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REGULAR ARTICLE

Cyclic dimers of tetrafluorobutatriene

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Abstract 1,1,4,4-Tetrafluorobutatriene polymerizes even at −78 °C within a short time yielding a red insoluble polymer. Possible closed-shell cyclic dimers and oligomers resulting from several reaction paths were analyzed by computational methods—with CCSDT/cc-pVTZ as the highest order calculation and several other calculations of lower level. For a better understanding of fluorination effects, the perhydrogen triene dimers were included in this study. The destabilization of the central cumulenic double bond of tetrafluorobutatriene relative to ethylene and the further destabilizing fluorine substitution makes the formation of most of the dimers exothermic with only one exception for the perfluoro derivatives. Astonishingly, the geometry of some of the discussed molecules is highly affected by fluorine substitution, while for others there is nearly no effect on the geometry of the carbon backbone. ^{19}F-NMR shifts of the potential dimers were calculated using the GIAO method.

Keywords Cumulenes · Dimerization · Coupled cluster · GIAO

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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1 Introduction

1,1,4,4-Tetrafluorobutatriene **1**, first prepared by Martin and Sharkey in 1959, is known to polymerize even at a temperature of −78 °C within a short time [1]. The pink to red polymer is insoluble in any common solvent. Attempts to prevent this undirected polymerization by addition of inhibitors, high dilution conditions, or very low temperature experiments, or a combination of these revealed no isolable dimeric or oligomeric species. Nevertheless, the polymerization in solution is observed by NMR spectroscopy, indicating a highly complex mixture of various compounds. Due to the unique properties of tetrafluorobutatriene, a defined polymer might show interesting properties since it is expected to be perfluorinated as well as hyperbranched [2].

Previously reported dimers of substituted butatrienes show an interesting structural diversity (as shown in Chart 1). While dimerization of the parent butatriene [3] results in a cyclooctadiyne [4], the all-chlorine triene [5] forms a [4]radialene-type dimer [5–7] and the all-phenyl triene [8] a head-to-head type dimer [9]. For the latter, the radialene-type dimer is also known but not as a product of dimerization, but from an unusual cyclization of an ate-type complex of a copper carbenoid derived from 1,1-dibromo-2,2-diphenylethylene [10].

In this respect, the nature of the potential closed-shell dimers and oligomers of tetrafluorobutatriene was investigated by computational methods.

The stabilities of the dimers were determined by CCSD(T)/cc-pVTZ//MP2/cc-pVTZ calculations with the GAUSSIAN 03 [11] program suite as the highest order calculations and on a variety of compound methods and lower-level computational methods. As reported previously, B3LYP calculations are inappropriate for the

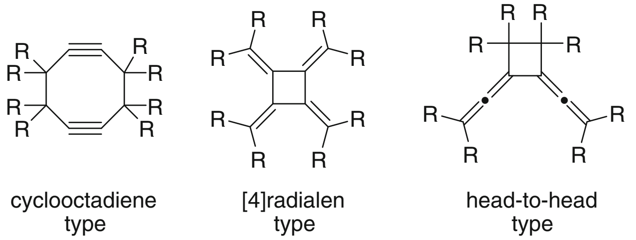


Chart 1 Types of butatriene dimers

presented problem due to the overestimation of the 1,2,3-triene stabilization energy [12, 13].

2 Results and discussion

Very recently, we reported on the partially hydrolyzed iron complex **2** shown in Chart 2 that contains two former tetrafluorobutatriene units and an inserted CO from $Fe(CO)_5$ [14].

Among others, the formation of this metal complex inspired us to study the dimerization reaction of **1** in more detail. Recently, a partially hydrolyzed trimer of tetrafluoroallene, the shorter cumulenic analogue of **1**, as well as a manganese complex of its dimer, could be structurally characterized [15].

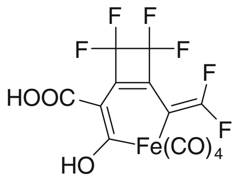
Additionally, mass spectrometry of a freshly oligomerized tetrafluorobutatriene sample showed signals attributed to trimers, tetramers, and even heptamers. In this work, we focused on the potential cyclic dimers since the iron complex is a direct hint to their existence. It should be mentioned that linear radical oligomerization/polymerization may also take place.

A first look at the structure of a symmetrically substituted 1,2,3-triene shows two potential reaction sites at the molecule. The reaction involves either the central double bond or one of the two terminal ones. Schemes 1 and 2 show the possible dimers.

Since the two molecules participating in a dimerization reaction do not have to react with the same reaction site, four potential dimers are imaginable as products of a formal [2 + 2]-cycloaddition reaction.

A symmetrical cycloaddition reaction results either in perfluoro[4]radialene **3** or in two different dimers substituted at the central cyclobutane ring by two fluoroallenyl units either on the same side of the ring (Z-Dimer, **7**) or on two opposite sites (E-Dimer, **8**).

Chart 2 Partially hydrolyzed iron complex 2



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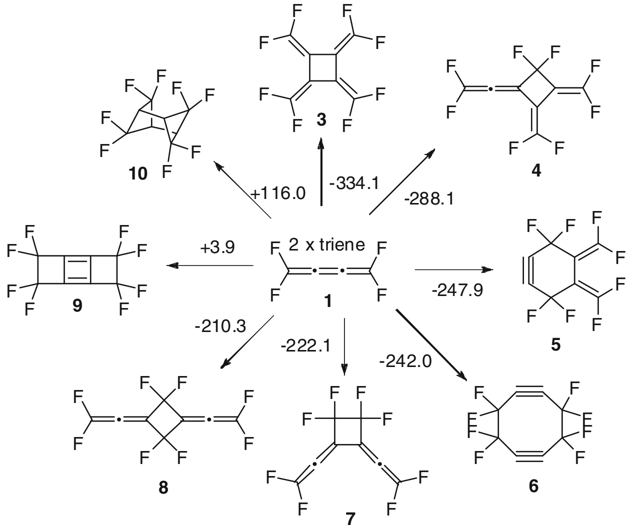
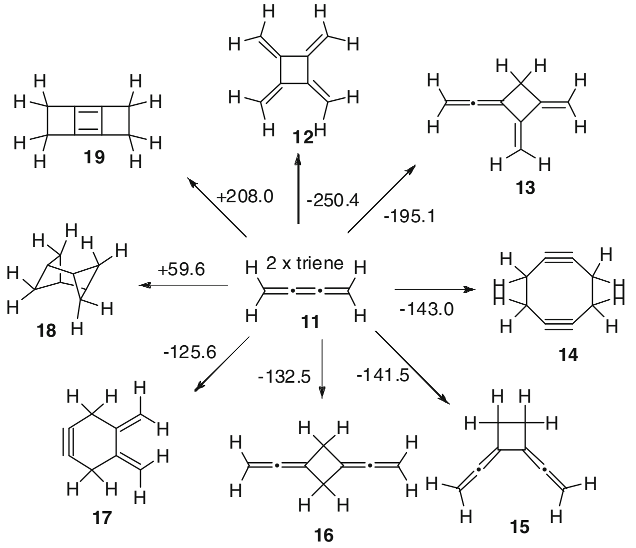


Scheme 1 Dimerization energies (kJ/mol) of several tetrafluorobutatriene dimers determined at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory including scaled ZPE correction (0 K) [16]



Scheme 2 Dimerization energies (kJ/mol) of several butatriene dimers determined at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory including scaled ZPE correction (0 K) [16]

An unsymmetrical cycloaddition on the other hand will produce some sort of head-to-middle dimer (**4**). The possibility of an intramolecular second [2 + 2]-cycloaddition either simultaneous to the first one or as a second step adds a fifth possible structure that will be further assigned as a “double dimer” **9**.

Thinking of a formal [4 + 2]-cycloaddition-reaction–Diels–Alder-type–the reaction product would be a bis(methylene)cyclohexyne **5**. Recently, we demonstrated that tetrafluorobutatriene readily undergoes Diels–Alder reactions with various enophiles [17]. A hypothetical second intramolecular Diels–Alder-type reaction would produce a sort of “double topped cyclohexadiene” **10**, clearly a highly unstable compound.

Finally, a potential biradical recombination reaction results in a cyclooctadiyne (**6**, known as the favored dimer [4] of the all-hydrogen 1,2,3-butatriene), which we investigated as the eight and last cyclic dimer.

As presented in Scheme 1, six of the potential closed-shell dimers are far more stable than the monomer, even such an exotic structure like the cyclohexyne structure **5**. The impressive instability of perfluorobutatriene is best displayed by the fact that a cyclobutadiene structure present in the “double dimer” **9,** i.e., a highly disfavored antiaromatic cyclic system [18], is in fact as unstable as the triene itself.

The most stable dimer is represented in the perfluoro as well as in the parent butatriene case by the radialene structures **3** and **12**. While it is 334.1 kJ/mol more stable than two of the triene molecules when the molecules are perfluorobutatrienes, it is only 250.4 kJ/mol more stable if all substituents are hydrogen atoms. In both cases, the molecule exhibits D_{4h}-symmetry with all atoms lying in the mirror plane.

In contrast to the perchloro[4]radialen, both structures are not puckered [6]. The difference in dimerization energy results most likely from the additional destabilization of the central double bond of tetrafluorobutatriene compared to that of butatriene [19].

Fluorination has a significant effect on both the bond lengths and the angles (Figs. 1, 2) of the perfluoro[4]radialen **3**. By fluorination, all C–C bond lengths decrease, the cyclobutane bond shrinkage of 0.013 Å represents the major effect, and the CF_2 vs. CH_2 bond angle is reduced by almost 7°. The difluoromethylene unit present in this molecule is also present in the molecules **4** and **5**. In all cases, the C–C double bond is approximately 1.33 Å in length, while the C–F bond is 1.31 Å in length. The F–C–F bond angle is approximately 111°. This demonstrates that the structure of the rest of the molecule has nearly no influence on the geometry of the difluoromethylene unit.

Interestingly, it was not the thermodynamically most stable dimer that was isolated by Kloster-Jensen and Wirz [4] from polymerized butatriene but instead the 1,5-cyclooctadiyne **14**. This finding is probably a result of the perfect suitability of the radialene **12** for subsequent Diels–Alder [20–22] reactions since all exocyclic double bonds are *s*-cis configurated. The diyne dimer was isolated in only 2% yield from a polymeric or oligomeric mixture.

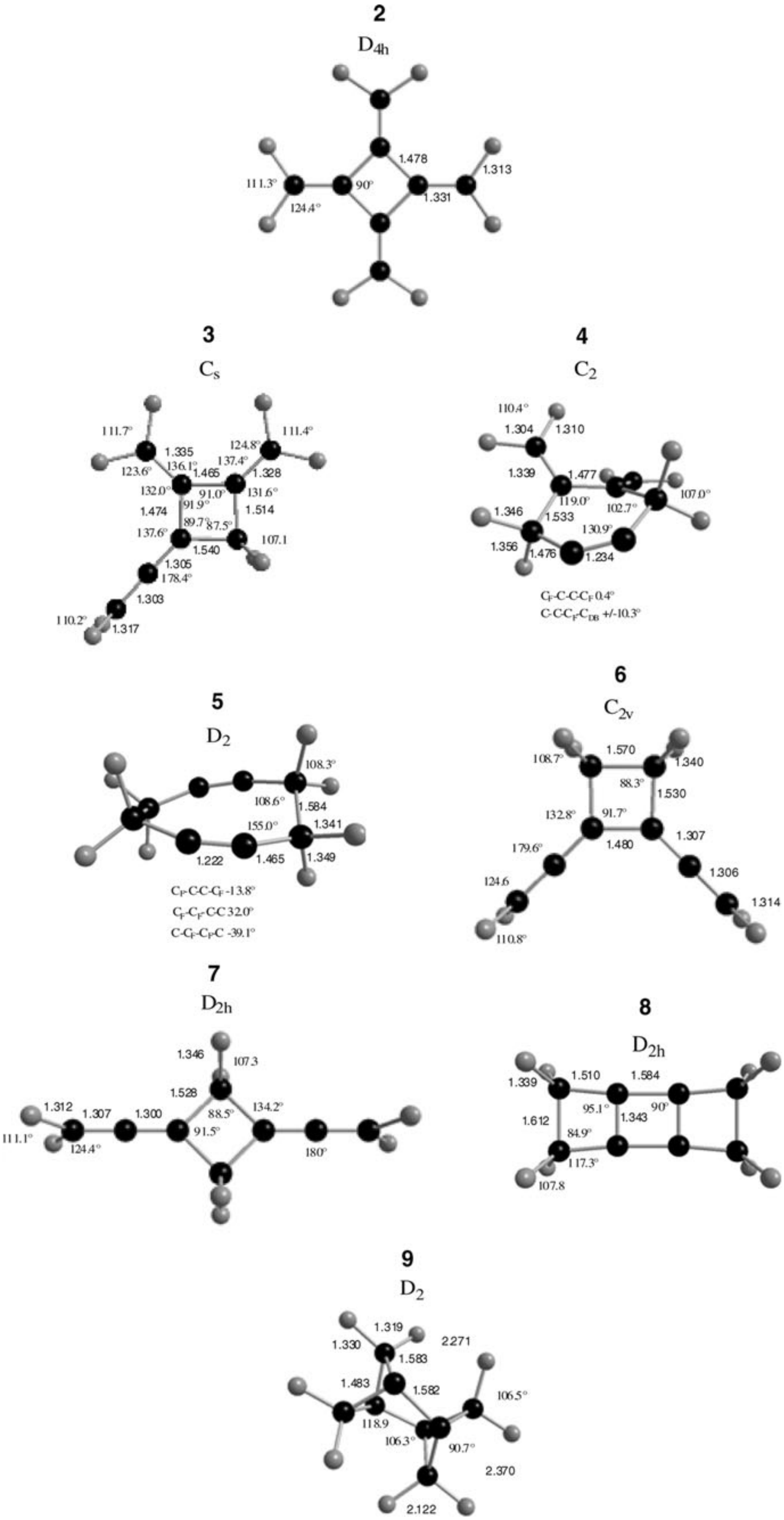
In both cases, the head-to-middle dimers **4** and **13** represent the second most stable structure. Again, the dimerization energy in the perfluoro case **4** is larger than the dimerization energy of **13** with a difference of 93.0 kJ/mol. The fluorination has major effects on the geometry of the molecule. Almost all C–C bonds in the cyclobutane ring of **4** are significantly shorter than in dimer **13** (0.011–0.018 Å). Both methylene double bonds as well as the terminal allenylidene C–C double bond are also shortened (up to 0.007 Å). The F–C-F bond angle at the allenylidene group is reduced by 8°. The maximum deviation of the cyclobutane ring angles from 90° decreases from 3.4° in the dimer **13** to 2.5° in the perfluorinated dimer **4**. The allenylidene group is also part of the molecules **7** and **8**. The structure of the rest of the molecule has little influence on the allenylidene unit. The C–C bond lengths are approximately 1.30–1.31 Å and C–F bond lengths 1.31 Å. The F–C-F angle matches 110–111°, similar to the angle in the difluoromethylene unit. It is only the C–C–C bond angle that is indeed slightly influenced. While in dimer **4** the perfect 180° allenylidene angle is distorted by 1.6°, it is nearly not distorted in the molecules **7** and **8**.

The diyne dimer is the third most stable dimer in the perhydrogen case and the forth most stable in the perfluorine case (structures **6** and **14**). It exhibits D_2-symmetry in both cases. The C–C triple (1.22 Å) bond as well as the adjacent single bond (1.47 Å) is nearly unaffected by the fluorination. This subunit appears again in the alkyne dimer **5** and **17** where both bonds are slightly longer by 0.01 Å. Consequently, the sp^3–sp^3 ring bond is affected by fluorination and elongated by 0.013 Å, resulting in a bond length of 1.584 Å. This bond length is significantly longer than the typical 1.54 Å for a carbon–carbon single bond. The bond angles in the ring differ only slightly with a maximum of 2°. All dihedral angles are stressed by a maximum of 7°.

It is very impressive that the alkyne dimer **5** in the all fluorine case is more stable than the diyne dimer **6** (5.8 kJ/mol). On the contrary, it is significantly less stable (17.4 kJ/mol) in the perhydrogen case (structures **14** and **17**). Both alkyne dimers have C_2-symmetry. One part of the molecule equals an 1,3-butadiene system similar to half of the radialene structure **3**. This part is in contrast to the radialene distorted by up to 53° in both cases (dihedral CCCC-angle). The single bond is shortened in the same manner as in the radialene, while the double bond is significantly less shortened (1.339 Å compared to 1.331 Å in the radialen).

The yne parts of both molecules exhibit equatorial and axial fluorine positions that are not equivalent. The axial fluorine–carbon bond is elongated by 0.01 Å compared to the equatorial one. The sp^2–sp^3 ring bond is elongated by 0.006 Å compared to the perhydrogen dimer **17**. The two remaining C–C bonds (triple bond and adjacent single bond) are again not affected by the fluorination. The same holds true for the angles within the molecule (less than 1° deviation). The only exception is the difluoromethylene angle that is reduced in the same manner as in the radialene.

Fig. 1 Optimized geometries (MP2/cc-pVTZ) of tetrafluorobutatriene dimers



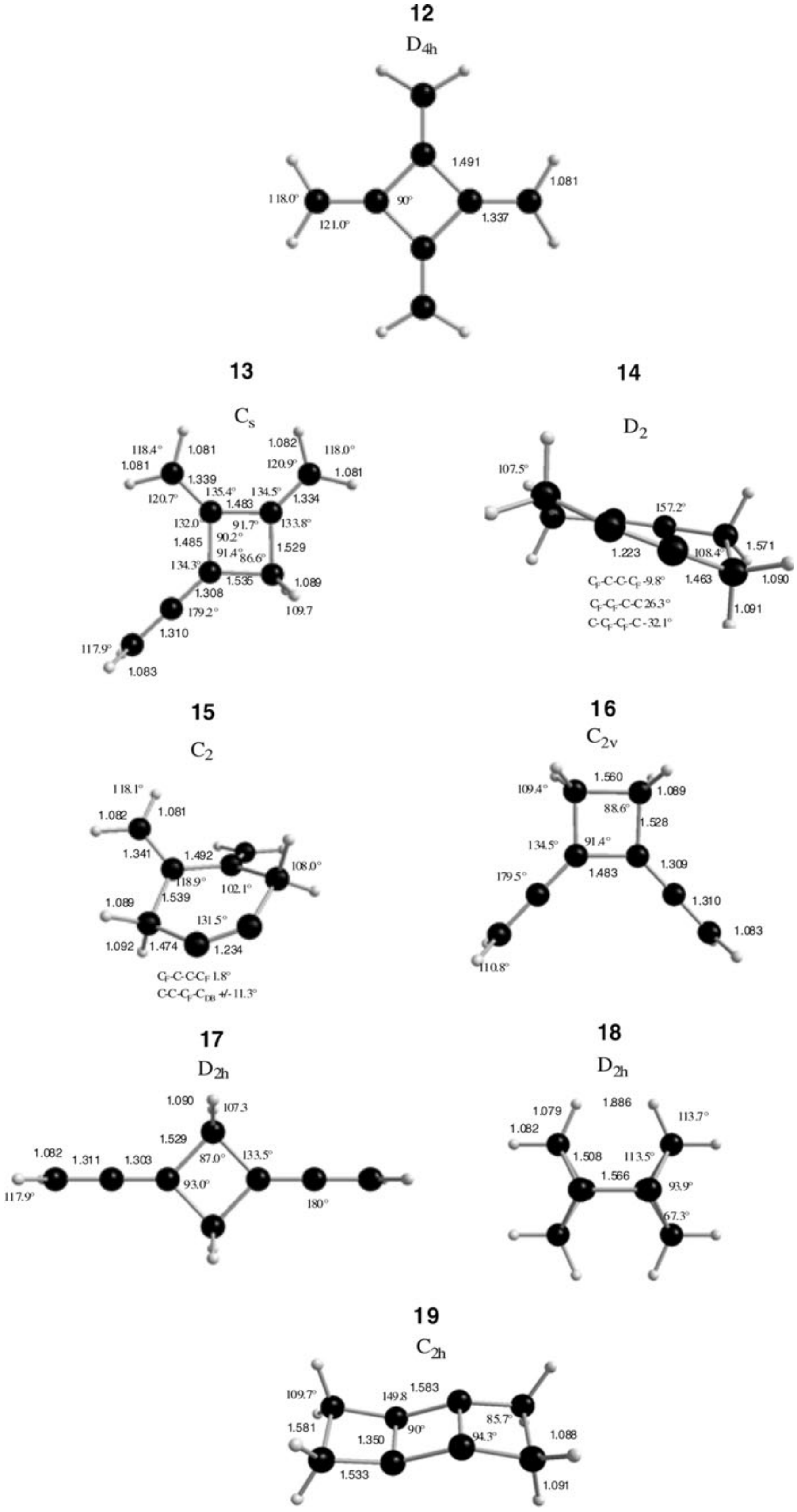


Fig. 2 Optimized geometries (MP2/cc-pVTZ) of butatriene dimers

The Z-dimer and the E-dimer (structures **7** + **8** and **15** + **16**) represent the last structures, resulting from a thermodynamically preferred dimerization. Both dimers are more stable than the alkyne dimer **17** in the perhydrogen case. The Z-dimer is more stable in the perfluoro (11.8 kJ/mol) as well as the perhydrogen case (9.0 kJ/mol). Most likely this results from the fact that the Z-dimers possess a conjugated allenic system, while the E-dimers have isolated allenic subunits. Consequently, a distortion of the central cyclobutane ring results from the conjugation. Regarding the perfluorinated molecules, the E-dimer has four identical 1.528 Å sp^2–sp^2 bonds while the Z-dimer has 2 bonds of 1.53 Å, an elongated bond between the two CF_2 groups 1.57 Å in length and a shortened single bond as part of the conjugated system between the two allenylidene subunits, 1.48 Å in length.

In comparison with octafluoro-1,2-dimethylenecyclobutane—the dimer of tetrafluoroallene—the cyclobutane ring bonds in the related Z-dimer are elongated by 0.02 Å. In contrast to that, the bond between the two CF_2 groups is identical in length to the analogous bond in the tetrafluoroallene dimer [23].

The sp^3–sp^3 ring bond is the only one in the cyclobutane subunit in which the Z-dimers **7** and **15** differ noticeably by fluorination. It is elongated by 0.01 Å if the molecule is fully fluorinated. Within the allenylidene subunits, C–C bond lengths differ only slightly. The cumulene bond on the ring side of the molecule is 0.006–0.007 Å shorter in the E-dimer **8** than in the Z-dimer **7**. This is again an effect of the conjugated allenic system on the Z-dimers The bond angles in the cyclobutane ring deviate about 1.5° from the ideal 90° in case of the fluorinated Z-dimer **7**, the non-fluorinated Z-dimer **15,** and the fluorinated E-dimer **8**. In the non-fluorinated E-dimer **16,** this deviation doubles to 3°. The allene units are not distorted within the E-dimers (**8** + **16**) and only slightly distorted within the Z-dimers (**7** and **15**) by a maximum of 0.5°.

The "double-dimer" **9** is only slightly destabilized in the perfluorine case in comparison with two free triene molecules (3.9 kJ/mol). In the perhydrogen case, double dimer **19** is the least stable one, destabilized by 208 kJ/mol in respect to two triene molecules. These energy differences again emphasize the additional destabilization of the cumulenic double bonds of perfluorobutatriene by fluorination.

The perfluorinated molecule **9** has D_{2h}-symmetry, and all carbon atoms are in the same plane. On the contrary, the perhydrogen dimer **19** has only C_{2h}-symmetry and the outer cyclobutene rings form two different planes, resulting in a C–C–C_H angle of 149.8°. The single bonds of the central cyclobutadiene ring in both cases are identical in length, while the double bonds are shortened by fluorination by 0.007 Å. The effect on the bond lengths of the outer cyclobutene rings is even more dramatic. The bond opposite to the double bond is stretched by fluorination by 0.031–1.612 Å. Furthermore, the C–H bonds are not equal: the *endo* C–H bond is 0.003 Å shorter than the *exo* C–H bond.

The last structures to be discussed are the double-capped cyclohexadienes **10** and **18**, respectively. They are highly destabilized in both cases. It is 116 kJ/mol less stable than two tetrafluorobutatriene molecules and just half, 59.6 kJ/mol, compared to two triene molecules. The non-fluorinated molecule has D_{2h}-symmetry which is distorted to D_2-symmetry by fluorination. As a result, the two equal bonds within the three membered rings (1.508 Å) of **18** become inequivalent (1.583 and 1.483 Å) in compound **10**. The central rectangle of the carbon atoms resembles much more a cyclobutane unit than a diene system. The C–C bond lengths are 1.566, 1.671 Å and 1.582, 1.765 Å in compound **18** and **10**, respectively. All fluorine atoms within molecule **10** are in close contact of 2.122 to 2.370 Å compared with the double van der Waals radii of 3.0–3.2 Å of fluorine [24]. The instability of the molecule clearly reflects these distances and distortion.

Higher spin states were also considered but do not play a significant role. Triplet states of all discussed molecules are at least 115 kJ/mol higher in energy with only one exception. The triplet states of both "double dimer" molecules are only slightly higher in energy compared with the singlet ground state (68 kJ/mol (F) and 20.3 kJ/mol (H), determined at the B3LYP/cc-pvtz level of theory).

To study methods and basis set effects, the dimerization energies of tetrafluorobutatriene were not only analyzed by the CCSD(T)/cc-pVTZ level of theory but also by the lower level methods (B3LYP [25, 26], B3PW91 [27], MP2) and compound methods. The complete basis set methods CBS-4 M [28], CBS-Q [29], CBS-QB3 [30], the G3 [31], and G3(MP2) [32] methods were chosen.

Values are only given for three different dimers in Table 1 and discussed below. The trends for all other dimers are comparable to this small test set.

As expected, B3LYP does not perform well on the given problem as it overestimates the triene stabilization energy and hence underestimates the dimerization energy. To our surprise, CBS-Q does also perform rather poorly. The other CBS and G3 methods in contrast perform very well. Taking the CCSD(T)/cc-pVTZ calculation as the most reliable value, B3LYP and CBS-Q deviate up to 123 kJ/mol and 61.9 kJ/mol, respectively. Whether one should take the CCSD(T) or G3 values as the best depends on preference, but they are known to give very similar results.

In the dimerization reaction of **1** forming the compounds **3**, **4**, **7,** and **8,** two double bonds are converted into four single bonds. Therefore, the relative amount of energy released per double bond during dimerization can be

Table 1 Dimerization energies (kJ/mol, 0 K) of perfluorinated butatriene-dependence on theoretical method

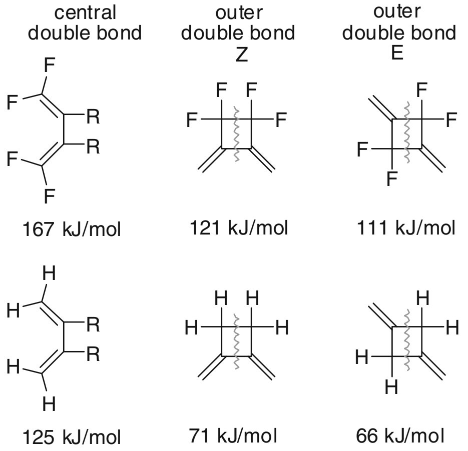
Level of theory/basis set	**3**	**9**	**7**
B3LYP/6-311G(d,p)	+53.9	+121.6	+61.4
B3LYP/6-311 ++G(3df,3pd)	+66.3	+123.0	+62.4
B3PW91/6-311G(d,p)	+23.6	+64.5	+37.0
MP2/6-311G(d,p)	−23.2	−21.8	−7.0
MP2/cc-pVTZ	−24.3	−25.8	−9.9
CBS-4 M	−11.8	−9.4	−5.1
CBS-Q	+61.9	+55.7	+43.1
CBS-QB3	−2.1	−5.4	−3.0
G3	+3.2	5.8	0.0
G3(MP2)	+9.0	+8.0	+3.8
CCSD(T)/cc-pVTZ//MP2/cc-pVTZ[a]	0.0	0.0	0.0

[a] Absolute values for CCSD(T): **3** −327.1, **9** +7.9 and **7** −222.0 kJ/mol

determined (shown in Scheme 3). The corresponding values for the hydrogen compounds are also given. Clearly observable is the additional destabilization of the triene double bonds by fluorination compared to the parent hydrogen compound.

As expected, the central double bond releases the highest amount of energy since two cumulenic centers are converted to two vinylic centers. The relative amounts of energy released per bond type are approximately additive.

To allow the identification of these compounds in the complicated mixture which is formed on the thermal decomposition of **1**, ^{19}F-NMR shifts were estimated by the gauge-independent orbital (GIAO) method using MP2/cc-pvtz [33–35]. The calculated shifts are given in Table 2. Since the calculated shift for tetrafluorobutatriene and a second reference compound 1,1,4,4-tetrafluorobutadiene differ only slightly from the observed value, the calculated shifts were not calibrated (tetrafluorbutatriene: 96.1 (93.4 calc.), 1,1,4,4-tetrafluorobutadiene: 80.1 and 86.8 (82.8 and 85.9 calc.) [36, 37]. The ^{19}F-NMR of freshly oligomerized tetrafluorobutatriene in solution shows two principal regions (between −60 and −95 ppm and between −105 and −120 ppm) where various signals appear. Based on calculations, cyclic dimers exhibit signals in the ^{19}F-NMR spectrum in exactly the same region. Nevertheless, it might be possible that linear oligomers derived by radical oligomerization are also responsible for some of the observed signals. Dimerizations of fluorinated double bonds may take place by a radical mechanism rather than a pericyclic mechanism, as recently proven by EPR spectroscopy for the cyclopolymerization of aromatic trifluorovinyl ethers [38]. EPR spectroscopy of a freshly prepared sample of tetrafluorobutatriene did not prove the existence of radical intermediates. Since most of the resulting dimers are themselves highly reactive molecules, it is not surprising that no specific dimer could be isolated up to now.



Scheme 3 dimerization energies released per bond type

Looking at iron complex **17**, it turns out that it is a partially hydrolyzed complex of the *Z*-dimer **22**. Two coordination sites of the central iron are occupied by the dimer. Whether the dimerization took place before coordination to the metal center or afterward remains unclear. *Z*-dimer **22** is the only dimer with two allenylidene units presented to the iron atom in a perfect cone angle and that is most likely the reason for its formation. Additionally, the cyclobutane side of the molecule is unreactive in contrast to the other dimers.

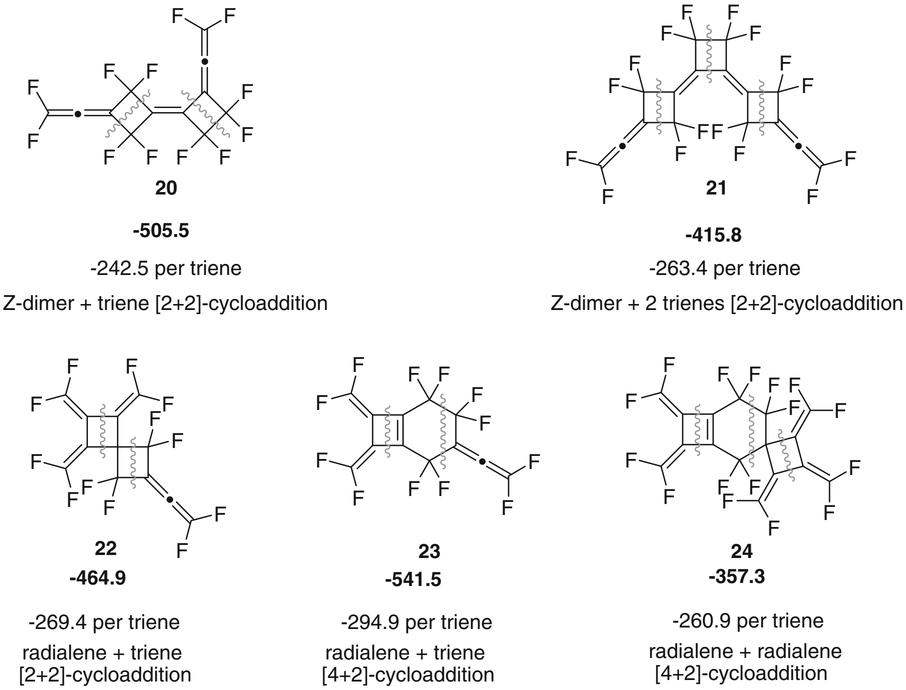
The next question to be answered concerns the fate of the dimers. Notwithstanding the highly destabilized dimers **9** and **10**, the question arises, why none of the six other potential dimers (**3**–**8**) has been isolated so far. Three of these dimers possess highly reactive allenylidene units, and three of them possess *s-cis* configurated butadiene units. Both units are potential sites for further reactions leading to an oligomeric or polymeric species. Assuming that most of these dimers are formed, reactions with **5** or any of its dimers yield an almost unlimited number of oligomeric species. This is in good agreement with the observed highly complex ^{19}F-NMR spectra with hundreds of detectable signals. This assumption also explains the insolubility of the polymer. Random buildup by different oligomerization paths forms a highly branched structure.

NMR findings indicate that the cyclic dimerizations take place. Theoretical calculations on dimers and oligomers are focused on the cyclic derivatives since an iron complex of a cyclic dimer was isolated and characterized previously.

Scheme 4 shows the plausible trimers and tetramers **20**–**24**. It is evident that subsequent cycloaddition reactions of these molecules with remaining triene are highly exergonic. Reactions between the dimers are also thermodynamically favorable as indicated by tetramer **39**. Additionally, it explains why the reaction does not stop at the

Table 2 Calculated ^{19}F chemical shifts

Dimer	^{19}F-shift(s)					
Radialene	−93.4					
Head-to-middle	−83.8	−85.6	−86.7	−87.3	−105.1	−113.8
Alkyne	−63.6	−64.0	−66	−88.5		
Diyne	−122.3	−28.1				
Z-dimer	−106.8	−128.1				
E-dimer	−93.1	−85.6				
Double dimer	−109.9					
Double-topped cyclohexadiene	−95.7	−103				



Scheme 4 oligomerization energies of tetrafluorobutatriene oligomers MP2/6-311G(d,p) level of theory including scaled ZPE correction (0 K)

dimeric stage but subsequent reactions lead to higher oligomers. Calculations were made at the MP2/6-311G(d,p) level of theory due to the size of the systems (up to 32 heavy atoms for the tetramers). As shown in Table 1, this theory level performs well on the given problem, only slightly overestimating the oligomerization energy.

3 Experimental

All calculations were made with the Gaussian 03 program package [11]. Geometries and vibrations were calculated at the MP2/cc-pVTZ level of theory (cc-pVTZ defined as correlation-consistent polarized valence-triple-ζ (Dunning) basis set) for the dimers and at the MP2/-6311G(d.p) level for trimers and tetramers. All structures represent local minima indicated by the absence of imaginary frequencies. For the tetramers, B3LYP/6-311G(d,p) level of theory was used for frequency calculation due to the size of the system. Final energies for the dimers were calculated at the CCSD(T)/cc-pVTZ (correlation-consistent polarized valence-triple-ζ (Dunning) basis set) level of theory and were corrected by the scaled MP2/cc-pVTZ zero point energy [16].

4 Conclusion

We were able to show that the polymerization of 1,1,4,4-tetrafluorobutatriene most likely involves the formation of cyclic dimers and oligomers. All dimers seem to be highly reactive and participate in further oligomerization reactions. Both the formation and further reactions of the dimers are highly exothermic processes.

It turned out that fluorination does have observable effects on the geometry of the discussed dimers as well as on their relative energies.

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