B.—3-Ethoxy-2-methylcyclohexene (0.18 mol) was treated as described above, yielding 6.6 g (38%) of mixed dienes. Glpc analysis yielded 41% **6**, 35% **7**, 22% **8**, and 2% **9**.

C.—3-Ethoxy-1-methylcyclohexene (0.18 mol) was treated as above yielding 7.0 g (41%) of mixed dienes. Glpc analysis yielded 18% **5**, 18% **6**, 46% **7**, 14% **8**, and 2% **9**.

Thermal Isomerization Reactions. General Procedure.—Mixtures of the three isomeric methyl-1,3-cyclohexadienes of known composition were added dropwise through a 22-mm Pyrex tube packed to a depth of 12 in. with $^{1}/_{16}$-in. Pyrex helices and externally heated at either 300, 325, or 350° as in the above elimination studies. The thermolysis products were isolated in a similar manner (90–95% recovery) and submitted to glpc analysis (Table II). Addition of 3-methylenecyclohexene did not affect the above reactions, and **8** survived quantitatively in all cases. Alumina studies were carried out under identical conditions of temperature and flow rate.

Registry No.—**1**, 27525-90-2; **2**, 27525-91-3; **3**, 27525-92-4; **4**, 23758-27-2; ethanol, 64-17-5.

The Molecular Structure of Perfluorobutyne-2 and Perfluorobutadiene-1,3 as Studied by Gas Phase Electron Diffraction

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The structures of two C_4F_6 isomers, perfluorobutadiene-1,3 and perfluorobutyne-2, have been determined by gas phase electron diffraction. The perfluorobutyne-2 was found to be linear with freely rotating CF_3 groups. The following parameters were determined: r_g values for $(C{\equiv}C) = 1.199 \pm 0.009$ Å; $(C{-}F) = 1.333 \pm 0.003$ Å; $(C{-}C) = 1.472 \pm 0.006$ Å; and $\angle CCF = 110.8 \pm 0.3°$. In contrast to the trans planar structure of butadiene-1,3, the perfluoro compound is in a nonplanar cisoid conformation, with a CCCC dihedral angle of 47.4 ± 2.4°. For the other structural parameters (r_g values): $(C{=}C) = 1.336 \pm 0.018$ Å; $(C{-}F) = 1.323 \pm 0.006$ Å; $(C{-}C) = 1.488 \pm 0.018$ Å; $\angle C{=}C{-}C = 125.8 \pm 0.6°$; $\angle F_7{-}C_2{=}C_1 = 121.0 \pm 1.8°$; and $\angle F_6{-}C_1{=}C_2 = 124.5 \pm 0.6°$. The above uncertainties were estimated errors set at three times the standard deviations as obtained from the converged least squares fitting of the calculated to the observed $qM(q)$ function.

Recent developments in experimental techniques, both diffraction and spectroscopic, and in computer reductions of data have led to accurate determinations of molecular structures and systematic studies of geometrical parameters as influenced by various types of substitution. It was recognized more than a decade ago[1,2] that C–C bond lengths vary with environment. Stoicheff[3] found empirical relations for C–C and C=C bond lengths in hydrocarbons as a function of the number of adjacent bonds or adjacent atoms. Little is known about the secondary effect,[4] of deviations due to adjacent heteroatoms, although Stoicheff[3] did notice a small change on the C=C bond length when Cl, Br, or F atoms were substituted for hydrogen. There is a suggestion of an "inductive" effect through two or more bonds by heteroatoms, but it has not been adequately documented. Of course, Stoicheff's relations do not apply to highly strained small ring molecules.[5,6]

Studies of fluoro compounds made in this laboratory have shown that substitution not only changes the length of the bond β to the site of substitution, but also alters the entire molecular conformation. For instance, perfluoroazomethane[7] was found to be cis instead of trans, as is the conformation for azomethane, and the third carbon atom of perfluoropropene may not be in the plane containing the $F_2C{=}C$ group.[8] This is a report on the molecular structures of two fluorocarbons, $F_3CC{\equiv}CCF_3$ and $F_2C{=}CFCF{=}CF_2$, which were investigated in order to shed additional light on the inductive effect produced by fluorine atom substitution.

Perfluorobutyne-2 was first studied by Sheehan and Schomaker,[9] who used visual estimates of plate densities. They reported (C–F) as 1.340 ± 0.020 Å, (C–C) as 1.465 ± 0.055 Å, (C≡C) as 1.22 ± 0.09 Å, and ∠FCF as 107.5 ± 1.0°, in agreement with corresponding geometrical parameters in $F_3CC{\equiv}CH$.[9] Infrared and raman spectra of $F_3CC{\equiv}CCF_3$ were obtained by Miller and Bauman.[10] Their data clearly indicate that D_{3d} selection rules were followed. Hence either the molecule has free internal rotation or a staggered conformation; they were unable to distinguish between them.

The structure of butadiene-1,3 with various degrees and types of substitution has been extensively investigated. In general, these were found to be in the trans-planar conformation.[11–14] However, in the cases with trihalogenation at the 1,1, and 3 positions, skew conformations were observed.[15] For the hexasubstituted species, there is strong evidence for a cisoid structure.[16,17] Robin and Brundle recorded the optical spectra of perfluorobutadiene-1,3 and interpreted their data as indicative of a cisoid structure, with the skeleton carbon dihedral angle of approximately 42°.[18] In view of this departure from the expected behavior of a conjugated system, it was

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[1] G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955).

[2] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

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[8] (a) J. Karle, A. H. Lowrey, C. F. George, and P. D'Antonio, private communication; (b) C. H. Chang, R. F. Porter, and S. H. Bauer, unpublished work.

[9] W. F. Sheehan, Jr., and V. Schomaker, *J. Amer. Chem. Soc.*, **74**, 4468 (1952).

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[13] R. A. Beaudet, *ibid.*, **42**, 3758 (1965).

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[17] J. C. Albright and J. Rud Nielsen, *J. Chem. Phys.*, **26**, 370 (1957).

[18] M. Robin and C. R. Brundle, *J. Amer. Chem. Soc.*, **92**, 5550 (1970).

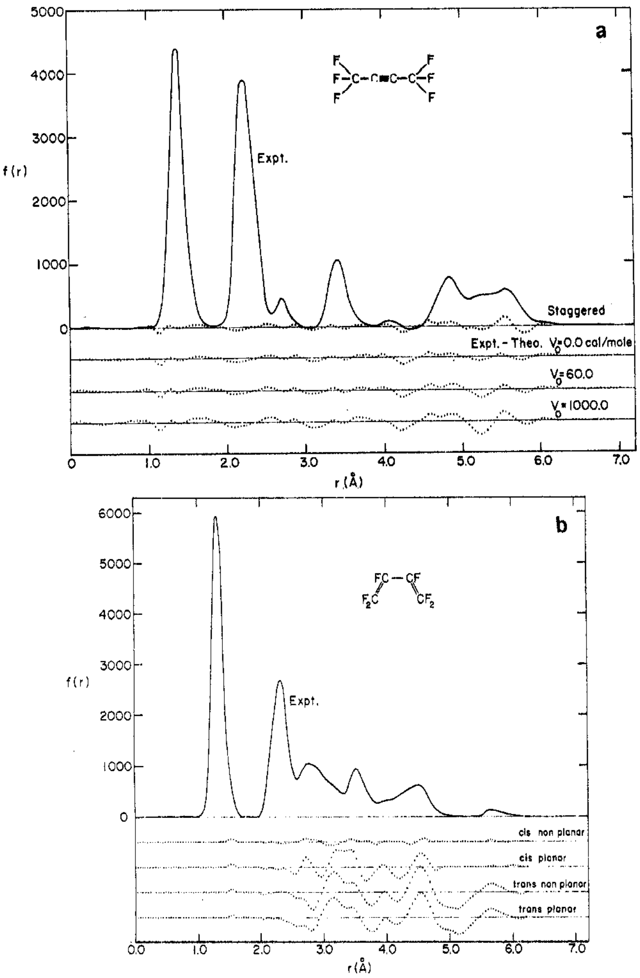

Figure 1.—The refined experimental radial distribution curves and difference curves between the experimental and calculated values for various models. In Figure 1a, the staggered conformation ($V_0 \rightarrow \infty$) appears to give a slightly better fit then does the curve with $V_0 = 1000$. This was possible only with unacceptably large l_{ij}'s.

decided to investigate the structure of this molecule more fully by electron diffraction.

Experimental Section

Both C_4F_6 were available commercially from Pennisular Chem-Research, Gainesville, Fla. Infrared spectra of the gases agreed with published data.[10,17] For each compound, three sets of convergent mode diffraction photographs were recorded with the Cornell dual mode apparatus.[19] Data were obtained for q = 4–30 Å^{-1} at 25 kV, at a nozzle-to-plate distance of 253 mm; q = 15–60 Å^{-1} at 60 kV, at a nozzle-to-plate distance of 253 mm; and q = 40–126 Å^{-1} at 60 kV, at a distance of 125 mm. All patterns were recorded on 4 × 5 in. Kodak electron image plates. Wavelengths and nozzle-to-plate distances were determined from analyses of magnesium oxide powder patterns taken concurrently with the sample photographs.

For each set of experimental conditions, a pair of plates, one light and one dark, were microphotometered on a modified double-beam Jarrel-Ash densitometer, fitted with a rotating stage.[20] The digital signal was recorded on punched paper tape at intervals of 100 μ for the short nozzle-to-plate distance and at 200 μ for the long distance. The conversion of the recorded transmittances to optical densities and then to intensities[21] was carried out on a modified DEC PDP-9 computer.

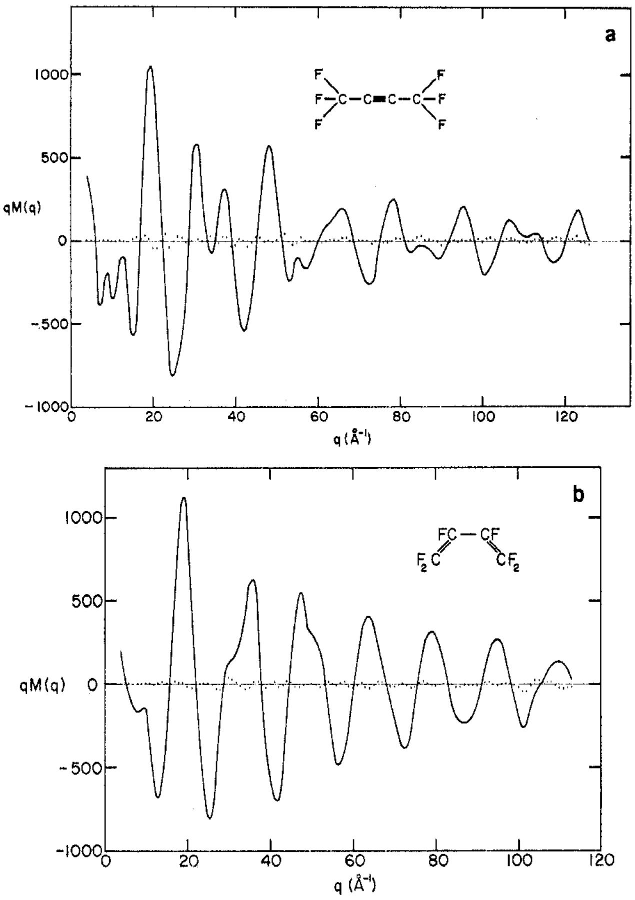

Figure 2.—The reduced experimental molecular scattering curves, $qM(q)$, and the difference curves between the experimental and the calculated values.

Structure Analysis.—The reduced diffracted intensities were analyzed by least squares fitting of the experimental $qM(q)$ curve[22] [$q \equiv (40/\lambda)\sin(\phi/2)$]. The atomic elastic and inelastic scattering factors of Tavard, *et al.*,[23] were used, as was the phase shift correction of Bonham and Ukaji.[24] In the least squares analysis a nondiagonal weighting matrix was inserted in the manner described by Morino.[25] Corrections were introduced to compensate for the anharmonicity of the molecular vibrations.[26,27] A very simple and rapid algorithm[28] for the calculation of the molecular cartesian coordinates was employed throughout the analysis. The radial distribution curve was used for background refinement;[29] the curve was also used to obtain initial parameter estimates.

Perfluorobutyne-2.—Reduced experimental data from q = 4–126 Å^{-1} have been included in the microfilm edition (Table IVa);[30] they have also been plotted along with the reduced backgrounds in Figure 4a.[30] The corresponding radial distribution curve is shown in Figure 1a, and the experimental molecular intensity curve $qM(q)$ is shown in Figure 2a. "Static" models were constructed in the preliminary least squares refinements by as-

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(29) I. L. Karle and J. Karle, *ibid.*, **17**, 1052 (1949).

(30) Table IVa,b, Table Va,b, and Figures 4a,b will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

suming that the molecule had either D_{3h} (eclipsed) symmetry, D_{3d} (staggered) symmetry, or an intermediate conformation with very large mean square amplitudes in the region 5.0–6.0 Å, contributed by long nonbonded F$\cdots$F distances. Three bond lengths, C–C, C≡C, and C–F, and the valence angle CCF were inserted as independent geometrical parameters; these were refined simultaneously with seven root mean square amplitude parameters, l_{ij}'s. They are l_{C-C}, $l_{C_1\cdots C_3}$, l_{C-F}, $l_{C_2\cdots F_5}$, $l_{C_3\cdots F_5}$, $l_{C_4\cdots F_5}$, $l_{F_5\cdots F_6}$; the atom designations are shown in Figure 3.

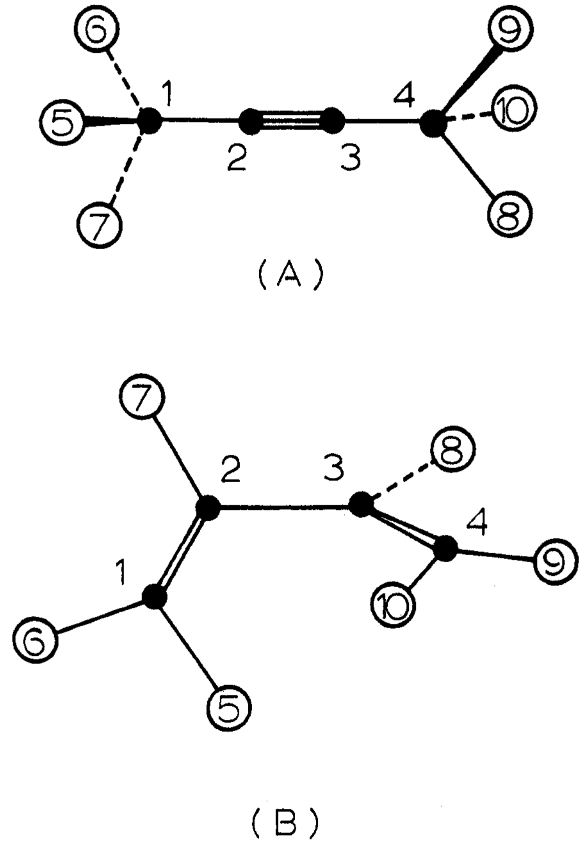

Figure 3.—Atom designation for $F_3CC{\equiv}CCF_3$ (A) and $CF_2{=}CFCF{=}CF_2$ (B).

Initial values for these 11 parameters were obtained from the RDR curves, reported bond lengths, and calculated root mean square amplitudes.[31] Since the l_{ij}'s for the long F$\cdots$F atom pairs are relatively insensitive to the least squares refinement, their values were constrained to those calculated by Elvebredd.[31] The optinum set of parameters for $F_3CC{\equiv}CCF_3$ are listed in Table I. As shown in Table Va,[30] correlations between the selected 11 parameters are small.

The question whether this molecule is best represented by a staggered conformation or by a free internal rotation model was investigated by careful study of the RDR curve in the region from r = 5.0–6.0 Å, contributed solely by the nonbonded F$\cdots$F distances. A threefold potential function, $V(\phi) = (1/2)V_0(1 + \cos 3\phi)$, was used to approximate the rotational barrier, and a Boltzmann satistical weight function inserted to weight all rotational conformations. The staggered form was assumed to be the minimum energy conformation. Then a sequence of "dynamic" models was tested by choosing a range of V_0's, while constraining the $l_{F\cdots F}$'s = 0.140 Å. The difference curves shown in Figure 1 indicate that, within the limits of our analysis, $V_0 \approx 0$; *i.e.*, the molecule has free internal rotation.

Perfluorobutadiene-1,3.—The experimental intensity curve for this model has been plotted in Figure 4b.[30] Several conformations were investigated, ranging in torsional angle from trans planar to cis planar. The experimental RDR and difference curves for these models are plotted in Figure 1b. All the trans models predict a sizable peak in the RDR curve which is 0.3 Å beyond the last peak in the experimental curve. Least squares analysis of the angular parameters proceeded without difficulty. However, determination of the bonded parameters proved troublesome. Examination of the correlation matrix (Table Vb)[30] reveals that the C–F and C═C bond lengths are −0.97 correlated. An iterative process was followed, in which first one of these two distances was constrained and all other parameters allowed to vary, and then the other distance was constrained, again allowing all parameters to vary. After several iterations it was possible to insert concurrent variations in both the C–F and C═C distances, along with the other parameters. It was essential that the initially inserted approximate values be quite close to the final model before this simultaneous variation converged. The RDR difference curve for the final model is labeled cis nonplanar in Figure 1b. The experimental $qM(q)$ curve and difference curve are shown in Figure 2b.

Table I

Least Squares Structure Parameters for $F_3CC{\equiv}CCF_3$ and $F_2C{=}CFCF{=}CF_2$

$F_3CC{\equiv}CCF_3$		$F_2C{=}CFCF{=}CF_2$	
C–C	1.472 ± 0.002[a]	C–C	1.488 ± 0.006
C≡C	1.199 ± 0.003	C═C	1.336 ± 0.006
C–F	1.333 ± 0.001	C–F	1.323 ± 0.002
∠CCF	110.8 ± 0.1	∠CCC	125.8 ± 0.2
l_{C-C}	0.053 ± 0.004 (0.046)[b]	$\angle C_1C_2C_7$	121.0 ± 0.2
$l_{C\equiv C}$	0.036 (fixed) (0.036)	$\angle C_3C_1F_6$	124.5 ± 0.6
$l_{C_1\cdots C_3}$	0.055 ± 0.006 (0.050)	∠CCCC	47.4 ± 0.8
$l_{C_1\cdots C_4}$	0.058 (fixed) (0.058)	l_{C-C}	0.051 (fixed)
l_{C-F}	0.046 ± 0.001 (0.044)	$l_{C=C}$	0.039 (fixed)
$l_{F_5\cdots F_6}$	0.058 ± 0.001 (0.058)	l_{C-F}	0.054 ± 0.001
$l_{C_2\cdots F_5}$	0.062 ± 0.002 (0.073)	$l_{C_2\cdots F_6}$	0.074 ± 0.002
$l_{C_3\cdots F_5}$	0.098 ± 0.003 (0.099)	$l_{F_7\cdots F_8}$	0.079 ± 0.003
$l_{C_4\cdots F_5}$	0.115 ± 0.006 (0.128)	$l_{C_1\cdots F_8}$	0.093 ± 0.006
		$l_{F_6\cdots F_7}$	0.077 (fixed)
		$l_{F_5\cdots F_6}$	0.054 (fixed)
		$l_{F_7\cdots F_9}$	0.134 (fixed)
		$l_{C_3\cdots F_{10}}$	0.128 (fixed)
		$l_{C_2\cdots F_9}$	0.109 (fixed)
		$l_{C_1\cdots C_3}$	0.107 (fixed)
		$l_{F_6\cdots F_{10}}$	0.129 (fixed)
		$l_{F_8\cdots F_9}$	0.135 (fixed)
		$l_{C_3\cdots C_4}$	0.110 (fixed)

[a] These are least squares standard deviations. [b] Calculated value from I. Elvebredd, *Acta Chem. Scand.*, **22**, 1606 (1968).

Discussion

Perfluorobutyne-2.—The C–F bond length of 1.333 ± 0.003 Å agrees well with previous studies of $F_3CC{\equiv}CH$[9] (1.335 ± 0.01 Å), $F_3CC{\equiv}CCH_3$[32] (1.340 Å), and $F_3CC{\equiv}CCF_3$[9] (1.340 ± 0.020 Å). However, the C≡C separation is shorter and the C–C bond lengths are longer in $F_3CC{\equiv}CCF_3$ than in $H_3CC{\equiv}CCH_3$.[4] As shown in Table II, this parallels the relative magnitudes in HC≡CF and $HC{\equiv}CCF_3$, and it is also interesting to notice that in the N═N system, the N═N bond is shortened and the N–C bond is lengthened by fluorine substitution. More accurate determinations of bond lengths in these molecules are required to substantiate these comparisons. Except for $l_{C_2\cdots F_6}$ the mean square amplitudes of vibration obtained in this study agree with those calculated by Elvebredd, within the experimental uncertainties.

Perfluorobutadiene-1,3.—The C–F bond length in this compound (1.323 ± 0.006 Å) is consistent with dimensions reported for similar species; its magnitude does not appear to be particularly sensitive to its molecular environment. Twisting of the molecules

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(31) Irene Elvebredd, *Acta Chem. Scand.*, **22**, 1606 (1968).

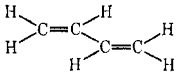
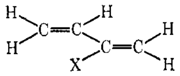
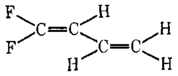
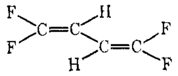
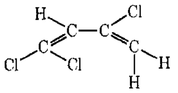
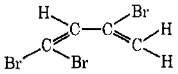
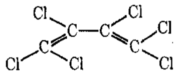
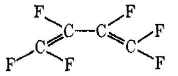
(32) V. W. Laurie, *J. Chem. Phys.*, **30**, 1101 (1959).

TABLE II

Compd	C≡C {N=N}	Δ (C≡C) Δ {N=N}	C–C {C–N}	Δ (C–C)	∠XCC	Ref
HC≡CH (r_0)	1.207					*a*
		−0.009				
HC≡CF (r_0)	1.198					*b*
HC≡CCH$_3$ (r_0)	1.207		1.458		110° 30′	*c*
		−0.006		+0.006		
HC≡CCF$_3$ (r_0)	1.201		1.464		107.5 ± 1.0° (FCF)	*d*
H$_3$CC≡CCH$_3$ (r_g)	1.213 ± 0.001		1.467 ± 0.001		110.7 ± 0.4°	*e*
		−0.014		+0.005		
F$_3$CC≡CCF$_3$ (r_g)	1.199 ± 0.009		1.472 ± 0.006		110.8 ± 0.3°	*f*
HN=NH (trans)	{1.238 ± 0.007}					*g*
		−0.024				
FN=NF (cis)	{1.214 ± 0.010}					*h*
H$_3$CN=NCH$_3$ (trans) (r_g)	{1.254 ± 0.003}		{1.474 ± 0.002}			*i*
		−0.018		+0.016		
F$_3$CN=NCF$_3$ (cis) (r_g)	{1.236 ± 0.015}		{1.490 ± 0.006}			*i*

[a] M. T. Christensen, D. R. Easton, B. A. Green, and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **238**, 15 (1956). [b] J. K. Tyler and J. Sheridan, *Proc. Chem. Soc.*, 119 (1960). [c] L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, **51**, 619 (1955). [d] W. F. Sheehan, Jr., and V. Schomaker, *J. Amer. Chem. Soc.*, **74**, 4468 (1952). [e] See ref 31. [f] This work. [g] A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968). [h] R. K. Bohn and S. H. Bauer, *Inorg. Chem.*, **6**, 309 (1967). [i] C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 5313 (1970).

TABLE III

Compd	Structure	Dihedral angle (φ = 0° cis planar)	Ref
Butadiene-1,3		φ = 180°	*a, b*
Haloprene X = F, Cl, Br, I		φ = 180°	*c, e*
1,1-Difluorobutadiene-1,3		φ = 180°	*f*
1,1,4,4-Tetrafluorobutadiene-1,3		φ = 180°	*g*
1,1,3-Trichlorobutadiene-1,3		φ = 50°	*e*
1,1,3-Tribromobutadiene-1,3		φ = 50°	*e*
Perchlorobutadiene-1,3		0° < φ < 90°	*d*
Perfluorobutadiene-1,3		φ = 42° φ = 47°	*h* *i*

[a] A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958). [b] D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962). [c] D. R. Lide, Jr., *J. Chem. Phys.*, **37**, 2074 (1962). [d] G. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953). [e] A. A. Bothner-by and D. Jung, *J. Amer. Chem. Soc.*, **90**, 2342 (1968). [f] R. A. Beaudet, *J. Chem. Phys.*, **42**, 3758 (1965). [g] R. A. Beaudet, *J. Amer. Chem. Soc.*, **87**, 1390 (1965). [h] C. R. Brundle and M. Robin, private communication. [i] This work.

from a planar conformation minimizes the π overlap conjugation; this accounts for the shortening of the C=C separation from 1.344 Å in butadiene-1,3[33] to 1.336 ± 0.018 and lengthening of Å, the C–C distance from 1.467 Å to 1.488 ± 0.018 Å. The large uncertainties in the two carbon–carbon bond lengths is attributed to the fact that their scattering is greatly overshadowed by the scattering from the six carbon–fluorine pairs.

The 47.4 ± 2.4° dihedral angle for the cisoid model is in quantitative agreement with the spectroscopic work of Brundle and Robin.[18] The unlikelihood of a completely cis structure due to fluorine–fluorine overlap has been discussed.[34] Examination of Table III documents the trend from trans planar to cisoid. It appears that 1,1,3 type of interaction is necessary for twisting the molecule out of the trans conformation. Perfluorobutadiene-1,3 has in effect two 1,1,3 interactions.

Registry No.—Perfluorobutyne-2, 692-50-2; perfluorobutadiene-1,3, 685-63-2.

Acknowledgments.—We wish to thank Dr. H. Mair for his initial work on perfluorobutyne-2. This work was supported partly by the National Science Foundation under Grant No. GP-7794 and the Material Science Center, Cornell University.

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