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Cooperativity effects in cyclic trifluoromethanol trimer: an ab initio study

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Abstract

For the first time, ab initio molecular orbital calculations are used to provide information on the dimer and cyclic trimer of trifluoromethanol. In order to better understand the system, the monomer is also investigated. Molecular geometries, binding energies, and harmonic vibrational frequencies of monomer, dimer and trimer are investigated at the Hartree–Fock Self-Consistent level using the 6-31+G(d,p), 6-31++G(2d,2p), and the 6-311++G(2d,2p) basis sets. Because the primary goal of this study is to examine cooperativity effects, particular attention is given to parameters such as O–O distances, electronic charge densities at the bond critical points, shifts in the stretching frequencies of the donor O–H bond, and the length of the donor O–H bond. The cooperativity factor found using the HF/6-311++G(2d,2p) method ranged from 1.49 to 1.90 for the three hydrogen bonds in the cyclic trimer. © 1998 Elsevier Science B.V.

Keywords: Ab initio; Hydrogen bonding; Cooperativity; Perfluoromethanol

1. Introduction

Trifluoromethanol has recently begun to receive attention based on its well-known role in the degradation of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). HFCs and HCFCs are beginning to replace the infamous chlorofluorocarbons (CFCs) which are widely believed to lead to the destruction of stratospheric ozone [1]. Trifluoromethanol is believed to be one of the eventual degradation products of HFCs and HCFCs, and is therefore, a compound that requires some attention.

CF₃OH has not been extensively studied by either theoretical or experimental means [[2], and references

therein]. Experimentally, it has often been considered too unstable to prepare and store in bulk. However, Asher et al. [2] prepared CF₃OH according to the procedure defined by Seppalt et al. [3,4] and found no decomposition after many days of storage at liquid nitrogen temperature. This suggests that trifluoromethanol may, in fact, be studied more extensively through experiment, either as a precursor or a check to theoretical work.

The primary goal of this study is to investigate the cooperativity of the cyclic trifluoromethanol trimer. Cooperativity was first described by Frank and Wen [5] in 1957 as the enhancement of a hydrogen bond by the formation of another hydrogen bond with either the donor or acceptor of the first hydrogen bond. Cooperativity is important because it helps explain

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Table 1

Total energies (E) given in hartrees, scaled zero-point energies (ZPE), basis set superposition error (BSSE), binding energies and enthalpies of dimerization and trimerization at 0 K (ΔH_0^0) in kcal mol⁻¹, O–O distances (R_{oo}) and elongation donor O–H bond with respect to the monomer (Δr) given in Å, cooperativity (A_b) as defined by Eq. (2)

6-31+G(d,p)	E	ZPE	BSSE	D_e	ΔH_0^0	R_{oo}	Δr	A_b
CF ₃ OH	– 411.6682	17.80						
(CF ₃ OH) ₂	– 823.34307	36.20	0.47	4.19	3.59	2.989	0.003	
(CF ₃ OH) ₃	– 1235.02148	54.80	1.26	10.59	9.19	2.866	0.006	1.52
						2.865	0.006	1.52
						2.865	0.006	1.95
6-31++G(2d,2p)								
CF ₃ OH	– 411.68007	17.80						
(CF ₃ OH) ₂	– 823.36561	36.10	0.28	3.43	2.93	3.024	0.003	
(CF ₃ OH) ₃	– 1235.05396	54.60	0.64	8.63	7.43	2.905	0.005	1.32
						2.905	0.005	1.32
						2.905	0.005	1.66
6-311++G(2d,2p)								
CF ₃ OH	– 411.78747	17.80						
(CF ₃ OH) ₂	– 823.58098	36.30	0.67	3.79	3.09	3.029	0.003	
(CF ₃ OH) ₃	– 1235.37723	54.60	1.38	9.30	8.10	2.896	0.005	1.49
						2.896	0.005	1.49
						2.896	0.005	1.90

the behavior of hydrogen bonded systems. As far as we know, no experimental or theoretical work has been done on trifluoromethanol dimers or trimers, no direct comparison can be made. However, a similar study was carried out for the cyclic trimer of methanol by Mó et al. [6], from which results are very comparable.

2. Computational details

All ab initio molecular orbital results were calculated using the Gaussian 94 program [7]. In order to efficiently complete this systematic study, the monomer was first fully optimized at the Hartree–Fock (HF) level of theory using the 6-31+G(d,p) basis set. The dimer and trimer structures at this basis set were fully optimized using the geometries of the corresponding methanol (dimer and trimer) found by Mó et al. [6] as starting points. These optimized structures were then used as starting geometries for the full optimization using the HF/6-31++G(2d,2p) and HF/6-311++G(2d,2p) basis sets. Table 1 lists the total energy of each optimized structure. Schematics of the dimer, and trimer optimized using

the HF/6-311++G(2d,2p) basis set can be seen in Fig. 1. Harmonic vibrational frequencies were also computed for each optimized structure using the same basis set as was used for geometry optimization. If the frequencies seen in Table 2 were to be compared with experimental results, a scaling factor of 0.89 is required caused by the well known overestimation of vibrational frequencies at the Hartree–Fock level of theory [8].

As well as providing the total energy of each structure, Table 1 lists the zero point energy (ZPE) which has been scaled by the empirical factor of 0.89. The dimerization and trimerization energies are easily determined by the following equation:

$$D_e = E(nmer) - nE(CF_3OH) \quad n = 2, 3 \quad (1)$$

The dimerization and trimerization enthalpies at 0 K are found by using the same formula, except that the energies are corrected by adding the corresponding scaled ZPE to each one. Basis set superposition error (BSSE) is also indicated on Table 1, as calculated using the full counterpoise method [9].

In order to better understand the key bonds within each structure, the bond critical points have been located. At these bond critical points, the charge

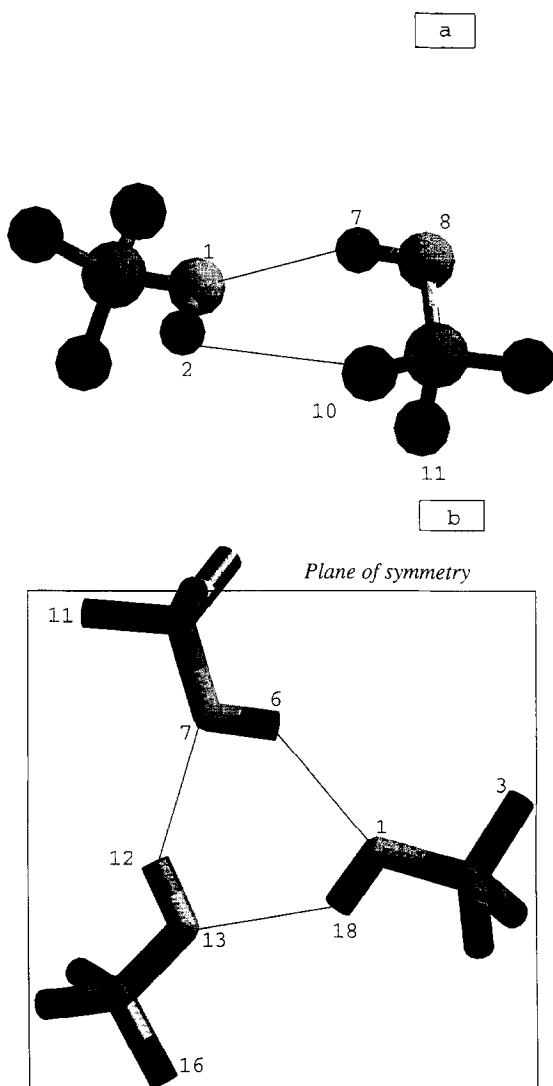


Fig. 1. Optimized structures obtained at the HF/6-311 + + G(2d,2p) level of theory (See appendix for *z*-matrix information). (a) Trifluoromethanol dimer. O(1)–H(7) = 2.177 Å; F(10)–H(2) = 2.669 Å; F(11)–H(2) = 3.502 Å; O(1)–H(7)–O(8) = 149.3 deg; F(10)–H(2)–O(1) = 101.7 deg. (b) Trifluoromethanol trimer (C_{3h}). Numbered atoms lie in the plane of symmetry. O(1)–H(6) = O(7)–H(12) = O(13)–H(18) = 2.145 Å; O(1)–O(7) = O(7)–O(13) = O(13)–O(18) = 2.896 Å; F(3)–H(6) = F(11)–H(12) = F(16)–H(18) = 3.466 Å; O(7)–H(6)–O(1) = 104.8 deg; H(12)–O(7)–H(6) = 135.3 deg.

densities, ρ , have been determined. This was implemented through the Gaussian 94 program [7], using the Atoms in Molecules theory of [10]. These charge densities indicate the strength of the bond

and are therefore useful in showing cooperative effects.

Finally, the cooperative effects themselves will be highlighted using several different indications. In order to quantitatively determine the cooperativity factor [11], the same method will be used as Mó et al. [6] highlighted in previous work. It is defined as the relative shifts in the frequency of the donor O–H stretching mode:

$$A_b = \Delta\nu_{OH} / \Delta\nu'_{OH} \quad (2)$$

where $\Delta\nu_{OH}$ is the change in the stretching frequency of the dimer with respect to the monomer, and $\Delta\nu'_{OH}$ is the change in the stretching frequency of the trimer with respect to the monomer.

3. Results and discussion

3.1. Geometries

It is instantly apparent when looking at the HF/6-311++G(2d,2p) optimized structures in Fig. 1 that the cyclic trimer contains a high degree of symmetry. This is mirrored by the harmonic vibrational frequencies, and the dipole moment of 0.002 D. It should be noted, however, that this structure does not represent a minimum on the potential energy surface, as three imaginary frequencies were found. The trimers optimized at the two lower basis sets showed a very similar structure, but no imaginary frequencies were present.

The cyclic trimer of trifluoromethanol has a distinctly circular shape. In fact, the plane defined by the three oxygen atoms is actually a plane of symmetry. A C_3 axis of rotation perpendicular to the plane of symmetry is also found. No C_2 axes are present, so this cyclic trimer belongs to the C_{3h} point group. In this structure all three trifluoromethanol molecules are equivalent and arranged in such a way as to minimize the repulsive interaction among the trifluoromethyl groups. The O–O distances are all equal to 2.896 Å and the H...O distances are equal to 2.145 Å. The corresponding OH...O and HO...H angles are all equal to 135 deg and 104.8 deg respectively. The latter angle is basically the same as that of a free molecule of water. In contrast, the three hydrogen bonds in the cyclic trimer of methanol

Table 2

Harmonic vibrational frequencies (cm⁻¹)

	^a CF ₃ OH	^a (CF ₃ OH) ₂ *		^a (CF ₃ OH) ₃		
O–H stretch	4157	4129	4101	4072	4072	4048
C–O stretch	1465	1451	1479	1503	1437	1437
O–H bend	1233	1245	1252	1287	1255	1255
O–H torsion	260	300	414	445	390	390
Other modes	1551	1548	1572	1559	1559	1550
	1347	1370	1331	1373	1363	1363
	989	992	987	996	992	992
	688	693	687	699	692	692
	677	678	676	682	680	677
	651	660	655	677	659	659
	491	494	531	586	510	510
	478	486	478	496	485	485
Intermolecular modes		111, 68, 42, 27, 21, 13		117, 104, 104, 83, 36, 36, 26, 26, 26, 10, 9, 8		
	^b CF ₃ OH	^b (CF ₃ OH) ₂ *		^b (CF ₃ OH) ₃		
O–H stretch	4158	4135	4102	4084	4072	4048
C–O stretch	1448	1436	1462	1484	1437	1437
O–H bend	1235	1243	1247	1272	1255	1255
O–H torsion	266	297	408	438	390	390
Other modes	1550	1548	1572	1556	1559	1550
	1322	1344	1308	1346	1363	1363
	983	986	981	990	992	992
	692	696	692	702	692	692
	679	680	679	681	680	677
	655	663	658	679	659	659
	490	492	522	552	510	510
	480	487	480	497	485	485
Intermolecular modes		101, 64, 39, 26, 20, 10		111, 95, 95, 73, 34, 34, 27, 22, 22, 11, 7, 7		
	^c CF ₃ OH	^c (CF ₃ OH) ₂ *		^c (CF ₃ OH) ₃		
O–H stretch	4153	4129	4104	4080	4080	4060
C–O stretch	1449	1436	1462	1486	1422	1422
O–H bend	1242	1252	1255	1284	1258	1258
O–H torsion	264	309	407	435	368	367
Other modes	1556	1556	1577	1565	1565	1558
	1340	1362	1324	1365	1356	1356
	993	996	991	1000	996	996
	695	700	694	705	699	699
	682	683	681	683	682	681
	657	665	660	681	663	663
	494	497	525	547	504	504
	482	490	483	499	489	489
Intermolecular modes		102, 66, 42, 29, 22, 13		110, 96, 96, 76, 31, 31, 26, 23, 23, – 5, – 15, – 15		

^a HF/6-31+G(d,p) results^b HF/6-31++G(2d,2p) results^c HF/6-311++G(2d,2p) results

* The first column of the dimer frequencies refers to the acceptor molecule.

Table 3

Charge densities (in e.a.u⁻³) at the bond critical points (ρ_c), as well as dipole moment (μ) given in Debyes

	6-31+G(d,p)				6-311++G(3d,3p)			
	C–O	O–H	HB	μ	C–O	O–H	HB	μ
CF ₃ OH	0.342	0.383		2.155	0.346	0.396		2.021
(CF ₃ OH) ₂	0.348 ^d	0.377 ^d	0.0146	2.064	0.352 ^d	0.390 ^d	0.0123	1.872
	0.333 ^a	0.378 ^a			0.339 ^a	0.392 ^a		
(CF ₃ OH) ₃	0.335	0.371	0.0151	0.003	0.341	0.386	0.0131	0.002
	0.335	0.371	0.0151		0.341	0.386	0.0131	
	0.335	0.371	0.0151		0.341	0.386	0.0131	

^d Donor; ^a acceptor.

found by Mó et al. [6] at the HF/6-311++G(2d,2p) level of theory, are not strictly equivalent. In this trimer, two methyl groups are in the same side of the O–O–O plane. Resulting from steric effects, the O–O distance corresponding to that between these two methyl groups is about 0.01 Å longer than the other two O–O distances. Likewise, the corresponding O...H distance is about 0.025 Å longer than the other two O...H distances. The HO...H angles are between 89 deg and 91 deg, and the OH...O angles between 149 and 150 deg.

The dimer of CF₃OH also has some significant differences compared to methanol. The most striking feature is the deviation in linearity of the hydrogen bond. Trifluoromethanol has a hydrogen bond angle of 149 deg, while the hydrogen bond of methanol was found to be nearly 177 deg by Mó et al. [6]. The donor and acceptor C–O–H angles are 0.3 deg smaller and 0.6 deg larger respectively than in the monomer. In addition, the hydrogen atom of the acceptor points preferably toward one of the fluorine atoms of the donor group. In fact, the H(2)–F(10) distance is ~2.67 Å which is ~0.80 Å smaller than the H(2)–F(11) distance (Fig. 1). All these geometrical features suggest the existence of a secondary hydrogen bond between a fluorine atom in the donor monomer and the OH group of the acceptor. Of course, the fluorine substitution also has some effect on the length of the C–O bond in the monomer. The fluorines make the carbon charge more positive, and thus shorten the C–O bond length from 1.400 Å in methanol [6] to 1.328 Å in trifluoromethanol. Dimerization produces a noticeable increase in the length of the acceptor C–O bond, while decreasing the donor C–O bond.

Upon trimerization, the C–O bond lengths return to a value that are fairly similar to the monomer. These observations are mirrored in the charge densities seen in Table 3. Upon dimerization, ρ_c for C–O increases for the donor molecule and decreases for the acceptor. An increase in ρ_c signals a stronger bond, and thus a shorter bond length. Upon trimerization, the charge density for the C–O bond moves closer to that of the monomer.

As was expected, the donor O–H bonds are lengthened upon dimerization and trimerization. This elongation of the donor O–H bond is shown in Table 1. In fact, cooperative effects may be quantified by these Δr values. A comparison of Δr between methanol and trifluoromethanol shows similar results. For trifluoromethanol, this value is 0.003 Å and 0.005 Å for the dimer and trimer, respectively. These values for methanol are slightly higher, at 0.004 Å and about 0.006 Å [6].

3.2. Harmonic vibrational frequencies

The harmonic vibrational frequencies for the monomer, dimer, and trimer at each basis set are listed in Table 2. As one would expect, there is a sizeable shift in the stretching mode of the donor O–H bond upon formation of a dimer. This shift is a red shift of 49 cm⁻¹ at the HF/6-311++G(2d,2p) basis set. This is very typical of hydrogen bonded systems, but 20 cm⁻¹ less than reported by Mó et al. for methanol [6]. However, the acceptor O–H stretching frequency also undergoes a red shift that is fairly sizeable. At the same basis set, this shift is 24 cm⁻¹.

This is much greater than the 5 cm^{-1} red shift seen upon the dimerization of methanol [6].

Another important mode of vibration which can be easily compared to that of methanol is the C–O stretch. In the case of the trifluoromethanol dimer, it is seen that the C–O acceptor band is red shifted about 13 cm^{-1} , while the donor C–O frequency is shifted to the blue by 13 cm^{-1} . This result compares very favorably with that seen for the case of methanol [6].

Dimerization also has strong effects upon the O–H torsional and O–H bending modes. Both torsional modes are blue shifted by very significant amounts; the acceptor is shifted by 55 cm^{-1} , while the donor is shifted by 143 cm^{-1} . The donor O–H bending mode is shifted upward 13 cm^{-1} , and the acceptor is also blue shifted by 10 cm^{-1} .

Many of the same qualitative trends seen upon dimerization are also noted upon trimerization of CF_3OH . The O–H stretching frequencies are affected by trimerization even more than dimerization. The red shift ranges from 73 cm^{-1} to 93 cm^{-1} . This increase in the red shift of the donor O–H stretch is one method of determining that cooperative effects are present. In fact, this frequency is actually used to quantify the cooperativity factor as seen in Eq. (2). The effect of trimerization also increases the shifts seen in the C–O stretching frequency. Two of the C–O stretches are red shifted by 27 cm^{-1} , while the other is blue shifted by 37 cm^{-1} . This is qualitatively the same trend as was seen upon dimerization. The same effect is seen in the torsional frequencies, and the O–H bending modes. Torsional frequencies are shifted to the blue by 103 cm^{-1} to 171 cm^{-1} . The O–H bend is also shifted to the blue, but by 16 cm^{-1} up to 42 cm^{-1} .

3.3. Cooperative effects

There are many parameters which can be indications of cooperative effects in a hydrogen bonded system. One of these is the O–O distance between each species of an n mer. Obviously, there is a tendency for the oxygen atoms of each molecule to repel one another. However, when the hydrogen bonding is favorable enough, it will slightly overcome this tendency. As seen in Table 1, the O–O distance moves from 3.029 \AA to 2.896 \AA when moving from the dimer to the trimer. This is a large decrease,

though it should be noted that this is partially due to the formation of a cyclic trimer. When compared to the cyclic trimer of methanol, the O–O distance of trifluoromethanol is at least 0.031 \AA smaller [6]. The decrease in the O–O distance for CF_3OH upon trimerization is also significant, at nearly 0.05 \AA more than the decrease seen in methanol [6].

The effects of cooperativity as noted by the O–O distance are backed by the cooperativity factor which was determined by Eq. (2). At the highest basis set, the cooperativity factor ranged from 1.49 to 1.90. This is slightly larger than that found for methanol, which was found to be from 1.42 to 1.84 by Mó et al. [6]. However, the dimerization and trimerization energies are smaller than those found in methanol [6]. One must also consider that the BSSE should be taken into account when looking at the dimerization and trimerization energies and enthalpies found in Table 1. After correction for the BSSE using the counterpoise method [9], the dimerization and trimerization energies of perfluoromethanol are $0.60\text{ kcal mol}^{-1}$ and $3.13\text{ kcal mol}^{-1}$ respectively, smaller than those of methanol. Finally, charge densities as calculated at the bond critical points are an indication of cooperative effects. These charge densities are shown in Table 3. One important trend to look for is the decrease of ρ_c for the O–H bond upon dimerization and trimerization. Because charge density is an indication of electron density, and thus bond strength, this decrease implies that the O–H bond is being slightly weakened. The weakening of this bond is due to the favorable hydrogen bonding. Cooperativity lowers the charge density even more, which is why ρ_c is lower in the trimer than the dimer for the O–H bond. Another indication of cooperativity is seen in the strengthening of the hydrogen bond in the trimer as opposed to the dimer. This is seen as an increase in ρ_c at the hydrogen bond upon trimerization.

4. Conclusions

This paper is, to our knowledge, the first ab initio study to explore dimer and trimer clusters of trifluoromethanol. The structures were systematically optimized, and harmonic vibrational frequencies were calculated from analytical second derivatives. Dimerization and trimerization caused noticeable

shifts in the frequencies of many vibrational modes. Not surprisingly, those involving the O–H bond were most dramatically affected. The shift in the donor O–H stretching frequency was used to calculate the cooperativity factor, which ranged from 1.49 to 1.90.

Cooperative effects were also evident by shorter O–O distances, increased donor O–H bond lengths, and charge densities computed at the bond critical points. Qualitatively, all of these parameters were also observed in the cyclic methanol trimer. Of course, some of the quantitative results were different, but the cooperativity factor is quite similar for each species [6]. This indicates that cooperativity is similar for methanol and trifluoromethanol.

The binding energies found for the dimer and trimer of CF_3OH are smaller than those found for methanol [6], as is the trimerization enthalpy at 0 K.

The study of correlation effects on the vibrational frequencies of the dimer and the trimer of perfluoromethanol as well as the search for a true minimum for the cyclic trimer at the HF/6-311++G(2d,2p) will be the subject of future work.¹ We will investigate whether the inclusion of correlation effects supports a symmetric cyclic trimer of perfluoromethanol corresponding to a minimum on the potential energy surface as found at the Hartree–Fock level and the two lower basis sets used in this paper, or rather a saddle point as found at the HF/6-311++G(2d,2p) level.

Acknowledgements

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¹ Recently we carried out a full HF/6-311 + + G(2d,2p) optimization for the cyclic trimer of methanol using the C_{3h} structure of $(\text{CF}_3\text{OH})_3$ as the initial guess. The final optimized structure was found to conserve the C_{3h} symmetry. Even though this structure is only 0.17 kcal mol⁻¹ less stable than the one found by Mó et al. [6], two imaginary frequencies were found. This result shows the flatness of the potential energy surface. It also suggests that a true minimum for the cyclic $(\text{CF}_3\text{OH})_3$ system may be closer to the minimum found in the methanol trimer. We are currently investigating this possibility.

Appendix

Z-matrix given by the HF/6-311++G(2d,2p) method. (distance in Å, angles in degrees)

Perfluoromethanol monomer

1	C						
2	O	1	1.328				
3	H	2	0.943	1	110.51		
4	F	1	1.299	2	108.81	3	180.00
5	F	1	1.314	2	112.04	3	60.00
6	F	1	1.314	2	112.04	3	-60.00

Perfluoromethanol dimer

1	O						
2	H	1	0.945				
3	C	1	1.334	2	111.14		
4	F	3	1.309	1	111.79	2	-60.00
5	F	3	1.309	4	107.31	1	-122.81
6	F	3	1.299	4	108.83	5	-117.62
7	H	1	2.177	3	135.80	2	167.04
8	O	7	0.946	1	149.25	3	-162.50
9	C	8	1.321	7	110.18	1	28.14
10	F	9	1.323	8	111.95	7	-56.36
11	F	9	1.314	10	106.30	8	-123.24
12	F	9	1.298	10	108.13	11	-116.29

Perfluoromethanol trimer

1	O						
2	C	1	1.331				
3	F	2	1.300	1	108.43		
4	F	2	1.310	3	108.68	1	121.80
5	F	2	1.310	3	108.68	4	116.40
6	H	1	2.145	2	143.44	3	-0.16
7	O	6	0.947	1	135.26	2	-179.89
8	C	7	1.331	6	111.81	1	-179.94
9	F	8	1.310	7	111.86	6	60.17
10	F	8	1.310	9	107.25	7	123.01
11	F	8	1.300	9	108.68	10	117.31
12	H	7	2.145	8	143.44	6	-179.89
13	O	12	0.947	7	135.21	8	179.97
14	C	13	1.331	12	111.81	7	-179.86
15	F	14	1.310	13	111.86	12	60.16
16	F	14	1.300	15	108.68	13	-119.68
17	F	14	1.310	15	107.25	16	-117.31
18	H	1	0.947	2	111.81	3	179.97

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