Crystal Structure Analysis of 1,1,4,4-Tetrafluorobutadiene and Experimental Determination of the Charge Density of 1,1,4,4-Tetrafluorobutatriene**

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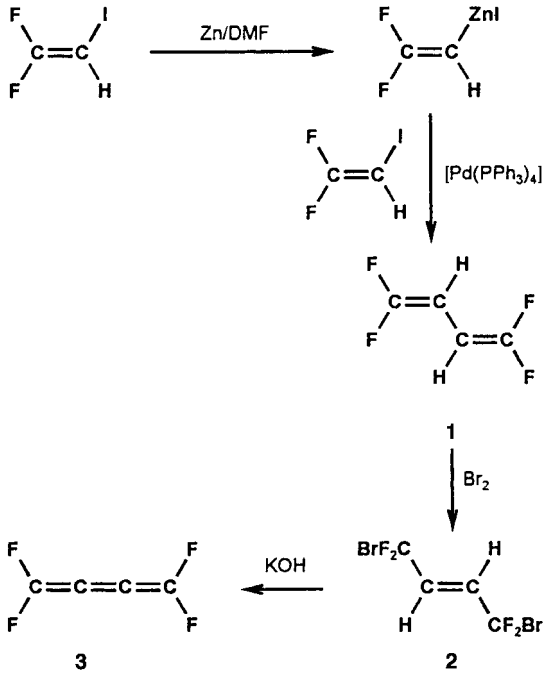
1,1,4,4-Tetrafluorobutatriene (**3**) is an extremely reactive molecule that was reported to explode on warming to its boiling point of about $-5\,^{\circ}C$ or even below on contact with air.[1] Nevertheless, ^{19}F NMR,[1] IR,[1, 2] Raman[2], and photoelectron (PE)[3] spectra were recorded, although the published multistep synthesis includes some low yield steps[4, 5] which additionally hinder a detailed study of its reactivity and structure.

Using palladium-catalyzed C–C coupling reactions,[6] we were able to develop an effective synthesis of 1,1,4,4-tetrafluorobutadiene (**1;** Scheme 1), which is the key compound in the synthesis of the cumulene **3** and furthermore should possess an interesting versatile chemistry of its own. Reaction of 2,2-difluoroiodoethene with zinc in DMF yields $F_2C{=}CZnI$.[7] The subsequent palladium-catalyzed C–C coupling reaction with 2,2-difluoroiodoethene gives good yields of the butadiene **1**; the yields of the other steps are likewise good.[1] Owing to the instability of **1** we modified the dehydrobromination reaction: 1,2-Dibromo-1,1,4,4-tetrafluorobut-2-ene (**2**) was passed over potassium hydroxide ($100\,^{\circ}C$) under vacuum (10^{-3} h Pa) and the triene **3** was collected in a trap kept at liquid nitrogen temperature. Compound **3** decomposes slowly even at $-80\,^{\circ}C$ forming a colorless solid and is best stored at $-196\,^{\circ}C$. In the presence of α-terpinene a viscous oil is formed on warming to ambient temperature.

Owing to the low boiling and melting points of the compounds, crystals had to be grown in situ directly on the diffractometer. Thus **1** and **3** were condensed into glass capillaries (o. d. 0.5 mm) using a glass vacuum line system on cooling with liquid nitrogen; the capillaries were sealed under vacuum, mounted on a goniometer head under low temperatures and brought into a cold gas stream of a diffractometer. Single crystals were grown by slow Φ rotation of the capillary



Scheme 1. Synthesis of **3**.

at 157.5 K for **1** and 143.0 K for **3** very close to the melting points of the compounds **1** and **3**, respectively.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit and possesses crystallographic C_i symmetry (Figure 1).[8] In the solid state the molecules have the s-*trans* conformation, which is the prevailing one in solution and the gaseous phase despite the

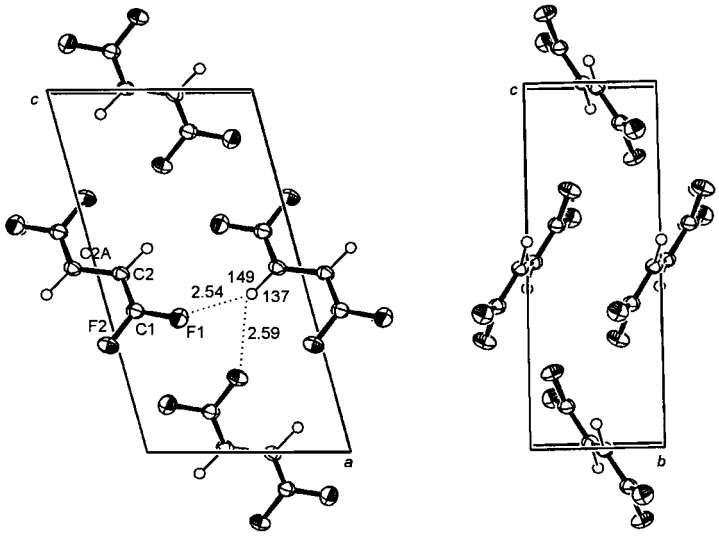


Figure 1. Unit cell of **1** (ORTEP,[33] 50% ellipsoids). Left: view along (010); right: view along (100). Short H–F contacts are drawn as dotted lines. Selected bond lengths [Å] and angles [°]: C1-F1 1.323(1), C1-F2 1.319(1), C1-C2 1.321(1), C2-C2A 1.450(2); F1-C1-F2 109.62(8), C1-C2-C2A 122.26(9).

large long-range fluorine coupling constants.[9] As expected, the C–C bond lengths alternate and the F1-C1-F2 bond angle is well below $120\,^{\circ}$. The packing of the molecules of **1** in the

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crystal is shown in Figure 1. The molecules are related by short H···F contacts along the *a* axis. A view on the *bc* plane shows the herring-bone arrangement of the molecules.

Compound **3** crystallizes in the monoclinic space group $P2_1/c$ (Figure 2),[8] and displays a crystal packing very similar to that of ethene[10] and tetrafluoroethene[11] The common motif again is the typical herring-bone arrangement.[12]

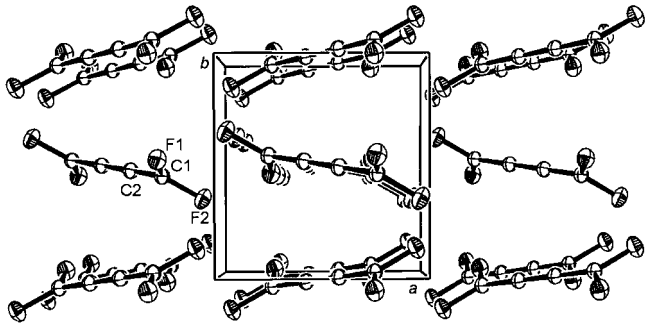

Figure 2. Unit cell of **3** (ORTEP,[33] 50% ellipsoids), view along (001).

The charge density $\rho(\mathbf{r})$ can be deduced theoretically from ab initio calculations at high level and experimentally from high-resolution X-ray diffraction data at low temperature.[13] The topological analysis of the charge density based on the theory of atoms in molecules (AIM) developed by Bader,[14, 15] allows a quantitative description of bonds and nonbonding interactions. Partitioning of a structure into submolecular regions (atoms or functional groups) provides a quantitative description of atomic properties such as atomic volumes and atomic charges. Since simple fluorinated alkenes are gaseous at ambient temperature, only a few crystal structure determinations or even charge density determinations have been carried out so far.[16–19] In pioneering work, Irngartiner et al. determined the charge density of cumulenes with bulky substituents.[20]

High resolution X-ray data were collected for **3**[8] and were used for a multipole refinement based on the Hansen–Coppens formalism[21] and a topological analysis using the program package XD was performed.[22]

The experimental static deformation densities for two perpendicular planes of **3** are represented in Figure 3a and 3b, from which the perpendicular π systems of the cumulene are clearly evident. In the molecular plane the electron density of the central double bond appears to be more elongated perpendicular to the bond axis than in the neighboring bonds; the opposite is seen in the plane perpendicular to the molecular plane. The charge density in the outer double bonds is shifted towards the fluorine substituents.

The results of the topological analysis of $\rho(\boldsymbol{r})$ at the bond critical points (BCPs; BCP at the location $\boldsymbol{r}_b$ is defined by $\nabla\rho(\boldsymbol{r}_b)=0$) enable a quantitative description of the bonds. The experimental results are found to be in good agreement with the theoretical ones (Table 1) except for the Laplacian $-\nabla^2\rho(\boldsymbol{r}_b)$ in the polar C–F bonds. These differences for polar

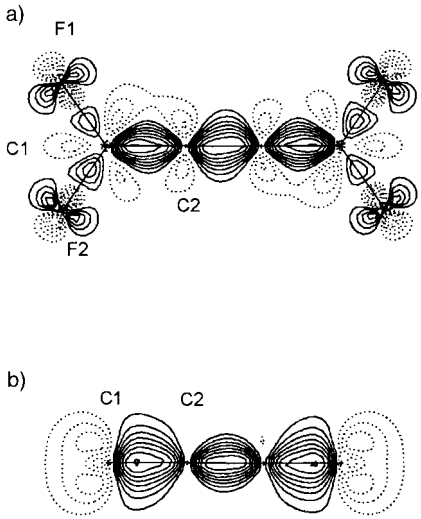

Figure 3. Experimental static deformation density in the molecular plane (a) and perpendicular to the molecular plane and parallel to the molecular axis (b). The contour intervals are at 0.1 e Å^{-3}, negative lines are dotted.

Table 1. Topological parameters at the BCPs of **3** (experiment/theory).[a]

Bond	Bond length [Å]	d_1 [Å][b]	$\rho(\boldsymbol{r})$ [e Å^{-3}]	$-\nabla^2\rho(\boldsymbol{r})$ [e Å^{-5}]	ε
C1–F1	1.3198(3)/1.3189	0.518/0.444	2.13(1)/1.97	25.0(1)/3.05	0.13/0.23
C1–F2	1.3222(3)/1.3189	0.533/0.444	2.20(1)/1.97	24.3(1)/3.05	0.08/0.23
C1–C2	1.3162(3)/1.3089	0.654/0.680	2.43(2)/2.44	24.0(1)/27.39	0.32/0.50
C2–C2′	1.2679(5)/1.2584	0.634/0.629	2.63(2)/2.57	30.5(1)/29.12	0.14/0.20

[a] Geometry optimization using B3LYP/6–311+G(3df).[31] [b] d_1 the distance of the first atom of a bond to the BCP.

bonds have been observed before.[16, 18, 23, 24] According to Coppens et al.[25] the main origin of these discrepancies is attributed to the nature of the radial functions in the experimental multipole model.

The topological parameters of the cumulated double bonds C1–C2 and C2–C2′ (the third double bond C2′–C1′ is equivalent to C1–C2 by crystallographic symmetry) reveal more interesting aspects. At the BCP of the shorter central bond the charge density and the negative Laplacian ($\rho(\boldsymbol{r}_b)=2.63$ e Å^{-3} and $-\nabla^2\rho(\boldsymbol{r}_b)=30.5$ e Å^{-5}) are significantly larger than for the neighboring longer bonds ($\rho(\boldsymbol{r}_b)=2.43$ e Å^{-3}and $-\nabla^2\rho(\boldsymbol{r}_b)=24.0$ e Å^{-5}. Thereby the charge density is not only concentrated on the fluorine atoms but also on the inner double bond. These experimental results agree very well with those of the theoretical topological analysis (Table 1).[14] There is a striking difference in the ellipticities ε[26] of the outer double bond ($\varepsilon=0.32$) and the inner double bond ($\varepsilon=0.14$). These results confirm the idea of sp-hybridization for the inner carbon atoms in cumulenes. The shorter bond length, the higher charge density, and the smaller ellipticity are attributed to the higher s-character for the central bond.

The partitioning of **3** into submolecular regions according to Bader[14, 15] can be deduced from the topology of $\rho(\boldsymbol{r})$. Atomic regions are limited by zero flux surfaces (ZFS) as boundaries. A ZFS is defined by Equation (1) ($\boldsymbol{n}$ = unit vector perpendicular to the surface).

$$\nabla\rho(\boldsymbol{r})\boldsymbol{n}(\boldsymbol{r}) = 0 \text{ at every point of the surface} \quad (1)$$

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The nuclear positions are local maxima of the charge density and thereby attractors of the gradient vector field $\nabla\rho(\boldsymbol{r})$. Figure 4 presents the gradient vector field $\nabla\rho(\boldsymbol{r})$ (experiment and theory) in the molecular plane. The atomic volume can be calculated from the ZFS. The atomic charges

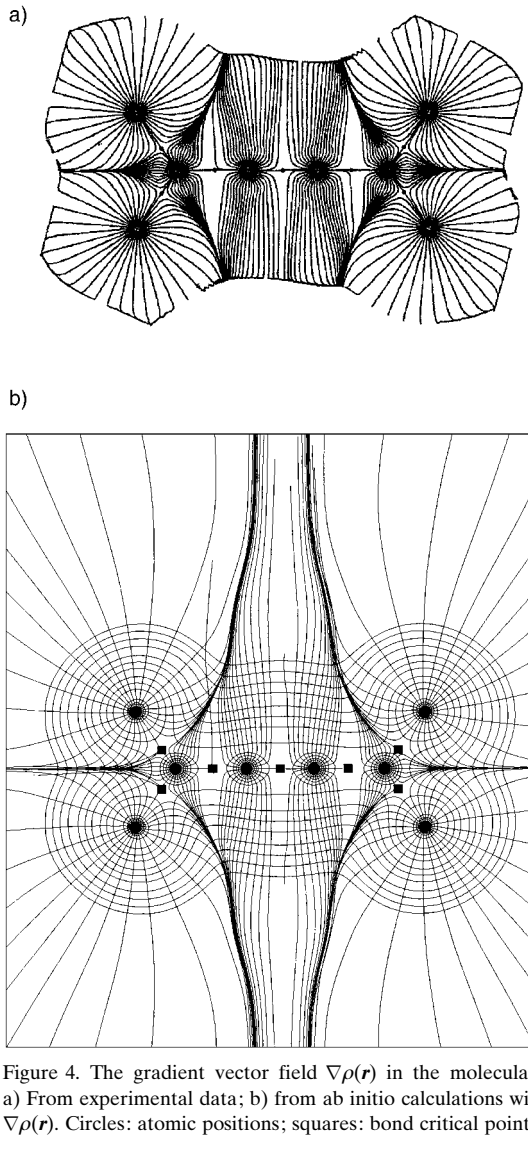

Figure 4. The gradient vector field $\nabla\rho(\boldsymbol{r})$ in the molecular plane of **3**. a) From experimental data; b) from ab initio calculations with isolines of $\nabla\rho(\boldsymbol{r})$. Circles: atomic positions; squares: bond critical points.

were obtained by integration of $\rho(\boldsymbol{r})$ over these volumes. The computation of atomic volumes and charges based on experimental data was performed by the use of the program TOPXD.[27, 28] The computation of these parameters by theory was performed with the program MORPHY 98.[29] Both, the experimental and theoretical results are in very good agreement (Table 2). The sum of the atomic volumes, derived by both methods, are equal to the cell volume[8] within an error of only 0.1 %. The high positive charge of +1.13 (experiment) and +1.267 (theory) at C1 gives an idea of the high reactivity (favored site for nucleophilic attack).

The electrostatic potential was calculated by using the method of Su and Coppens[30] on the basis of experimental data. This calculation considers a molecule of **3** extracted from the crystal but still containing the polarization effects induced by intermolecular interactions. Figure 5 displays an isosurface representation of the electrostatic potential. As expected, the negative potential is concentrated around the fluorine atoms and the positive potential along the molecular axis; the electrostatic potential corresponds to the crystal packing in a kind of a herring-bone motif.

Table 2. AIM volumes and charges of 3 (experiment/theory).[a]

Atom	Charge [e]	Volume [Å^3]
F1	−0.593/−0.636	15.58/15.94
F2	−0.591/−0.636	15.96/15.95
C1	+1.130/+1.267	7.86/7.47
C2	+0.053/+0.002	15.51/15.56

[a] Geometry optimization using B3LYP/6−311+G(3df).[31]

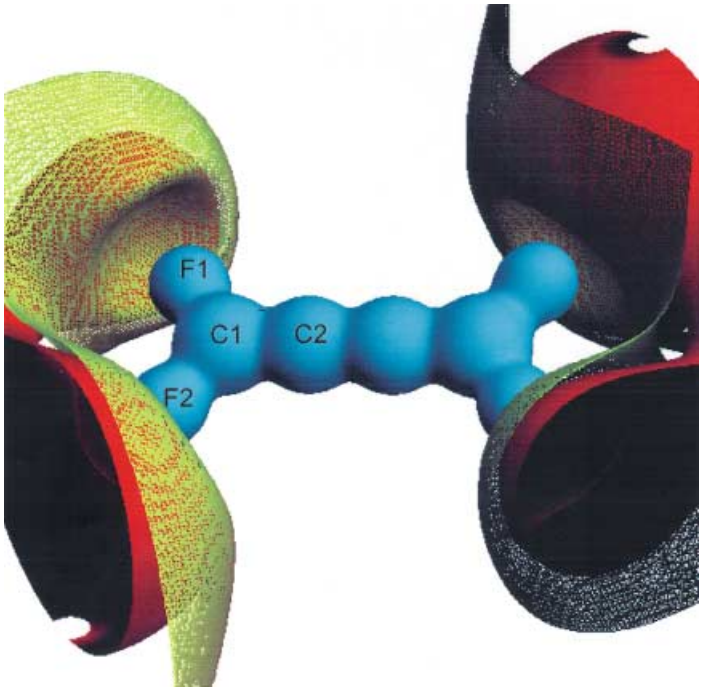

Figure 5. Three-dimensional distribution of the electrostatic potential based on experimental data for **3;** three isopotential surfaces are shown: blue 0.50, red −0.03, and net 0.00 e Å^{-1}.

Experimental Section

1: 1-Iodo-2,2-difluoroethene (13 g, 68.45 mmol) was added dropwise to activated zinc powder (8 g) in DMF (50 mL) at 60 °C and stirred for 1 h at 60 °C. The solution of the zinc reagent was added to $[Pd(PPh_3)_4]$ (2 g, 1.7 mmol, 2.5 mol %) in a second flask. After the mixture had been warmed to 75 °C, 1-iodo-2,2-difluoroethene (13 g, 68.45 mmol) was added slowly. The temperature of the reflux condenser was adjusted to 5 °C during the addition and to 20 °C after the addition. The reaction temperature was maintained at 75 °C for an additional 4 h. The product was collected as a colorless liquid in a trap kept at −78 °C. Purification by fractional condensation under vacuum (10^{-3} h Pa) yielded **1** (5.7 g, 45 mmol) in the trap kept at −120 °C. IR (gas): $\tilde{\nu}$ = 3122 vw, 1740 sh, 1715 vs, 1321 s, 1172 m 1140 w, 949 m, 922 s, 826 w 739 vw, 548 vw cm^{-1} (in agreement with literature data[32]); the ^{19}F and ^{1}H NMR spectra exhibit the pattern of an AA′BB′XX′ spin system which was already analyzed earlier.[9] ^{1}H NMR ($CDCl_3$): δ = 4.52 (m); ^{19}F NMR($CDCl_3$): δ = −86.77 (m), −88.09 (m); ^{13}C{^{1}H} NMR: δ = 72.3 (m), 155.6 (m).

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2: Compound **1** (5.4 g, 42 mmol) was condensed onto Br_2 (6.7 g, 42 mmol) in CH_2Cl_2 (10 mL) in a 100 mL glass flask. The reaction mixture was stirred for 5 h at ambient temperature. Fractional condensation under vacuum yielded **2** (6.2 g, 51.5 %) as a pale yellow liquid in the trap kept at $-60\,^{\circ}C$. ^1H NMR ($CDCl_3$): $\delta = 6.33$ (m); ^{19}F NMR ($CDCl_3$): $\delta = -50.3$ (m); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 114.2$ (t, $^1J(^{19}F,^{13}C) = 301$ Hz; CF_2), 129.3 ($^2J(^{19}F,^{13}C) = 27$ Hz, $^3J(^{19}F,^{13}C) = 7$ Hz; CH).

3: Compound **2** (1 g, 3.5 mmol) was passed over KOH which was filled into a U-shaped tube heated to $90\,^{\circ}C$ by evaporation under vacuum (10^{-3} h Pa). The volatile materials were collected in traps kept at $-78\,^{\circ}C$ (starting material **2**) and $-196\,^{\circ}C$ (**3**). This was repeated until practically all starting material **2** had reacted. A yield of 43 % was determined by $p/V/T$ measurement; m.p. $-130\,^{\circ}C$; ^{19}F NMR (CD_2Cl_2, 193 K): $\delta = -96.1$ (s); $^{13}C\{^{19}F\}$ NMR (CD_2Cl_2, 193 K): $\delta = 147.8$, 158.9; IR (gas): $\tilde{\nu} = 1732$, 1281, 973, 939, 536 cm^{-1}; Raman (250 mW, 193 K): $\tilde{\nu} = 2137$ m, 2103 vw, 1374 vw, 984 w, 951 w, 788 w, 724 m, 475 vs, 374 w, 351 m, 185 m cm^{-1}.

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[8] Crystal structure analysis. A SMART-CCD (BRUKER-AXS) diffractometer was used for the data collection. **1**: The structure was solved by direct methods and refined using full-matrix least-squares methods (SHELX97[34]); monoclinic, $P2_1/n$, $a = 5.8897(11)$, $b = 3.8205(7)$, $c = 10.971(2)$ Å, $\beta = 105.145(4)^{\circ}$, $V = 238.28(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.757$ g cm^{-3}, $T = 120$ K, 4297 reflections measured, 861 crystallographically independent ($R_{int} = 0.087$), and 794 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $2\theta_{max.} = 66^{\circ}$, $R(F_{obs}) = 0.037$, $wR(F^2)_{all} = 0.115$, 42 parameters, anisotropic displacement parameters, H atoms isotropic. **3**: monoclinic, $P2_1/c$, $Z = 2$, $a = 5.9421(2)$, $b = 6.3092(2)$, $c = 5.8648(2)$ Å, $\beta = 90.93(1)^{\circ}$, $V = 219.84(2)$ Å^3, $\rho_{calcd} = 1.87$ g cm^{-3}, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å (graphite monochromator), $T = 90$ K, $\sin\theta/\lambda_{max} = 1.29$ Å^{-1}, 25 284 reflections measured, 3686 crystallographically independent ($R_{int} = 0.028$), and 2571 reflections with $F_o > 3\sigma(F_o)$, $R(F_o) = 0.026$, $R_w(F_o) = 0.025$, The structure was solved by direct methods (SHELX97[34]). The multipole refinement[22] uses structure factors with $F_o(\boldsymbol{H}) > 3\sigma(F_o(\boldsymbol{H}))$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-169644 (**1**) and CCDC-169643 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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