

## ***Ab initio* calculations of fundamental frequencies for isomeric difluorobenzenes**

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**Abstract.** *Ab initio* computations of harmonic frequencies for the three isomeric difluorobenzenes have been carried out using the MO technique with split valence 3-21 G basis set. The computed frequencies have been compared with the experimental frequencies. The computed frequencies have been scaled with empirical scale factors in order to correct for the systematic errors originating in the limitations of the theoretical model. It was found necessary to use different scaling factors for the planar and non-planar modes.

**Keywords.** Isomeric difluorobenzenes; harmonic frequencies; molecular orbital technique.

### **1. Introduction**

The accurate prediction of vibrational spectra of polyatomic molecules has been one of the goals of quantum theoretical studies. In recent years, *ab initio* molecular orbital theory has become a powerful tool for the calculation of vibrational frequencies of polyatomic molecules (Pulay 1981). Most of these studies are based on the method developed by Pulay (1969, 1977) in which forces acting on the nuclei for a molecular structure slightly displaced from its equilibrium configuration are directly calculated. The second derivatives of the potential energy with respect to the positional coordinates of the nuclei are then obtained numerically. Techniques and computer programmes featuring direct analytical evaluation of the second derivatives of the Hartree-Fock energy with respect to the nuclear coordinates have also been developed and shown to be practical (Pople *et al* 1979; Thomsen and Swanston 1973).

It is now realized that calculations employing split valence basis sets may yield vibrational frequencies which agree well with experimental values (after being scaled) as regards their general behaviour even though calculated values are usually 10–12% higher (Pulay and Meyer 1971; Pulay and Meyer 1974; Pople *et al* 1981; Wiberg and Wendoloski 1984). The calculated frequencies are often adjusted via simple scaling procedures so as to give a 'best fit' to the experimental vibrational

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frequencies. Two scaling procedures are in use. One of these (Pople *et al* 1981) directly scales the calculated frequencies while the second procedure scales the various force constants (Pulay and Meyer 1974). Scaling of the force constants grants us more flexibility in checking/modifying the vibrational assignments, especially if data from one molecule are to be used for other similar molecules. The direct scaling of the frequencies is also often used, since effects due to electron correlation, anharmonicity corrections etc. are not known well enough. Pople *et al* (1979) have pointed out that the whole concept of empirical scaling is of course conceptually unsatisfactory and is continued only as a practical necessity.

The present article reports the *ab initio* computation of the harmonic vibrational frequencies of the three isomeric difluorobenzenes using the HF/3-21 G basis set. A CNDO/2 study of the out-of-plane vibrations of these molecules has been made earlier by Torok *et al* (1976). It has already been noted by Pople *et al* (1981) that the use of the HF/3-21 G basis set provides accuracy comparable to the improved basis set HF-6-31 G\* and is also less expensive.

## 2. Method of calculation

The vibrational frequencies have been calculated at Hartree-Fock level using 3-21 G basis set (Binkley *et al* 1979). Let the system consists of  $N$  nuclei having  $3N$  nuclear coordinates. The energy  $E$  is calculated as a function of the  $3N$  nuclear coordinates  $x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N$ . Let us denote these by  $R_i$  ( $i = 1, 2, 3, \dots, 3N$ ). If  $m_i$  be the mass associated with the coordinate  $R_i$  so that  $m_1 = m_2 = m_3$  is the mass corresponding to the first nucleus and so on and  $r_i$  be a small change in  $R_i$ , then the classical equation of motion is

$$m_i \ddot{r}_i = - \sum_j f_{ij} r_j, \quad (1)$$

$f_{ij}$  being the force constants. In terms of mass weighted force constants,

$$f'_{ij} = f_{ij} m_i^{-1/2} m_j^{1/2} \quad (2)$$

and (1) can be written as

$$\ddot{r}_i = - \sum_j f'_{ij} r_j. \quad (3)$$

For a normal mode atomic displacements have the form

$$r_i = a_i \exp(2\pi \nu(-1)^{1/2} t), \quad (4)$$

and therefore, (3) reduces to

$$\sum_j f'_{ij} a_j = 4\pi^2 \nu^2 a_i, \quad (5)$$

where  $a_i$  are the amplitudes of the normal coordinates. The eigen-values  $4\pi^2 \nu^2$  are obtained by diagonalizing the mass weighted force constants  $f'_{ij}$ .  $\nu$  are the harmonic frequencies and the eigen vectors  $r_i$  give the amplitudes of the normal coordinates. Six of the  $3N$  frequencies corresponding to the translational and the

rotational motions of the molecule will be zero and the remaining  $3N-6$  frequencies will correspond to the internal vibrations. The force on the nuclei and the force constants are calculated by the first and second energy derivatives respectively, which are represented by the expressions

$$f_i = \frac{\partial E}{\partial R_i} \quad (6)$$

and

$$f_{ij} = \frac{\partial^2 E}{\partial R_i \partial R_j} \quad (7)$$

These quantities have been evaluated using a computer program developed by Pople *et al* (1979). However, the integral involved in the second derivatives of the energy has been obtained numerically because of computer storage problems. All calculations have been performed on a VAX-11/750 computer. The geometrical parameters used for the calculations of vibrational frequencies are:  $r(\text{C}-\text{C}) = 1.397 \text{ \AA}$ ,  $r(\text{C}-\text{H}) = 1.084 \text{ \AA}$ ,  $r(\text{C}-\text{F}) = 1.350 \text{ \AA}$ ,  $\angle \text{C}-\text{C}-\text{C} = \angle \text{H}-\text{C}-\text{C} = \angle \text{F}-\text{C}-\text{C} = 120^\circ$ . An *ab initio* evaluation of the geometries of the fluorobenzenes with a discussion of the most reliable geometry has been given by Boggs *et al* (1982). However, since the above transformation (5) is valid at a stationary point of the energy surface, the use of a geometry optimised using a basis set other than the one used here (3-21G) would not have any significance. Therefore, no effort was made to consider any geometry optimization.

### 3. Results and discussion

The computed harmonic frequencies together with the experimental frequencies (Pearce *et al* 1973; Eaton and Steele 1973; Eaton *et al* 1976; Varsányi 1974) and the tentative assignments for *ortho*-, *meta*- and *para*-difluorobenzenes are presented in table 1.

The average value for the ratio  $\nu_{\text{exp}}/\nu_{\text{cal}}$  considering all the frequencies was found to be 0.89 for the three molecules. Therefore, a scale factor of 0.89 may be proposed as correcting for the deficiencies in the SCF method as well as for the anharmonic nature of the experimental frequencies. A larger deviation is found between calculated and observed frequencies for the non-planar modes as compared to that for the planar modes and the computed non-planar frequencies usually have much higher magnitudes than the observed ones. Other workers (Wiberg and Wendolosky 1984) have also made similar observations. The average  $\nu_{\text{exp}}/\nu_{\text{cal}}$  for planar frequencies was found to be 0.93 whereas for the non-planar frequencies it was 0.8. The use of a single scale factor of 0.89 for planar and non-planar frequencies gives an average error of  $64 \text{ cm}^{-1}$  whereas the use of two different scale factors of 0.93 and 0.80 gives an average error of only  $28 \text{ cm}^{-1}$ . Therefore, different scale factors of 0.93 and 0.80 are used for planar and non-planar frequencies respectively. The fact that the scale factors needed for out-of-plane modes are lower than those for the in-plane ones has been emphasized earlier by Pulay *et al* (1981) and indicates that a scaling of the calculated frequencies

**Table 1.** Theoretical and experimental vibrational frequencies ( $\text{cm}^{-1}$ ) for *o*-, *m*- and *p*-difluorobenzenes with 3-21G basis set.

Molecules	Species	Theoretical Frequencies			Experimental frequencies	Vibrational assignments*	
		Cal.	Exp./Cal.	Scaled			
<i>o</i> -Di-fluoro-benzene		3275	0.941	3046	3081	$\nu(\text{C-H})$ (2)	
		3257	0.935	3029	3045	$\nu(\text{C-H})$ (20b)	
		1716	0.935	1596	1605	$\nu(\text{C=C})$ (8a)	
		1674	0.904	1557	1514	$\nu(\text{C=C})$ (19b)	
		1426	0.906	1326	1292	$\nu(\text{C-F})$ (7a)	
		1342	0.948	1248	1272	$\nu(\text{C=C})$ (14)	
		1139	1.011	1059	1152	$\beta(\text{C-H})$ (9a)	
		1106	0.927	1029	1025	$\beta(\text{C-H})$ (18b)	
		811	0.940	754	762	$\nu(\text{C-C})$ (1)	
		641	0.886	596	568	$\alpha(\text{C-C-C})$ (6a)	
		289	0.993	269	287	$\beta(\text{C-F})$ (15) <sup>c</sup>	
		3267	0.937	3038	3060	$\nu(\text{C-H})$ (20a)	
		3243	—	3016	—	$\nu(\text{C-H})$ (7b)	
	<i>b</i> <sub>2</sub>	1733	0.934	1612	1618	$\nu(\text{C=C})$ (8b)	
		1617	0.910	1504	1472	$\nu(\text{C=C})$ (19a)	
		1432	0.875	1332	1253	$\beta(\text{C-H})$ (3)	
		1339	0.901	1245	1206	$\nu(\text{C-F})$ (13)	
		1216	0.907	1131	1103	$\beta(\text{C-H})$ (18a)	
		951	0.901	884	857	$\alpha(\text{C-C-C})$ (12)	
		587	0.930	546	546	$\alpha(\text{C-C-C})$ (6b)	
		476	0.924	443	440	$\beta(\text{C-F})$ (9b)	
		1183	0.785	946	929	$\gamma(\text{C-H})$ (17b)	
		955	0.784	764	749	$\gamma(\text{C-H})$ (11)	
		<i>b</i> <sub>1</sub>	582	0.773	466	450	$\phi(\text{C-C-C-C})$ (16b)
			358	0.768	286	275	$\gamma(\text{C-F})$ (10a)
			1222	0.794	978	970	$\gamma(\text{C-H})$ (5)
<i>a</i> <sub>2</sub>	1082	0.776	866	840	$\gamma(\text{C-H})$ (17a)		
	877	0.802	702	703	$\phi(\text{C-C-C-C})$ (4)		
	659	0.892	527	588	$\phi(\text{C-C-C-C})$ (16a)		
	237	0.827	190	196	$\gamma(\text{C-F})$ (10b)		
<i>m</i> -Di-fluoro-benzene	<i>a</i> <sub>1</sub>	3273	0.943	3044	3087	$\nu(\text{C-H})$ (2)	
		3270	—	3041	—	$\nu(\text{C-H})$ (20a)	
		3249	0.938	3022	3049	$\nu(\text{C-H})$ (7a)	
		1725	0.930	1604	1605	$\nu(\text{C=C})$ (8a)	
		1563	0.927	1454	1449	$\nu(\text{C=C})$ (19a)	
		1466	0.871	1363	1277	$\nu(\text{C-F})$ (13)	
		1174	0.908	1092	1066	$\beta(\text{C-H})$ (18a)	
		1094	0.921	1017	1008	$\alpha(\text{C-C-C})$ (12)	
		804	0.914	748	735	$\nu(\text{C-C})$ (1)	
		580	0.903	539	524	$\alpha(\text{C-C-C})$ (6a)	
		332	0.997	308	331	$\beta(\text{C-F})$ (9a)	
		3262	0.949	3034	3096	$\nu(\text{C-H})$ (20b)	
		<i>b</i> <sub>2</sub>	1755	0.919	1632	1613	$\nu(\text{C=C})$ (8b)
	1645		0.906	1530	1490	$\nu(\text{C=C})$ (19b)	
	1466		0.912	1363	1337	$\beta(\text{C-H})$ (3)	
	1333		0.945	1240	1260	$\nu(\text{C=C})$ (14)	
	1310		0.884	1218	1158	$\beta(\text{C-H})$ (9b)	
	1140		0.982	1060	1120	$\beta(\text{C-H})$ (18b)	

Table 1.

Molecules	Species	Theoretical Frequencies			Experimental frequencies	Vibrational assignments*
		Cal.	Exp./Cal.	Scaled		
<i>p</i> -Di-fluoro-benzene	$b_1$	1027	0.929	955	954	$\nu(\text{C-F})$ (7b)
		572	0.899	532	514	$\alpha(\text{C-C-C})$ (6b)
		499	0.958	464	478	$\beta(\text{C-F})$ (15)
		1221	0.801	977	978	$\gamma(\text{C-H})$ (5)
		1135	0.749	908	850	$\gamma(\text{C-H})$ (17b)
		991	0.776	793	769	$\gamma(\text{C-H})$ (11)
		829	0.811	663	672	$\phi(\text{C-C-C-C})$ (4)
		569	0.805	455	458	$\phi(\text{C-C-C-C})$ (16b)
		286	0.804	229	230	$\gamma(\text{C-F})$ (10b)
		1131	0.777	906	879	$\gamma(\text{C-H})$ (17a)
	$a_2$	725	0.826	580	599	$\phi(\text{C-C-C-C})$ (16a)
		306	0.820	245	251	$\gamma(\text{C-F})$ (10a)
	$a_g$	3273	0.942	3044	3084	$\nu(\text{C-H})$ (2)
		1766	0.916	1642	1617	$\nu(\text{C=C})$ (8a)
		1405	0.886	1307	1245	$\nu(\text{C-F})$ (7c)
		1298	0.880	1207	1142	$\beta(\text{C-H})$ (9a)
		905	0.948	842	858	$\nu(\text{C-C})$ (1)
		500	0.902	465	451	$\alpha(\text{C-C-C})$ (6a)
		3256	0.948	3028	3088	$\nu(\text{C-H})$ (20a)
		1693	0.892	1574	1511	$\nu(\text{C=C})$ (19a)
		1412	0.858	1313	1285	$\nu(\text{C-F})$ (13)
		1105	0.916	1028	1012	$\beta(\text{C-H})$ (18a)
	$b_{1u}$	805	0.916	747	737	$\alpha(\text{C-C-C})$ (12)
		3271	0.926	3042	3028	$\nu(\text{C-H})$ (20b)
		1541	0.933	1433	1437	$\nu(\text{C=C})$ (19b)
		1226	0.989	1140	1212	$\nu(\text{C=C})$ (14)
		1130	0.960	1051	1085	$\beta(\text{C-H})$ (18b)
		347	1.009	323	350	$\beta(\text{C-F})$ (15)
		3257	0.947	3029	3084	$\nu(\text{C-H})$ (7b)
		1684	—	1566	—	$\nu(\text{C=C})$ (8b)
		1455	0.883	1353	1285	$\beta(\text{C-H})$ (3)
		717	0.886	667	635	$\alpha(\text{C-C-C})$ (6b)
	$b_{2u}$	477	0.910	444	434	$\beta(\text{C-F})$ (9b)
		1210	0.779	968	943	$\gamma(\text{C-H})$ (17a)
		534	0.758	427	405	$\phi(\text{C-C-C-C})$ (16a)
		1037	0.771	830	800	$\gamma(\text{C-H})$ (10a)
1199		0.774	959	928	$\gamma(\text{C-H})$ (5)	
858		0.807	686	692	$\phi(\text{C-C-C-C})$ (4)	
446		0.841	357	375	$\gamma(\text{C-F})$ (10b)	
1057		0.788	846	833	$\gamma(\text{C-H})$ (17b)	
645		0.781	516	504	$\phi(\text{C-C-C-C})$ (16b)	
184		0.902	147	166	$\gamma(\text{C-F})$ (11)	

\*Numbers within parenthesis following each assignment correspond to mode of vibration (Wilson 1934).

$\nu$ : Stretching;  $\beta$ : in-plane bending;  $\alpha$ : C-C-C angle bending;  $\gamma$ : out-of-plane bending; and  $\phi$ : torsion about C=C bond.

may be more appropriate. It has also been observed that for planar frequencies  $\Delta\nu$  is below  $30\text{ cm}^{-1}$  for frequencies below  $1100\text{ cm}^{-1}$  and below  $70\text{ cm}^{-1}$  for frequencies above  $1100\text{ cm}^{-1}$ . For the non-planar frequencies  $\Delta\nu$  is below  $30\text{ cm}^{-1}$  except for the  $588\text{ cm}^{-1}$  frequency (mode-16a) in *o*-difluorobenzene and the  $850\text{ cm}^{-1}$  frequency (mode-17b) in *m*-difluorobenzene.

The assignments of the fundamental frequencies for *o*-, *m*-, and *p*-difluorobenzenes presented in table 1 are based on the assignments made by earlier workers (Pearce *et al* 1973; Eaton and Steele 1973; Eaton *et al* 1976; Varsányi 1974) and are essentially identical to those given by Varsányi (1974) except for the cases discussed below.

For *o*-difluorobenzene, Varsányi (1974) has assigned the frequency  $1272\text{ cm}^{-1}$  to the C-F stretching mode (7a). The *ab initio* results show that the normal mode corresponding to this frequency amplitude does not involve any movement of the fluorine atoms. Instead the *ab initio* calculated frequency  $1426\text{ cm}^{-1}$  corresponding to the experimental frequency  $1292\text{ cm}^{-1}$  which has earlier (Varsányi 1974) been assigned to the Kekule C=C stretching mode-14 does involve a displacement of fluorine atoms. Therefore, we now assign the observed frequencies  $1272$  and  $1292\text{ cm}^{-1}$  to the C=C stretching mode-14 and the C-F stretching mode-7a respectively. This is consistent with their  $a_1$  symmetry.

The two interesting and widely discussed vibrational modes in substituted benzenes are the ring breathing (mode-1) and the trigonal C-C-C angle bending (mode-12). In disubstituted benzenes the interaction of these vibrational modes with vibrational modes involving substituent(s) motions (usually C-X stretchings) gives rise to two observed frequencies, one in the region  $750\text{--}825\text{ cm}^{-1}$  and the other in the region  $990\text{--}1050\text{ cm}^{-1}$ , both of which usually appear in the Raman spectrum with good intensities. One of these frequencies is usually attributed to the ring breathing or the C-C-C trigonal bending mode. The frequencies of magnitude  $762\text{ cm}^{-1}$  and  $1025\text{ cm}^{-1}$  observed as the strongest lines in the Raman spectrum of *o*-difluorobenzene are assigned to the ring breathing mode and the C-H in-plane bending modes, respectively (Varsányi 1974). The *ab initio* calculations show that the frequency  $762\text{ cm}^{-1}$  involves just the radial motion of all atoms which is the characteristic nature of the ring breathing mode. On the other hand, the frequency  $1025\text{ cm}^{-1}$  does not involve the displacement of any fluorine atoms nor of the corresponding carbon atoms. The earlier assignment (Varsányi 1974) of the frequency  $1025\text{ cm}^{-1}$  to the C-H in-plane bending mode thus seems to be reasonably correct. The trigonal C-C-C angle bending mode assigned by Varsányi (1974) to a frequency at  $857\text{ cm}^{-1}$  is also supported by our calculations.

The assignments for the *m*-difluorobenzenes are identical to those given by Varsányi (1974) and are supported by our computations.

We have noted that for frequencies above  $1100\text{ cm}^{-1}$  the difference between the computed and the observed magnitudes is below  $70\text{ cm}^{-1}$ . The same holds true for *p*-difluorobenzene also except for the two frequencies observed at  $1212\text{ cm}^{-1}$  (mode- $b_{1u}$ ) and at  $1285\text{ cm}^{-1}$  (mode- $b_{2u}$ ). These frequencies had been assigned to the C-F stretching (mode-13) and the C-C stretching (mode-14) vibrations, respectively. The corresponding calculated magnitudes for the modes 13 and 14 are  $1412$  and  $1226\text{ cm}^{-1}$  which after scaling become  $1313$  and  $1140\text{ cm}^{-1}$  respectively. Thus, if the earlier assignments are retained  $\Delta\nu(\nu_{\text{cal}} - \nu_{\text{obs}})$  for the two cases are  $101$  and  $145\text{ cm}^{-1}$  respectively which are far larger than  $\Delta\nu$ 's ( $\sim 70\text{ cm}^{-1}$ ) for other

frequencies above  $1100\text{ cm}^{-1}$ . However, if we interchange the assignments of the observed frequencies  $\Delta\nu$  is reduced to 72 and  $28\text{ cm}^{-1}$ , respectively, well within the expected limit. Both the modes are infrared-active and the normal mode with the frequency  $1285\text{ cm}^{-1}$  involves displacement of the fluorine atoms whereas the normal mode with the frequency  $1212\text{ cm}^{-1}$  does not involve any displacement of F atoms. The interchange of assignments is thus justified and we assign the frequencies 1212 and  $1285\text{ cm}^{-1}$  to the C=C stretching (mode-14) and to the C-F stretching (mode-13) respectively. The interchange of the assignments for these two frequencies seems to be justified by an additional experimental observation explained in the following paragraph.

The magnitudes of the six C=C stretching frequencies decrease in going from benzene- $\text{h}_6$  to benzene- $\text{d}_6$  and one would expect a similar pattern in going from *p*-difluorobenzene- $\text{h}_4$  to *p*-difluorobenzene- $\text{d}_4$ . In contrast, the magnitudes of the C-F stretching frequencies are not expected to be affected appreciably in going from  $\text{C}_6\text{F}_2\text{H}_4$  to  $\text{C}_6\text{F}_2\text{D}_4$ . In the infrared spectrum of *p*-difluorobenzene- $\text{h}_4$ , two fundamentals were observed in the region  $1200\text{--}1300\text{ cm}^{-1}$ , namely, 1212 and  $1285\text{ cm}^{-1}$ , whereas in the infrared spectrum of *p*-difluorobenzene- $\text{d}_4$  (Gates *et al* 1969) only a single fundamental at  $1287\text{ cm}^{-1}$  was observed. It seems logical to assume that the frequency  $1285\text{ cm}^{-1}$  in the normal compound corresponds to the frequency  $1287\text{ cm}^{-1}$  in the deuterated compound and is a C-F stretching rather than a C=C stretching fundamental. In the infrared spectrum of *p*-difluorobenzene- $\text{d}_4$  the only frequency which may be correlated with the  $1212\text{ cm}^{-1}$  of *p*-difluorobenzene- $\text{h}_4$  is  $1133\text{ cm}^{-1}$  which can therefore be assigned to the C=C stretching mode.

#### 4. Conclusions

The breathing mode is observed to decrease considerably in magnitude as compared to its magnitude ( $992\text{ cm}^{-1}$ ) for benzene in all the three cases, whereas the trigonal C-C-C angle bending mode is observed to be reduced in magnitude for the *o*- and the *p*-isomers, but retains its magnitude ( $1008\text{ cm}^{-1}$ ) in the *m*-isomer. Interestingly enough, the breathing mode has its lowest magnitude of  $735\text{ cm}^{-1}$  and the trigonal bending mode its highest magnitude of  $1008\text{ cm}^{-1}$  for the *m*-isomer whereas the breathing mode has its highest magnitude of  $858\text{ cm}^{-1}$  and the trigonal bending mode has its lowest magnitude of  $737\text{ cm}^{-1}$  for the *p*-isomer. Therefore, we may conclude that in the *m*-isomer the breathing mode mixes strongly with other modes whereas the trigonal bending mode mixes only slightly. On the other hand it seems that in the *p*-isomer the trigonal bending mode interacts strongly with other modes and it is the breathing mode which interacts only slightly. The magnitude of the Kekule C=C stretching mode is found to be in decreasing order on going from the *o*- to the *m*- to the *p*-isomer suggesting a decreasing mixing with other modes. Out of the two C-F stretching modes, one mode is always taken to correspond to mode-13 of benzene. This mode is observed to have magnitudes of 1206, 1277 and  $1285\text{ cm}^{-1}$  for the *o*-, *m*- and *p*-isomers, respectively. The other C-F stretching mode is described by the mode-7a in the *o*- and the *p*-isomers and as mode-7b in the *m*-isomer. The C-F stretching (mode-7a) for the *o*- and *p*-isomers is observed to have nearly equal magnitudes whereas for

Table 2.

Normal mode specification	<i>o</i> -Difluoro-benzene	<i>m</i> -Difluoro-benzene	<i>p</i> -Difluoro-benzene
C-F stretching	1292 (7a) 1206 (13)	954 (7b) 1277 (13)	1245 (7a) 1285 (13)
Ring breathing	762	735	858
Trigonal bending	857	1008	737
Kekula C=C	1272	1260	1212

the *m*-isomer (mode-7b) it is observed to have considerably reduced magnitude which may be due to its interaction with other C-F/ring modes. The frequencies corresponding to the two C-F stretchings, the ring breathing, the trigonal C-C-C angle bending and the Kekule C=C stretching modes are summarised in table 2.

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