(6) and 132.5(6) (**2c**) as well as between 131.8(8) and 132.8(8) (**3c**). [c] Individual values between 105.9(4) and 107.7(4) (**2c**) as well as between 106.4(6) and 108.4(6) (**3c**).

(trifluoromethyl) compounds by careful trap-to-trap condensations under vacuum. Finally, shaking these precursors with mercury in sealed tubes gave tetrakis(trifluoromethyl)diphosphane[27] (**2c**) and -diarsane[28] (**3c**) in good yields. Spectroscopically pure samples were obtained by repeated fractional condensations (traps at −45 and −196 °C) under vacuum, resulting, however, in a loss of about 50%.

Crystal Growth. Small amounts of diphosphane **2c** or diarsane **3c** were distilled under vacuum into the tips of Lindemann glass capillaries of 0.3 and 0.1 mm diameter, respectively. The samples were sealed, mounted on a Weissenberg camera, cooled to a temperature far beyond the respective melting point (Table 1) with a standard cooling device, and rinsed with a few drops of liquid nitrogen. When crystallization had been achieved, the temperature was raised to 1 to 2 °C below the melting point, and the sample was molten *almost* completely by use of a very fine, gently warmed wire. Slow recrystallization and further annealing for 12 h yielded single crystals, the quality of which had to be tested by means of oscillation photographs.

Collection and Reduction of X-ray Data. Capillaries with monocrystalline samples were enclosed in a lengthwise divided, precooled metal cylinder of appropriate size, immersed in liquid nitrogen and transferred to a Siemens P3 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 71.073$ pm). Automated centering of 30/28 selected reflections of **2c**/**3c** with ($25° < 2\Theta < 36°$) and least-squares routines were employed to obtain the cell parameters; characteristic crystallographic data are summarized in Table 1. From the dimensions of the unit cell and *E* value statistics (**2c**) or systematic absences (**3c**), respectively, the correct space groups were derived. Additional integral absences ($k + l = 2n + 1$) present in the diffraction pattern of **3c** and arising from an A type pseudo-centering are not valid for 56.8% of the reflections in question.

Solution and Refinement of Crystal Structures. Phases were determined with statistical methods[29] and the structures were refined on F^2 by full-matrix least-squares methods with the SHELXL-93[30] program and scattering factors of the neutral atoms[31] as included in this program. For diphosphane **2c**, 20 reflections with highly negative intensities had to be excluded from the calculations; for diarsane **3c** an absorption correction with the DIFABS[32] procedure was applied. In the final difference maps, maximum and minimum electron densities were 0.96/0.99 and $-0.66/-0.33 \times 10^{30}$ e m^{-3}. The final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Electron Diffraction. The electron diffraction intensities were recorded with a Gasdiffractograph[33] at 25 and 50 cm nozzle-to-plate distances applying an accelerating voltage of ca. 60 kV. To obtain appropriate vapor pressures of about 20 mbar, the sample reservoirs had to be cooled to −10 and −3 °C for **2c** and **3c**, respectively; the inlet system and gas nozzle, however, were kept at room temperature. The photographic plates were analyzed with standard methods[34] and molecular intensities in s-ranges from 0.02 to 0.18 and 0.08 to 0.35 pm^{-1} were used for the structure analyses $\{s = (4\pi/\lambda)\sin \theta/2,\ \lambda =$ electron wavelength, $\theta =$ scattering angle$\}$. Averaged intensities of **3c** are shown in Figure 1.

Results of Structure Determinations

Solid State Molecular Structures. Although tetrakis(trifluoromethyl)diphosphane (**2b**) and -diarsane (**3b**) crystallize in

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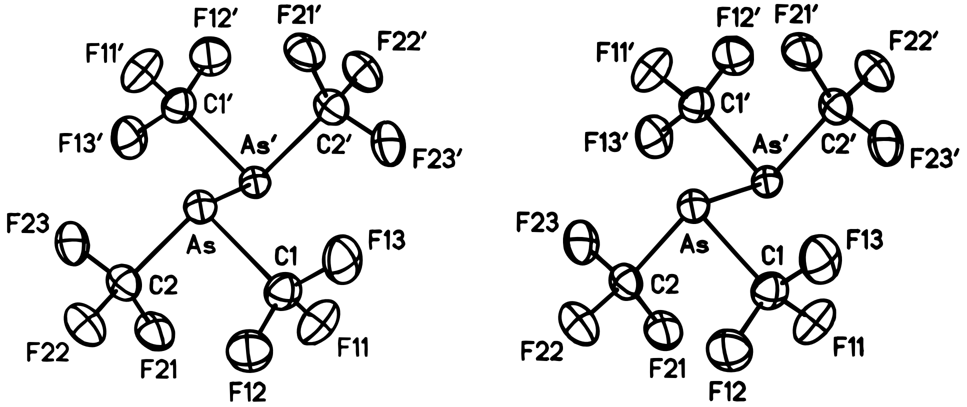

Figure 2. Molecular model of tetrakis(trifluoromethyl)diarsane (**3c**) in stereoscopic view showing the atom-labeling scheme and displacement ellipsoids at a 30% level of probability. Primed and unprimed atoms are symmetry related by a center of inversion.

different space groups (Table 1), the molecules of either compound adopt the trans conformation—a result which has been deduced already from vibrational spectroscopic studies.[23,25] The highest possible symmetry C_{2h} ($2/m$) of the free species, however, is reduced to C_i ($\bar{1}$) in the solid. Selected bond lengths and angles as well as characteristic torsional angles are listed in Table 3. Since corresponding molecular parameters are rather similar except for the E−E′ and E−C distances, we present a structural diagram for the diarsane **3c** only (Figure 2); the same atomic labeling scheme applies for diphosphane **2c**. Major deviations of 4.7° and 9.5° only are observed for the bond angles E′−E−C2 (96.6(1)° vs 91.9(2)°) and the torsional angles E′−E−C1−F12 (−154.2(3)° vs −144.7(5)°; Table 3), respectively.

Crystal Structures. Whereas tetramethyldiphosphane (**2b**) and -diarsane (**3b**) have been found to crystallize isotypically in space group $C2/m$,[6] such a relationship cannot be detected with respect to either of the crystal structures of the nonisotypic tetrakis(trifluoromethyl) derivatives **2c** ($P\bar{1}$) and **3c** ($P2_1/c$). Nevertheless, the packing of molecules in the solid shows certain similarities (Figure 3). In all three structure types the molecules are arranged in distorted hexagonal layers, but differences arise from the mutual directions of the homonuclear bonds and the normal vectors of the layer planes. These directions are virtually parallel in the structures of the tetramethyl compounds; with the tetrakis(trifluoromethyl) derivatives **2c** and **3c** considerable tilts, however, can be observed. In both cases the major component of the tilt comprises a rotation of the individual molecules around their pseudo-2-fold axes. The relative direction of rotation, however, is different, resulting in a characteristic decrease or increase of layer thickness for tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**), respectively.

Gas-Phase Structures. The radial distribution functions (RDFs) were calculated from the electron diffraction intensities by Fourier transformation. The curve obtained for **3c** is shown in Figure 4; it looks similar to that of **2c**, the reproduction of which we can therefore do without. Analyses of the RDFs clearly demonstrate the trans conformer predominating in both compounds. The geometric parameters were determined by least-squares fittings of the molecular intensities modified with a diagonal weight matrix, applying known complex scattering factors.[35]

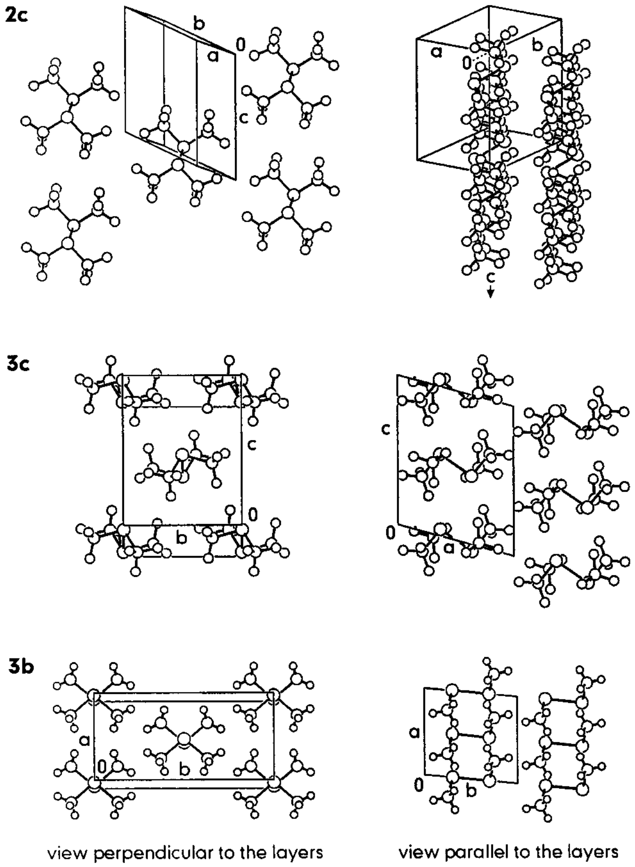

Figure 3. Crystal structures of tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**) as compared with the crystal structure of the tetramethyl derivative **3b**. Parallel projections in corresponding directions and of equal scale are given.

The overall molecular symmetry was constrained to C_{2h}; additionally, a local C_{3v} symmetry was assumed for the CF_3 groups introducing a variable angle between the C_3 axis and the E−C vector. From ab initio calculations this tilt is found to be directed toward the lone pair of E. Furthermore, since a dihedral angle C−E−C−F of 180° indicates an exactly staggered arrangement of the trifluoromethyl group with respect to the geminal C−E bond, the highest absolute value ϕ of this set of parameters is most appropriate to describe the torsional orientation of the CF_3 substituents. Vibrational amplitudes for similar distances were collected in groups; further assumptions are evident from Table 4. These constraints being established, eight geometric parameters (Table 5) and nine vibrational amplitudes lk (see Table 4 for numbering) were refined simultaneously. The following correlation coefficients had values larger than |0.6|: C−F/F−C−F = 0.74, P−P−C/C−P−C = −0.60, tilt/$l4$ = − 0.92, C−P−C/$l5$ = 0.62 for **2c** and As−As−C/ϕ = −0.73, tilt/$l4$ = −0.94, As−As−C/$l5$ = 0.60 for **3c**.

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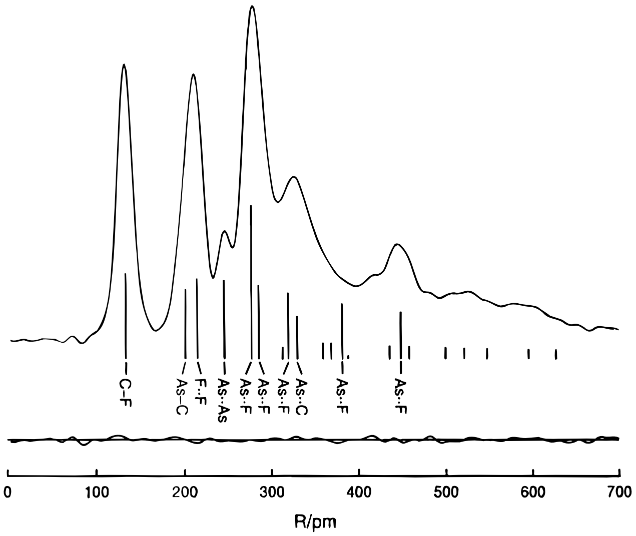

Figure 4. Experimental radial distribution function for **3c** and difference curve. The positions of important interatomic distances are indicated by vertical bars.

Table 4. Interatomic Distances and Vibrational Amplitudes (pm) from GED Analyses for the Tetrakis(trifluoromethyl) Compounds **2c** and **3c**[a]

	$(F_3C)_2P-P(CF_3)_2$ (**2c**)			$(F_3C)_2As-As(CF_3)_2$ (**3c**)		
	distance	amplitude		distance	amplitude	
C−F	134	4.8(2)	*l*1	134	4.4(3)	*l*1
E−C	190	4.5(5)	*l*2	201	6.2(8)	*l*2
E−E	225	6.0[5][b]		245	6.8(5)	*l*3
F···F	215	5.7(4)	*l*3	215	5.7[c]	
E···F	266−275	8.2(9)	*l*4	276−286	8.1(10)	*l*4
C···C	288			296		
F···F	260−292	25.0[c]		271−317	25.0[c]	
E···C	309	9.0[c]		330	10.0[c]	
E···F	315	21.9(55)	*l*5	320	18.7(28)	*l*5
C···F	315−324			313−368		
E···F	347	25.0[c]		318	25.0[c]	
F···F	350−359	25.0[c]		360−369	25.0[c]	
C···C	360			388		
C···F	396	23.4(62)	*l*6	405	27.7(53)	*l*6
F···F	440−445			436−458		
C···F	409	12.2(27)	*l*7	418	11.0(14)	*l*7
E···F	432			448		
C···C	461	23.0[c]		488	23.0[c]	
F···F	447−468			462−498		
C···F	486−504	28.0[c]		505−541	28.0[c]	
F···F	519−547	26.8(89)	*l*8	512−555	31.3(77)	*l*8
C···F	566	25.0[c]		590	25.0[c]	
F···F	576−681	31.3(96)	*l*9	595−703	27.6(80)	*l*9

[a] Error limits are 3σ values. [b] Not refined but varied within the given range in order to estimate the possible systematic error for the refined parameters. [c] Not refined.

Additional least-squares refinements were performed for mixtures of trans and gauche conformers, the gauche structures constrained to C_2 symmetry. Except for the bond angles around E and the E−E distances, the molecular parameters of both conformers were assumed to be equal. As a result of ab initio calculations the two angles E−E−C1 and E−E−C2 in the gauche conformers of **2c** and **3c** differ by 12.5° and 12.4°, respectively, and with respect to the trans conformers the E−E bonds of the gauche forms are shortened by 4.1 and 2.2 pm, respectively (Table 6). These differences were used as constraints in the least-squares refinements. Furthermore, the dihedral angles between the two lone pairs lp-E−E-lp were set to the HF/6-311+G* values of 93.0° and 94.8°. In case of diphosphane **2c** the agreement factor R decreases slightly when a 15% contribution of the gauche form is assumed and increases strongly with a value higher than 25%. A ratio of 15:85, the uncertainty of which is estimated to be ±10%, corresponds to a difference in free enthalpy of

$$\Delta G^\circ = G^\circ(\text{gauche}) - G^\circ(\text{trans}) = -1.0(4)\ \text{kcal/mol}$$

Neglecting entropy differences between the two conformations except for deviating multiplicities, we obtain an enthalpy value

$$\Delta H^\circ = -1.4(4)\ \text{kcal/mol}$$

As for the structure of diarsane **3c** the agreement factor R increases when taking small amounts of the gauche conformer into consideration. The final results of the GED analyses are listed in Tables 4 (vibrational amplitudes) and 5 (geometric parameters).

Results of Theoretical Calculations

Methods. To rationalize the energetical and geometrical differences between the possible conformers of tetrakis(trifluoromethyl)diphosphane **2c** and -diarsane **3c**, we carried out ab initio investigations including the hydrazine derivative **1c** and using Hartree−Fock (HF) as well as density functional theory (DFT) methods with the 6-311+G* basis set. As to the DFT level of theory, Becke's three parameter gradient-corrected exchange functional was applied along with the gradient-corrected correlation functional of Lee, Yang, and Parr[56] (B3LYP). Using the program Gaussian 94[57] and introducing either redundant internal or Cartesian coordinates, we optimized three distinct conformers each for compounds **1c**, **2c**, and **3c**:

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Table 5. Molecular Parameters (pm, deg) of Tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**) as well as of the Corresponding Methyl Derivatives **2b** and **3b** from X-ray Diffraction (XRD), Gas Electron Diffraction (GED), and Quantum Chemical Calculations (ab initio)

	$(F_3C)_2P{-}P(CF_3)_2$ (**2c**)			$(F_3C)_2As{-}As(CF_3)_2$ (**3c**)		
	XRD[a]	GED[b]	ab initio[a,c]	XRD[a]	GED[b]	ab initio[a,c]
E−E	224.6(2)	224.8(11)	227.2	246.3(1)	245.2(6)	248.9
E−C	188.3(4)	189.6(4)	190.0	201.3(7)	201.2(4)	201.3
C−F	131.7(4)	133.7(2)	131.3	132.4(2)	133.6(2)	131.5
E−E−C	96.9(3)	96.2(10)	98.0	93.3(14)[d]	94.6(7)	96.1
C−E−C	96.3(2)	98.8(28)	98.4	94.5(3)	94.5(17)	96.1
F−C−F	107.1(3)	107.4(2)	107.8	107.0(3)	107.2(3)	107.7
tilt(CF_3)[e]	4.5(5)	4.2(12)	4.3	4.2(7)	4.2(15)	4.0
C−E−C−F (ϕ)[f]	−171.9(3)	−174.8(41)	−174.9	−168.2(5)	−175.7(34)	+178.2
% trans	100	85(10)	−	100	100(10)	−

	$(H_3C)_2P{-}P(CH_3)_2$ (**2b**)			$(H_3C)_2As{-}As(CH_3)_2$ (**3b**)		
	XRD[a,g]	GED[b,h]	ab initio[a,c]	XRD[a,g]	GED[b,i]	ab initio[a,c]
E−E	221.2(1)	219.2(9)	222.8	242.9(1)	243.3(2)	244.9
E−C	183.8(1)	185.3(3)	185.5	196.5(3)	197.3(2)	197.3
E−E−C	98.3(1)	101.1(7)	98.3	96.2(1)	95.4(5)	97.9
C−E−C	98.8(1)	99.6(10)	98.9	96.7(2)	95.3(11)	97.9
% trans	100	100[j]	−	100	40(15)	−

[a] Mean values are given for nonunique parameters. Error limits are σ values. [b] r_a parameters; error limits are 3σ values. [c] HF/6-311+G*. [d] Mean of two strongly deviating values (see Table 3). [e] Tilt between the C_3 axis of the CF_3 group and the E−C bond toward the lone pair of E (see text). [f] A ϕ value of 180° corresponds to a staggered orientation of the CF_3 group with respect to the geminal E−C bond. [g] Reference 6. [h] Reference 36. [i] Reference 37. [j] The torsional angle C−P−P−C was refined to 164(23)°; a mixture of gauche and trans conformers was ruled out owing to a poor agreement between calculated and experimentally obtained radial distributions (ref 36).

Table 6. E−E and E−C Bond Lengths (pm) of R_4E_2 Compounds at HF/6-311+G* Level of Theory (calcd) in Different Conformations along with Experimental Data (expt); Substituents R Listed in Order of Increasing −I Effect[64]

		E−E				E−C	
E	source	R = CH_3 (**b**)	R = H (**a**)	R = CF_3 (**c**)	R = F (**d**)	R = CH_3 (**b**)	R = CF_3 (**c**)
N (**1**)	calcd (gauche)	140.9	141.0[a]	135.4	140.2[b]	144.4, 144.9	142.6, 143.2
	calcd (trans)	144.8	144.5[a]	149.2	143.3[b]	145.4	146.8
	calcd (cis)	146.5	144.5[a]	150.2	147.6[b]	144.9	145.9
	expt	140.1(4); 70% gauche[e]	144.7(2); 100% gauche[g]	140.2(20); 100% gauche, nearly D_{2d}[f]	148.9(4)[c]; 149.2(7)[d]; 53(3)% trans[c]; 71(8)% trans[d]	146.3(1)[e]	143.3(10)[f]
P (**2**)	calcd (gauche)	221.8	222.2[h]	223.1	229.3[i]	185.3, 185.5	189.2, 189.5
	calcd (trans)	222.8	223.8[h]	227.2	227.7[i]; 230.1[j]	185.5	190.0
	calcd (cis)	227.0	226.1[h]	230.0	234.0[i]	185.5	189.8
	expt	219.2(9)[k]; 60% gauche[n]	221.91(4)[l]; 221.8(4)[m]; >50% gauche[o]	224.8(11); 85(10)% trans	228.1(6); 100% trans[p]	185.3(3)[k]	189.6(4)
As (**3**)	calcd (gauche)	244.7[q]	245.2	246.7	−	197.3, 197.2[q]	200.7, 201.0
	calcd (trans)	244.9[q]	245.9	248.9	−	197.3[q]	201.3
	calcd (cis)	249.0	248.3	252.1	−	197.3	201.1
	expt	243.3(2)[r]; 60(15)% gauche[r]; 75% *trans*[s]	−	245.2(6); 100(10)% trans	−	197.3(2)[r]	201.2(4)

[a] For previous calculations see refs 38 and 39. [b] Reference 39; ab initio calculations with basis set 6-31G*; for more recent results on the gauche and trans conformers see ref 40. [c] Reference 41; GED study; convergence of the torsional angle at 67.1(10)°. [d] Reference 42; GED study; convergence of the torsional angle at 64.2(37)°. [e] Reference 43; GED study; convergence of the torsional angle at 78.5(41)°. [f] Reference 44; GED study. [g] Reference 45; GED study taking rotational constants from microwave spectra into account. [h] For previous calculations see refs 39, 46, and 47. [i] Reference 48; MP2 calculations with 6-311+G* basis set; for previous results see ref 39. [j] Reference 49; B3LYP calculations with basis set 6-311G(3df). [k] Reference 36; GED study; convergence of the torsional angle at 164(23)°. [l] Reference 50; microwave spectroscopic study at −60 °C; convergence of the torsional angle at 74.0(22)°, but the presence of a small amount of the trans conformer could not be ruled out. [m] Reference 51; GED study at +20 °C; convergence of the torsional angle at 81°, but a mixture of rotamers or even free rotation could not be excluded. [n] Reference 52; vibrational spectroscopic results. From photoelectron spectra a predominance of the trans form has been derived; ref 53. [o] Reference 54; photoelectron spectroscopic study. [p] Reference 19; GED study. [q] For previous calculations see ref 55. [r] Reference 37; GED study. [s] Reference 55; determined on the basis of a new assignment of the photoelectron spectrum published in ref 24.

trans with C_{2h}, gauche with C_2, and cis with C_{2v} symmetry. The calculated stationary points at the B3LYP/6-311+G* level of theory were characterized by their Hessian matrix. The calculated relative energies are given in Table 7 along with information regarding the stationary points. The s and p orbital contributions to the lone pairs of the central atoms are based on the natural bond orbital (NBO) analyses[58] implemented in the program mentioned above.

Relative Energies of Conformers. The relative energies of the optimized structures at the HF/6-311+G* level of theory (Table 7) reveal that the C_2 symmetrical conformer should be the most stable form of tetrakis(trifluoromethyl)hydrazine (**1c**) and -diphosphane (**2c**). On the one hand, this result supports the significance of the gauche effect, which has been well-known

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Table 7. Calculated Relative Energies (kcal/mol) of $R_2E{-}ER_2$ Compounds, for the Trifluoromethyl Derivatives at Various Levels of Theory

		HF/6-311+G*	B3LYP/6-311+G*			
		R = CF_3 (**c**)			R = H (**a**)	R = CH_3 (**b**)
E	symmetry	E_{rel}[a]	E_{rel}[a]	$E_{rel,\ ZPE}$[a]	$E_{rel,\ ZPE}$[a]	$E_{rel,\ ZPE}$[a]
N (**1**)	C_2 (gauche[b])	0.0[c]/1(15)[d]	0.0	0.0	0.0	0.0
	C_{2h} (trans)	+43.6	+39.1	+38.9	+2.8	+5.5
	C_{2v} (cis)	+61.1	+54.2	+53.5	+9.8/1(552)[d]	+18.6/1(169)[d]
P (**2**)	C_2 (gauche[b])	0.0	0.0	0.0	0.0	0.0
	C_{2h} (trans)	+1.5	+0.4	+0.3	+0.0	−1.2
	C_{2v} (cis)	+11.7	+10.0	+9.9	+3.6/1(286)[d]	+6.3/1(87)[d]
As (**3**)	C_2 (gauche[b])	0.0	0.0	0.0	0.0	0.0
	C_{2h} (trans)	−0.8	−1.9	−1.8	−0.6	−1.4
	C_{2v} (cis)	+7.8	+6.5	+6.5	+2.2/1(157)[d]	+3.6/1(53)[d]

[a] Relative energies (E_{rel}); relative energies corrected by zero point energies ($E_{rel,\ ZPE}$). [b] The energies of the gauche conformers are set to zero. [c] The C_2 symmetrical conformer is characterized as an extremely flat transition state with an imaginary frequency. An optimization without symmetry constraints reveals a minimum of the same energy. [d] Number and value (i cm^{-1}) of the imaginary frequency for the transition state.

from the structures of the parent compounds hydrazine (**1a**)[45] and diphosphane (**2a**);[50,51] on the other hand, it does not agree with our experimental findings from X-ray and gas electron diffraction of diphosphane **2c**. Unlike this compound, theoretical calculations on diarsane **3c** show the C_{2h} symmetrical trans conformer to be stabilized by 0.8 kcal/mol (Table 7; HF/6-311+G* value) with respect to the gauche conformer. This outcome corresponds very well with the exclusive observation of the trans conformer in both the solid and the gaseous state.

As far as the choice of different basis sets is concerned, Jursic[49] has shown for tetrafluorodiphosphane (**2d**) that even the extension of the 6-311G(d) approximation by two additional sets of polarization functions and a set of f-type functions (6-311G(3df)) does not lead to a significant improvement in modeling the P−P bond length. From this point of view, the use of diffuse functions appeared reasonable in order to account for the numerous lone pairs of compound **2c** and **3c**, respectively. Furthermore, since the extended basis set seemed to be flexible enough for a description of the electronic structures, the lack of dynamic electron correlation within the Hartree−Fock method was regarded as responsible for the contradiction specified above. Therefore, we applied the B3LYP density functional theory, which is known to consider electron correlation effects comparably to the MP2 method for various types of molecules. As deduced from the relative energies, these calculations at the B3LYP/6-311+G* level qualitatively give the same picture as the HF/6-311+G* results: compared with the trans form the nitrogen compound (**1c**) as well as the phosphorus compound **2c** prefers the gauche conformation by 39.1 and 0.4 kcal/mol, respectively, whereas for diarsane **3c** the trans form is favored by 1.9 kcal/mol (Table 7; E_{rel} values). Additionally, the inclusion of zero-point vibrational energies (ZPEs) does not change the qualitative outcome of these calculations as shown by the $E_{rel,\ ZPE}$ values.

The contradiction of the conformational preference of compound **2c** between experiment and theory has to be seen in the light of the theoretical model applied. Although the B3LYP DFT method and the basis set perform very well in numerous cases, it would be an overinterpretation to argue on such small energy differences as calculated for the gauche and trans conformers of **2c**. Of course explicit correlation methods and the consideration of temperature would yield more reliable results. For molecules of this size, however, correlation methods such as post SCF or CI calculations are too demanding in terms of computer resources. Since the gas-phase structures of the molecules have been determined at room temperature, one might think about thermal corrections of the energetical results. To perform this for the trans conformer of **2c**, however, would require adequate calculations for a transition state. Furthermore, the corrections to be expected should be of the same order of magnitude as the actual energy differences. In conclusion, one can extract from the calculations on compound **2c** that the trans and gauche conformers of this molecule are very similar in energy, but the theoretical level employed cannot be used to decide unambiguously which conformer is preferred. In polar solvents, however, the gauche conformers are expected to be more stable because of the dipole moment as observed in 1,2-dichloroethane.[59]

Interactions of the Lone Pairs. At first sight, one might assume that the conformational preference of compounds **1c**, **2c**, and **3c** is driven by the gauche effect, i.e., by a tendency to minimize lone-pair repulsions in a virtually orthogonal arrangement of the corresponding orbitals. This conformation is characterized by a degeneracy of the two highest occupied molecular orbitals and a zero splitting Δ. However, such a general preference of gauche conformers is not reflected in the experimental findings, and an explanation by the gauche effect holds only if the lone-pair orbitals show a high degree of p character. Very recently, however, for tetramethyldiphosphane (**2b**), -diarsane (**3b**), and -distibane Sztáray and Szalay[55] have shown the s orbitals of the central atoms to contribute significantly to the lone-pairs. As a consequence, in the gauche conformers the splitting Δ does deviate from zero and, on the whole, the gauche effect is of minor significance for these compounds; lone-pair as well as steric repulsions are minimized by adopting the trans conformation accordingly. Population analyses based on natural bond orbitals[58] for the tetrakis(trifluoromethyl) derivatives **1c**, **2c**, and **3c** support this conclusion in that the s character of the lone pairs is calculated for the gauche conformers to be 0.2%, 64.3%, and 76.5%, respectively. As far as the heavier congeners **2c** and **3c** are concerned, it does not change significantly with conformation. In the hydrazine compound **1c**, however, the s character of the nitrogen lone pairs varies between 0.2% (gauche), 7.3% (cis), and 19.8% (trans).

Calculations on the tetramethyl derivatives give similar results with respect to their conformational preferences (Table 7): the hydrazine **1b** with its almost pure p-type lone pairs adopts the gauche conformation, whereas the corresponding diphosphane **2b** and diarsane **3b** prefer the trans conformation as described already by Sztáray and Szalay.[55] NBO analyses on the gauche conformers of **1b**, **2b**, and **3b** result in s characters of the lone

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(59) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616.

pairs of 14.8%, 55.5%, and 67.6%, respectively. The influence of different substituents on these values is demonstrated further by the result that in the gauche conformers of the parent compounds **1a**, **2a**, and **3a** the s-type contributions are 21.7%, 34.3%, and 68.0%. The percentage for hydrazine (**1a**) seems to be relatively high with respect to the observation that this compound does prefer the gauche conformation. Nevertheless, the splitting Δ of the lone-pair orbitals is much larger for the trans conformation indicating the larger lone-pair repulsion in the C_{2h} symmetrical rotamer.

Calculated Structures. In Table 6 selected structural parameters calculated for the tetrahydrogen (**a**), tetramethyl (**b**), and tetrakis(trifluoromethyl) (**c**) dipnicogenanes R_4E_2 (E = N, P, As) are compared with experimentally determined values. As the HF/6-311+G* optimized data show a higher degree of consistency, they are given preference to the density functional results. However, even these HF calculations lead to central P−P and As−As distances of 227.2 and 248.9 pm in the trans conformers which are about 3 pm longer than those obtained from the gas-phase (P−P, 224.8(11); As−As, 245.2(6) pm) and solid-state structure determinations (P−P, 224.6(2); As−As, 246.3(1) pm). These differences do not seem to be a correlation effect since the B3LYP values of the trans conformers of **2c** and **3c** are even larger (P−P, 230.5; As−As, 252.6 pm). Remarkably, extensive ab initio and density functional studies by Jursic[49] using the basis set 6-311G(d) have shown that such calculations fail to reproduce the P−P bond length of tetrafluorodiphosphane (**2d**) correctly and that the gradient-corrected B3LYP hybrid method gives the best results (230.1, Table 6). Furthermore, H. F. Schaefer, III, and co-workers have pointed out that, in general, B3LYP calculations on second-row elements lead to overestimated bond lengths.[60] Nevertheless, only theoretical methods open an opportunity to study the entire set of possible rotamers in order to derive geometrical and energetical trends.

In this respect some results of our work are worth a discussion in detail: To begin with, the calculations on the tetrahydrogen (**a**) and tetramethyl compounds (**b**) lead to nearly identical E−E bond lengths for each pair of conformers (Table 6). This coincidence is in contrast to the experimental findings at first sight; but the accuracy and the comparability of these values may be questionable, e.g. due to inappropriate constraints introduced into the GED structure analyses[39] or to an uncertain rotameric composition of the gaseous state. As far as the tetrakis(trifluoromethyl) derivatives **1c**, **2c**, and **3c** are concerned, however, in *nearly* all conformers the central E−E distances are calculated to be longer by about 2−5 pm compared to the corresponding tetrahydrogen (**a**) and tetramethyl compounds (**b**). This result may best be attributed to interactions between lone pairs of the fluorine atoms and the σ^*_{E-E} orbital, which lengthen the central E−E bond. Most remarkably, the gauche conformer of **1c** does not fit in this series of molecules insofar as the calculated N−N bond length is 5.5 pm shorter compared with tetramethylhydrazine (**1b**). Furthermore, the structure optimization leads to an almost D_{2d}-symmetrical molecule with nearly planar nitrogen atoms. This result is supported by experiment; a qualitative MO model based on an interaction between the σ bonds of either C_2N fragment and the p_π orbital of the adjacent nitrogen atom has been proposed.[44]

A second trend is found with respect to the correlation between E−E bond lengths and different conformations (Table 6). For the series of tetrahydrogen (**a**), tetramethyl (**b**), and tetrakis(trifluoromethyl) compounds (**c**) our calculations predict that the C_2 symmetrical gauche conformer should have the shortest and the higher symmetrical C_{2v} (cis) structure the longest E−E bond—a result already published by others[39] for hydrazine and diphosphane as well as for their tetrafluoro derivatives. More recent calculations[48] on tetrafluorodiphosphane (**2d**), however, predicted the trans rotamer to have the shortest P−P bond (Table 6). To our point of view, the graduation of bond lengths reflects the steric requirements of the substituents as well as the repulsion between the two lone-pair orbitals increasing in each sequence of gauche, trans, and cis conformers.

Third, in all conformers the calculated E−C bond lengths of tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**) are found to be longer by about 4 to 5 pm compared to the tetramethyl derivatives **2b** and **3b** (Table 6). A reverse situation, however, is met with the gauche conformers of the corresponding pair of hydrazines; here the N−C bond lengths of the tetrakis(trifluoromethyl) compound **1c** are definitely shorter by 2 to 3 pm with respect to tetramethylhydrazine (**1b**)—a phenomenon which is in accordance to experimental results. The electrostatic model[14] cited in the beginning might give an explanation of this observation, especially since it takes the reverse polarization of the E−C bonds, where nitrogen on one hand carries a negative and phosphorus or arsenic on the other hand carries a positive partial charge, into account. Furthermore, NBO analyses show the C−N bonds of tetrakis(trifluoromethyl)hydrazine (**1c**) to consist of $sp^{1.91}$ orbitals at nitrogen and $sp^{2.41}$ orbitals at carbon. In contrast, phosphorus and arsenic use almost pure p-type orbitals in their respective E−C bonds.

As already mentioned in the Introduction, a term called *altruistic covalent interaction* has been discussed in the literature[12] in order to account for the elongated E−C bond lengths of e.g. tris(trifluoromethyl)phosphane in comparison to the corresponding trimethyl derivative. Early MO calculations at the relatively low HF/3-21G$^{(*)}$ level have failed so far to confirm the suggested concept that a 3d-orbital contribution of phosphorus strengthens the C−F and weakens the P−C bonds altruistically.[16] In contrast, detailed NBO analyses reveal the absence of a significant d-orbital participation and show nonbonding interactions of the fluorine lone pairs with σ^*(P−C) orbitals to be responsible for the elongation of the P−C bonds in tris(trifluoromethyl)phosphane.[61] Interactions of the same type have been detected for the title compounds tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**). The hydrazines **1b** and **1c** do not fit to this scheme, probably because of the reverse polarization of the N−C bonds.

Discussion

The molecular parameters of tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**) (Table 5) as obtained by X-ray and gas electron diffraction are in excellent agreement, if error limits and systematic differences between these two methods of structure determination are taken into account. Furthermore, the gas-phase values correspond fairly well with the results of HF quantum chemical calculations which reproduce the experimental bond lengths and angles within small ranges of about ±4 pm and ±2°, respectively; just one somewhat larger difference of about 6° is found for the torsional angle C−E−C−F of the CF_3 groups in diarsane **3c** (+178.2° vs −175.7(34)°). To sum up the findings of our investigations, the gas electron diffraction study on compound **2c** published by Hodges, Su, and Bartell[19] more than twenty years ago is clearly in error with regard to the short P−P bond length of

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(60) Ma, B.; Lii, J.-H.; Schaefer, H. F., III; Allinger, N. L. *J. Phys. Chem.* **1996**, *100*, 8763.

(61) A detailed study on the origin of the so-called altruistic effect is underway: Maulitz, A. H., to be published.

218.2(16) pm as well as the wide P−P−C and C−P−C angles of 106.7(7)° and 103.8(8)°, respectively.

As far as tetramethyldiphosphane (**2b**) is concerned, the relatively short P−P bond length of 219.2(9) pm (Table 5) obtained by McAdam, Beagley, and Hewitt[36] from a gas electron diffraction study is presumed to be too short, too. Already Downs, Rankin, and co-workers[37] have pointed out that this investigation might be incorrect in that a conformationally homogeneous composition of the gas phase had been assumed. It should also be revised especially since a single-crystal X-ray structure determination at -155 ± 3 °C[6] reveals a more reasonable value of 221.2(1) pm.

The replacement of all methyl substituents for trifluoromethyl groups in solid diphosphane **2b** and diarsane **3b** leads to an elongation of the E−E bonds by 3.4 pm in either case and to an increase of the average E−C distance by 4.5 and 4.8 pm, respectively (Table 5). On the basis of very similar electronegativities identical alterations are indeed expected for the phosphorus and arsenic compounds. Furthermore, the averaged E−C bond lengths of solid tetrakis(trifluoromethyl)diphosphane (**2c**, 188.3(4) pm) and -diarsane (**3c**, 201.3(7) pm) agree very well with corresponding parameters of 186.7(14) and 201.2(15) pm published for tetrakis(trifluoromethyl)tetraphosphetane[62] and -tetraarsetane.[63] In these two compounds, however, the introduction of only one electronegative substituent on each pnicogen atom quite obviously leaves the E−E bonds in the four-membered rings unaffected; with lengths of 221.3(5) and 245.4(1) pm they do not deviate from standard values[18] of 221 and 246 pm, respectively. Moreover, both the E−E−C and C−E−C angles decrease slightly when going from the methyl to the trifluoromethyl derivatives (Table 5). An analogous behavior of mononuclear phosphanes and sulfanes has been attributed to the influence of increasing group electronegativity and a decreasing repulsion of the bonding electron pairs; because of relatively long E−C bonds (E = P, S) the simultaneous increase in the volume of the substituents has no noticeable steric effect.[14]

More than twenty years ago, Yokozeki and Bauer worked out a correlation of C−F bond lengths in $R-E-CF_3$ molecules versus the electronegativity of element E. From the diagram given in their review,[13] virtually identical averaged C−F bond lengths of about 133.5 pm can be taken for trifluoromethyl-substituted phosphanes and arsanes; remarkably, values of 133.7(2) and 133.6(2) pm have been determined by gas electron diffraction analyses of **2c** and **3c**, respectively (Table 5). In contrast to these results, the average C−F bond lengths of 131.7(4) and 132.4(2) pm only as obtained from the solid state are too short; obviously these values are biased by relatively large displacement parameters of the fluorine atoms (Table 2).

Since the structural parameters of many gaseous compounds are now available either by experiment or by calculations at a satisfactorily high level for different conformers, we decided to extend the compilation of E−E bond lengths in Table 6 by the corresponding values of tetrafluorohydrazine (**1d**) and -diphosphane (**2d**). Unfortunately, structural data are not known for all diarsanes of this group. If the compounds are listed with respect to an increasing −I effect[64] of their substituents, some remarkable trends are observed. In the diphosphane series, the experimentally determined P−P bond length increases monotonically starting from 221.91(4) pm for diphosphane itself (**2a**)[65] up to 228.1(6) pm for the tetrafluoro derivative **2d**. An analogous observation holds for the As−As bond length of tetramethyl- (**3b**, 243.3(2) pm) and tetrakis(trifluoromethyl)diarsane (**3c**, 245.2(6) pm).

In the hydrazine series the situation is found to be more complicated. Even though the methyl and hydrogen substituents show a similar inductive effect, for still unknown reasons the experimentally determined N−N bond lengths in the gauche conformers of hydrazine itself (**1a**, 144.7(2) pm) and its tetramethyl derivative (**1b**, 140.1(4) pm) differ by more than 4 pm. In contrast to this observation, our calculations result in nearly identical parameters of 141.0 and 140.9 pm, respectively (Table 6). To solve this problem, one has to realize that on one hand the experimental result for compound **1a**, based on a joint analysis of electron diffraction intensities and rotational constants,[45] is highly reliable. On the other hand it is well-known that the HF approximation in combination with large basis sets predicts N−N bonds too short.[66] However, since the coincidence of calculated values has to be regarded as correct, we suggest that the experimental value for compound **1b** is wrong with a high degree of probability.

The unusually short N−N bond of tetrakis(trifluoromethyl)-hydrazine (**1c**, 140.2(20) pm) and its correlation with the almost D_{2d} symmetrical gauche structure of the molecule has already been mentioned. Again, with 135.4 pm this parameter is calculated too short. Furthermore, replacement of the four hydrogen atoms in hydrazine itself (**1a**) for fluorine in **1d** is accompanied by a strong elongation of the N−N bond (144.7(2) vs 149.2(7) pm, Table 6, expt); this long distance, which has to be taken as a weighted average of the trans and gauche values, could not be reproduced correctly by HF/6-31G* calculations[39] (trans 143.3 pm, gauche 140.2 pm; Table 6). More realistic, but still not satisfying parameters of 153.5 and 147.1 pm resulted from a recent study at the B3LYP/6-311+G(2d) level.[40]

Theoretical calculations clearly point out that the gauche effect does not determine the most stable conformation of tetrakis(trifluoromethyl)diphosphane (**2c**) and -diarsane (**3c**). On the contrary, since the lone-pair orbitals of phosphorus and arsenic show a high degree of s character and, therefore, the gauche conformation cannot minimize the lone-pair repulsions, the trans conformation with weaker steric interactions is favored. This preference is supported further by the increasing s character of the lone-pair orbitals. As a consequence of the high p character of the nitrogen lone pairs, however, the conformation of the hydrazines is dominated by the gauche effect.

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Supporting Information Available: A complete listing of total energies and Cartesian coordinates of the optimized structures. X-ray crystallographic files, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

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