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## Theoretical potential functions and vibrational analysis for halocarbonyl azides CXO–NNN (X=F, Cl and Br)

Received: 5 November 2002 / Accepted: 31 January 2003 / Published online: 2 April 2003  
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**Abstract** The structural stability of halocarbonyl azides CXO–NNN (X=F, Cl and Br) was investigated by DFT and MP2 calculations using the 6-311++G\*\* basis set. From the calculations, the molecules were found to have an *s-cis*↔*s-trans* conformational equilibrium with *cis* being the lower-energy form. Full energy optimizations were carried out for the transition states and the minima at the B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels, from which the rotational barriers were calculated to be of the order 8–10 kcal mol<sup>-1</sup>. The vibrational frequencies were computed at the DFT-B3LYP level and the vibrational assignments for the normal modes of the stable conformers were made on the basis of normal coordinate calculations.

**Keywords** Vibrational spectra and assignments · Rotational barriers · Fluorocarbonyl azide · Chlorocarbonyl azide · Bromocarbonyl azide

### Introduction

The structural stability of a series of halocarbonyl isocyanates CXO–N=C=O, where X is F, Cl, or Br, has been investigated by theoretical and experimental methods and both agreed that the molecules exist only in the planar *cis* and *trans* conformations at ambient temperature. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16] The conformational behavior and the size of the rotational barrier of the compounds were found to be greatly influenced by the extent of interaction between the CXO group and both the –N=C=O group and the lone-pair on the nitrogen. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15,

Taken in part from the thesis of K.S. Al-Ghamdi that will be submitted to Chemistry Department at KFUPM, in partial fulfillment of the M.S. degree.

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16] The vibrational spectra and conformational behavior of fluorocarbonyl isocyanate CFO–N=C=O, [1, 2, 3, 4] chlorocarbonyl isocyanate CClO–N=C=O, [5, 6, 7, 8, 9, 10, 11, 12, 13, 14] and bromocarbonyl isocyanate CBr–N=C=O [13, 15, 16] have been the subject of many studies in the last two decades.

The *cis* conformation of fluorocarbonyl isocyanate (isocyanate group eclipsing the carbonyl oxygen) was found to be of a lower energy than the *trans* form on the basis of theoretical and experimental results. [2, 3] In the case of chlorocarbonyl isocyanate, different computational studies at the Hartree–Fock and the second order Moller–Plesset levels of calculation using different basis sets showed that the *cis* form of the molecule is the more stable. [6, 8, 13] However, from some experimental studies, it was noticed that the *trans* conformer (isocyanate group eclipsing the chlorine atom) is 0.6 kcal mol<sup>-1</sup> lower in energy than the *cis* one. [6, 7, 9] It was also found that, when additional polarization functions were used at the MP2 level, [6] the predicted stability of chlorocarbonyl isocyanate is in fair agreement with experimental results with an energy difference of 0.73 kcal mol<sup>-1</sup>. Moreover, the stability of bromocarbonyl isocyanate has been reported in the fluid and solid states, and the *trans* conformer was found to be 1.21 kcal mol<sup>-1</sup> more stable than the *cis* form. [15, 16] In this molecule, the theoretical data did not contradict experimental results.

In a more recent theoretical study at the B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels, [17] fluoro-, chloro-, and bromocarbonyl isocyanates were predicted to have *cis*–*trans* rotational barriers of about 2–3 kcal mol<sup>-1</sup>. The reverse conformational behavior of the bromide can be explained as a result of pronounced steric forces that stabilize the *trans* form with the bromine atom being directed away from the lone-pair on the nitrogen atom of the isocyanate group.

In the present study we investigate the corresponding series of azides CXO–NNN with both DFT-B3LYP and ab initio MP2 calculations for purposes of comparison. We optimized the energies of the possible conformers of

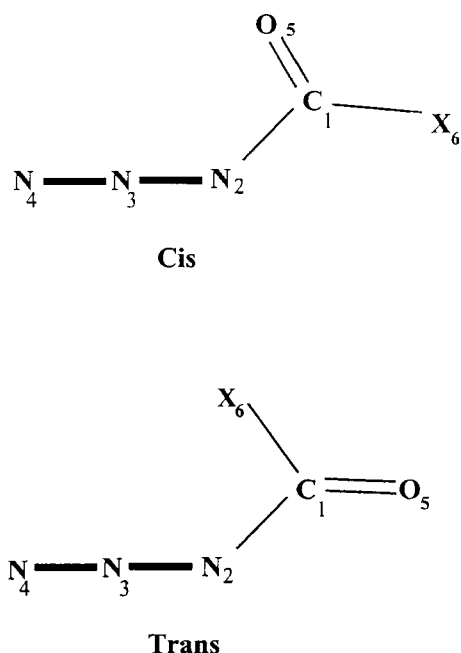


Fig. 1 Atom numbering for halocarbonyl azides in the *cis* (upper) and *trans* (lower) conformers

halocarbonyl azides and calculated the potential functions for the internal rotations of the three molecules. Additionally, we calculated the vibrational wavenumbers and spectra for the molecules at the DFT-B3LYP/6-311++G\*\* level. Then, we carried out normal coordinate analyses and derived the potential energy distributions (PED) among symmetry coordinates of all vibrational modes for the stable conformers of the molecules. The vibrational assignments of the normal modes were made based on comparison with experimental results and

calculated PED values. The results of the work are presented herein.

### Ab initio calculations

The Gaussian 98 program, [18] running on an IBM RS/6000 43P model 260 workstation, was used to carry out density functional B3LYP calculations. The extended 6-311++G\*\* basis set was employed at the ab initio MP2 and the DFT-B3LYP levels of calculations to optimize the structures and predict the energies, rotational constants and dipole moments of the series of CXO-NNN (where X=F, Cl or Br) in their stable conformations. From full energy optimization, the *cis* and the *trans* conformations were found to be the energy minima for the three molecular systems (Fig. 1). The optimized structural parameters of the molecules in their stable *cis* and *trans* conformations were calculated at both the MP2 and the DFT levels and are shown in Tables 1 and 2.

### Asymmetric torsional potential functions

Potential scans for the internal rotation about the C-N single bond in fluoro-, chloro-, and bromocarbonyl azides were obtained by allowing the OCNN dihedral angles ( $\varphi$ ) to vary from  $0^\circ$  (*cis* position) to  $180^\circ$  (*trans* position). Full geometry optimizations at each of the fixed dihedral angles ( $\varphi$ ) of  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ ,  $75^\circ$ ,  $90^\circ$ ,  $105^\circ$ ,  $120^\circ$ ,  $135^\circ$ ,  $150^\circ$ , and  $165^\circ$  were carried out for the three molecules. Then, full energy optimization was performed at the transition state TS of each of the three molecules. The computed relative energies and barriers to interconversion at the MP2/6-311++G\*\* and the DFT-B3LYP/6-311++G\*\* levels of calculation are listed in Tables 3 and

Table 1 Calculated structural parameters, total dipole moment, and rotational constants at DFT-B3LYP/6-311++G\*\* level for the *cis* and *trans* conformations of fluorocarbonyl (X=F), chlorocarbonyl (X=Cl), and bromocarbonyl (X=Br) azides

Parameter	Fluoride		Chloride		Bromide	
	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>
Bond length (Å)						
$r(\text{C}_1\text{-N}_2)$	1.397	1.392	1.404	1.395	1.403	1.394
$r(\text{N}_2\text{-N}_3)$	1.250	1.250	1.280	1.250	1.256	1.247
$r(\text{N}_3\text{-N}_4)$	1.121	1.122	1.141	1.123	1.121	1.122
$r(\text{C}_1\text{=O}_5)$	1.187	1.180	1.213	1.182	1.189	1.180
$r(\text{C}_1\text{-X}_6)$	1.337	1.366	1.831	1.815	1.940	1.995
Bond angle (deg)						
$(\text{C}_1\text{N}_2\text{N}_3)$	114.2	117.4	116.5	119.4	113.8	119.7
$(\text{N}_2\text{N}_3\text{N}_4)$	172.3	171.3	168.5	170.8	172.3	170.7
$(\text{N}_2\text{C}_1\text{O}_5)$	129.7	125.5	129.1	123.4	128.2	123.5
$(\text{N}_2\text{C}_1\text{X}_6)$	107.2	112.3	108.2	115.8	108.6	115.8
$(\text{N}_3\text{N}_2\text{C}_1\text{O}_5)$	0.0	180.0	0.0	180.0	0.0	180.0
Dipole moment (Debye)						
$(\mu_t)$	1.87	2.34	1.95	2.25	1.54	2.20
Rotational constants (MHz)						
<i>A</i>	11,529	11,128	9,283	5,000	9,212	3,438
<i>B</i>	2,513	2,675	1,584	2,482	1,098	1,976
<i>C</i>	2,063	2,157	1,353	1,659	981	1,255

**Table 2** Calculated structural parameters, total dipole moment, and rotational constants at MP2/6-311++G\*\* level for the *cis* and *trans* conformations of fluorocarbonyl (X=F), chlorocarbonyl (X=Cl), and bromocarbonyl (X=Br) azides

Parameter	Fluoride		Chloride		Bromide	
	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>
Bond length (Å)						
$r(C_1-N_2)$	1.401	1.396	1.410	1.403	1.410	1.401
$r(N_2-N_3)$	1.253	1.253	1.255	1.250	1.258	1.249
$r(N_3-N_4)$	1.147	1.148	1.148	1.149	1.148	1.149
$r(C_1=O_5)$	1.193	1.185	1.199	1.191	1.198	1.190
$r(C_1-X_6)$	1.333	1.361	1.741	1.780	1.916	1.965
Bond angle (deg)						
$(C_1N_2N_3)$	112.7	116.5	112.4	118.4	112.2	118.6
$(N_2N_3N_4)$	172.0	171.0	172.6	170.9	172.5	170.6
$(N_2C_1O_5)$	129.5	125.3	127.4	122.7	127.7	123.0
$(N_2C_1X_6)$	107.0	112.0	108.6	115.1	108.5	115.4
$(N_3N_2C_1O_5)$	0.0	180.0	0.0	180.0	0.0	180.0
Dipole moment (Debye)						
( $\mu$ )	2.39	3.14	1.93	3.12	1.90	3.08
Rotational constants (MHz)						
A	11,435	11,152	9,979	5,088	9,290	3,418
B	2,516	2,660	1,678	2,487	1,106	2,023
C	2,062	2,148	1,436	1,670	989	1,271

**Table 3** Computed relative energies and rotational barriers (kcal mol<sup>-1</sup>) at B3LYP/6-311++G\*\* and MP2/6-311++G\*\* levels of calculations in fluoro-, chloro-, and bromocarbonylazide

	Fluorocarbonylazide	Chlorocarbonylazide	Bromocarbonylazide
B3LYP/6-311++G** <sup>a, b</sup>			
Relative energy	1.757	1.186	0.640
<i>Cis-Trans</i> barrier	9.977	9.287	8.798
<i>Trans-Cis</i> barrier	8.220	8.101	8.158
Corrected relative energy	1.556	1.123	0.651
Corrected <i>cis-trans</i> barrier	9.639	9.030	8.587
Corrected <i>trans-cis</i> barrier	8.082	7.910	7.937
MP2/6-311++G** <sup>c</sup>			
Relative energy	2.215	1.581	0.778
<i>Cis-Trans</i> barrier	10.115	9.431	8.999
<i>Trans-Cis</i> barrier	7.900	7.850	8.220

<sup>a</sup> The calculated total energy of fluoro-, chloro- and bromocarbonyl azides in the *cis* conformation at B3LYP/6-311++G\*\* level are: -377.48069, -737.82646 and -2851.74621 hartrees, respectively

<sup>b</sup> The zero-point corrections by B3LYP/6-311++G\*\* calculation of fluoro-, chloro- and bromocarbonyl azides in the *cis* conformation are: 0.02486, 0.02295 and 0.02223 hartrees, respectively

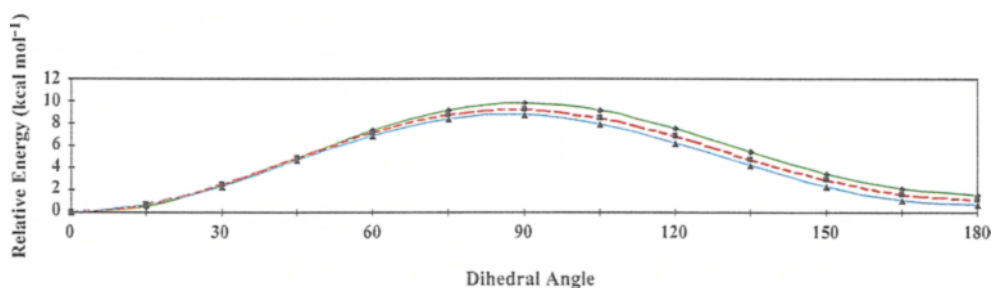
<sup>c</sup> The calculated total energy of fluoro-, chloro- and bromocarbonyl azides in the *cis* conformation at MP2/6-311++G\*\* level are: -376.60112, -736.57066 and -2849.41618 hartrees, respectively

**Table 4** Calculated potential constants (kcal mol<sup>-1</sup>) at B3LYP/6-311++G\*\* level for the asymmetric torsion in fluorocarbonylazide, chlorocarbonylazide, and bromocarbonylazide

Potential constant	Fluoride	Chloride	Bromide
$V_1$	1.214	0.421	-0.002
$V_2$	9.043	8.775	8.440
$V_3$	0.404	0.549	0.637
$V_4$	-0.145	-0.065	-0.153
$V_5$	-0.042	0.020	0.008
$V_6$	-0.058	-0.014	0.012

**Table 5** Internal coordinate definitions (for atom denotation see Fig. 1) for fluorocarbonyl (X=F), chlorocarbonyl (X=Cl), and bromocarbonyl (X=Br) azides

No.	Coordinate	Definition
1	$C_1-N_2$	Stretch R
2	$C_1-O_5$	Stretch S
3	$C_1-X_6$	Stretch P
4	$N_2-N_3$	Stretch T
5	$N_3-N_4$	Stretch Z
6	$C_1N_2N_3$	Bend $\delta$
7	$N_2N_3N_4$	Bend $\mu$
8	$O_5C_1N_2$	Bend $\phi$
9	$X_6C_1N_2$	Bend $\theta$
10	$O_5C_1X_6$	Bend $\epsilon$
11	$C_1-X_6$	Wag $\omega$
12	$N_2N_3N_4$	Wag $\chi$
13	$O_5C_1N_2N_3$	Torsion $\tau$



**Fig. 2** Potential curves for the internal rotation in fluorocarbonyl (green line), chlorocarbonyl (red line), and bromocarbonyl (blue line) azides as determined by ab initio calculations at the B3LYP/6-311++G\*\* level (Table 13)

**Table 6** Symmetry coordinates for halocarbonylazides

Species	Description	Symmetry coordinate <sup>a</sup>	
A'	C-X	Stretch	S <sub>1</sub> =P
	NNN	Antisymmetric stretch	S <sub>2</sub> =T-Z
	C=O	Stretch	S <sub>3</sub> =S
	NNN	Symmetric stretch	S <sub>4</sub> =T+Z
	CXO	In-plane bend (rock)	S <sub>5</sub> =φ-ε
	C-N	Stretch	S <sub>6</sub> =R
	CXO	In-plane bend (scissor)	S <sub>7</sub> =φ+ε-2θ
	NNN	In-plane bend	S <sub>8</sub> =μ
	CNN	In-plane bend	S <sub>9</sub> =δ
A''	CXO	Out-of-plane bend (wag)	S <sub>10</sub> =ω
	NNN	Out-of-plane bend	S <sub>11</sub> =χ
	Asymmetric torsion		S <sub>12</sub> =τ

<sup>a</sup> Not normalized

**Table 7** Calculated vibrational frequencies (cm<sup>-1</sup>) at B3LYP/6-311++G\*\* level for the *cis* conformer of fluorocarbonylazide

Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act. <sup>a</sup>	Depol. ratio	Obs. <sup>b</sup>	PED <sup>b</sup>
A'	v <sub>1</sub>	2300	365.3	65.6	0.4		88%S <sub>2</sub> , 12%S <sub>4</sub>
	v <sub>2</sub>	1863	646.1	23.1	0.3	1849	91%S <sub>3</sub>
	v <sub>3</sub>	1309	523.4	1.1	0.1		56%S <sub>4</sub> , 29%S <sub>6</sub>
	v <sub>4</sub>	1166	420.3	1.6	0.2	1162	52%S <sub>1</sub> , 17%S <sub>4</sub> , 12%S <sub>6</sub> , 10%S <sub>7</sub>
	v <sub>5</sub>	929	47.2	7.6	0.1	886	37%S <sub>6</sub> , 17%S <sub>1</sub> , 10%S <sub>9</sub> , 10%S <sub>4</sub>
	v <sub>6</sub>	709	12.6	7.8	0.3		26%S <sub>7</sub> , 25%S <sub>1</sub> , 20%S <sub>9</sub> , 19%S <sub>8</sub> , 11%S <sub>5</sub>
	v <sub>7</sub>	531	2.1	2.2	0.2	564	30%S <sub>8</sub> , 29%S <sub>5</sub> , 18%S <sub>6</sub> , 14%S <sub>7</sub>
	v <sub>8</sub>	483	0.3	1.8	0.6	493	43%S <sub>5</sub> , 28%S <sub>7</sub> , 19%S <sub>8</sub> , 60%S <sub>9</sub> , 27%S <sub>8</sub> , 3%S <sub>7</sub>
	v <sub>9</sub>	174	0.8	6.1	0.6		60%S <sub>9</sub> , 27%S <sub>8</sub> , 13%S <sub>7</sub>
A''	v <sub>10</sub>	747	32.5	0.3	0.8	750	100%S <sub>10</sub>
	v <sub>11</sub>	564	5.8	0.5	0.8		90%S <sub>11</sub> , 11%S <sub>12</sub>
	v <sub>12</sub>	34	0.0	2.0	0.8		89%S <sub>12</sub> , 10%S <sub>11</sub>

<sup>a</sup> IR intensities and Raman activities are calculated in km mol<sup>-1</sup> and Å<sup>4</sup> amu<sup>-1</sup> respectively

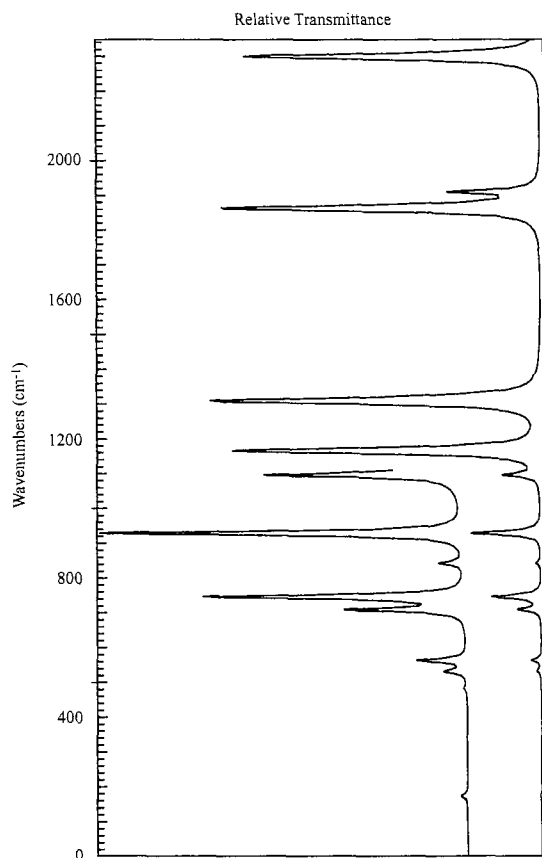
<sup>b</sup> Observed wavenumbers for the *cis* conformer of fluorocarbonyl isocyanate from [3]

4. Also, the zero-point corrections, the corrected relative energies and the corrected energy barriers in this series of molecules were computed at the DFT-B3LYP/6-311++G\*\* level and are shown in Table 4. The torsional potential was represented as a Fourier cosine series in the dihedral angle ( $\varphi$ ):  $V(\varphi) = \sum (V_n/2)[1 - \cos(n\varphi)]$ , where the potential coefficients from  $V_1$  to  $V_6$  are considered adequate to describe the potential function. The results of the energy optimizations at the B3LYP level were used to calculate the six coefficients by least-squares fitting for

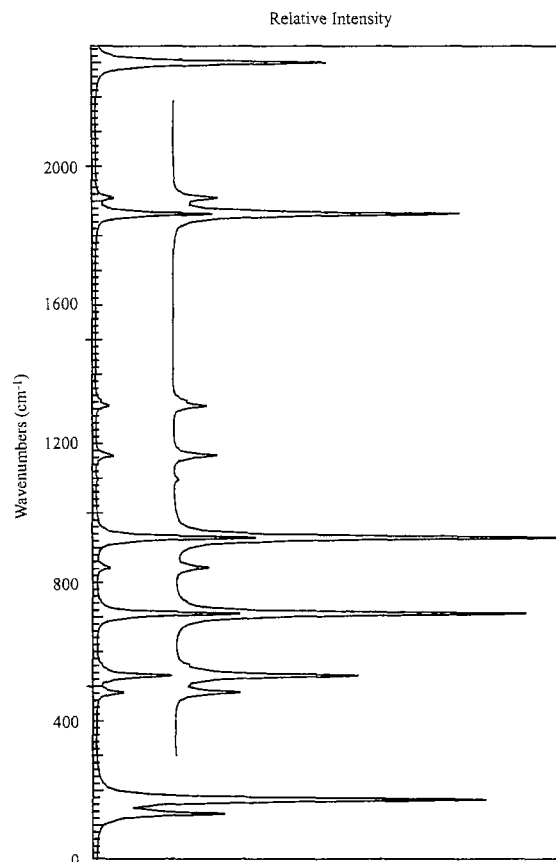
the three systems (Table 5). The potential functions of halocarbonyl azides are shown in Fig. 2.

### Vibrational frequencies and normal coordinate analyses

Halocarbonyl azides in their planar conformations have C<sub>s</sub> symmetry. The 12 vibrational modes in these molecules span the irreducible representations: 9 A' and 3 A''. The A'



**Fig. 3** Calculated vibrational infrared spectrum of fluorocarbonyl azide at 300 K by the DFT-B3LYP/6-311++G\*\* calculation



**Fig. 4** Calculated vibrational Raman spectrum of fluorocarbonyl azide at 300 K by the DFT-B3LYP/6-311++G\*\* calculation

modes should be polarized, whereas the A'' modes should be depolarized in the Raman spectra of the liquid.

Normal coordinate analyses were carried out for the stable conformers of the molecules as described previously. [19, 20] The internal and symmetry coordinates of the three molecules are listed in Tables 5 and 6. The potential energy distributions (PED) for each normal mode among the symmetry coordinates of the molecules were calculated and are given in Tables 7, 8, 9, 10, 11 and 12. A complete assignment of the fundamentals was proposed based on the calculated PED values, infrared band intensities, Raman line activities, and depolarization ratios. The data of the vibrational assignments are listed in Tables 5, 6, and 7.

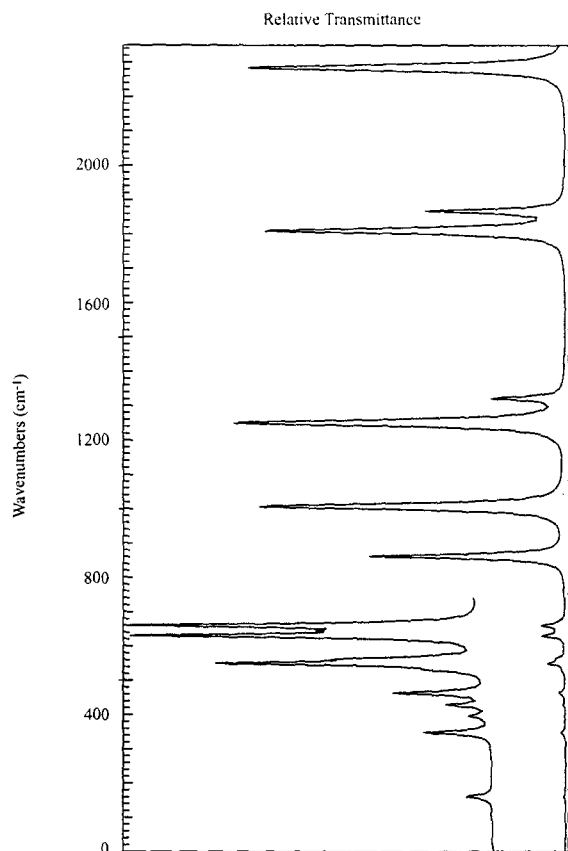
The vibrational infrared and Raman spectra were calculated using the computational methods described previously. [19, 20] To calculate the Raman spectra, the frequencies  $\nu_j$ , the scattering activities  $S_j$ , and the depolarization ratios  $\rho_j$  were obtained from DFT-B3LYP/6-311++G\*\* calculation. The calculated vibrational Raman and infrared spectra of the three molecules are shown in Figs. 3, 4, 5, 6, 7, and 8. A complete vibrational assignment of the fundamentals was proposed. The assignments were made based on the calculated PED and comparison with similar ones.

### Calculation of vibrational spectra

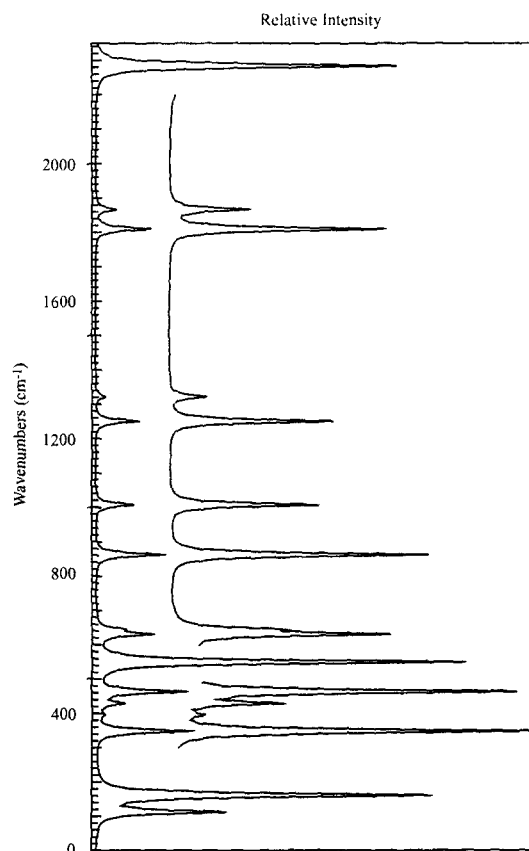
We calculated the vibrational infrared and Raman spectra for halocarbonyl azide using the computational methods previously described. [20, 21] To calculate the Raman spectra we used the frequencies  $\nu_j$ , the scattering activities  $S_j$ , and the depolarization ratios  $\rho_j$  as calculated on the DFT-B3LYP/6-311++G\*\* level. The temperature was set to be 300 K in calculating both the Raman and the infrared spectra. The calculated vibrational Raman and infrared spectra of the *cis* and *trans* of the three halocarbonyl azides are shown in Figs. 3, 4, 5, 6, 7, and 8.

### Discussion

The interesting properties and electronic structure of organoazides [22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40] have recently attracted our attention to investigate the structure and vibrational spectra of formyl azide. [39] Formyl azide was predicted to exist in the planar *cis* and *trans* conformations as a result of pronounced conjugation effects with the non-planar *gauche* conformation being a transition state. The *cis* conformer of the molecule was predicted to be the



**Fig. 5** Calculated vibrational infrared spectrum of chlorocarbonyl azide at 300 K by the DFT-B3LYP/6-311++G\*\* calculation



**Fig. 6** Calculated vibrational Raman spectrum of chlorocarbonyl azide at 300 K by the DFT-B3LYP/6-311++G\*\* calculation

**Table 8** Calculated vibrational frequencies ( $\text{cm}^{-1}$ ) at B3LYP/6-311++G\*\* level for the *trans* conformer of fluorocarbonylazide<sup>a</sup>

Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act. <sup>a</sup>	Depol. ratio	Obs. <sup>b</sup>	PED <sup>b</sup>
A'	$\nu_1$	2293	370.9	81.9	0.3		88% $S_2$ , 11% $S_4$
	$\nu_2$	1910	794.6	41.4	0.3	1831	91% $S_3$
	$\nu_3$	1325	343.5	5.4	0.2		55% $S_4$ , 33% $S_6$
	$\nu_4$	1096	292.2	2.3	0.3	1110	21% $S_7$ , 21% $S_6$ , 20% $S_4$ , 10% $S_1$
	$\nu_5$	843	37.5	7.9	0.1	858	64% $S_1$ , 22% $S_6$
	$\nu_6$	705	27.0	8.1	0.4	560	40% $S_5$ , 29% $S_9$
	$\nu_7$	548	1.8	2.7	0.4	520	42% $S_7$ , 19% $S_5$ , 18% $S_6$
	$\nu_8$	487	0.4	2.1	0.7		38% $S_8$ , 29% $S_5$ , 28% $S_7$
	$\nu_9$	182	0.9	3.1	0.6		61% $S_9$ , 26% $S_8$
A''	$\nu_{10}$	731	31.1	0.4	0.8	742	100% $S_{10}$
	$\nu_{11}$	537	8.8	0.4	0.8		91% $S_{11}$
	$\nu_{12}$	113	0.3	0.9	0.8		92% $S_{12}$

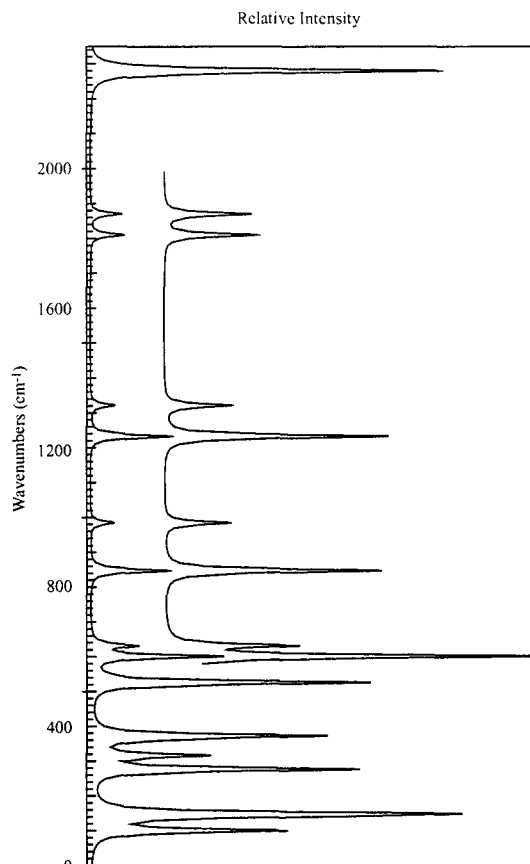
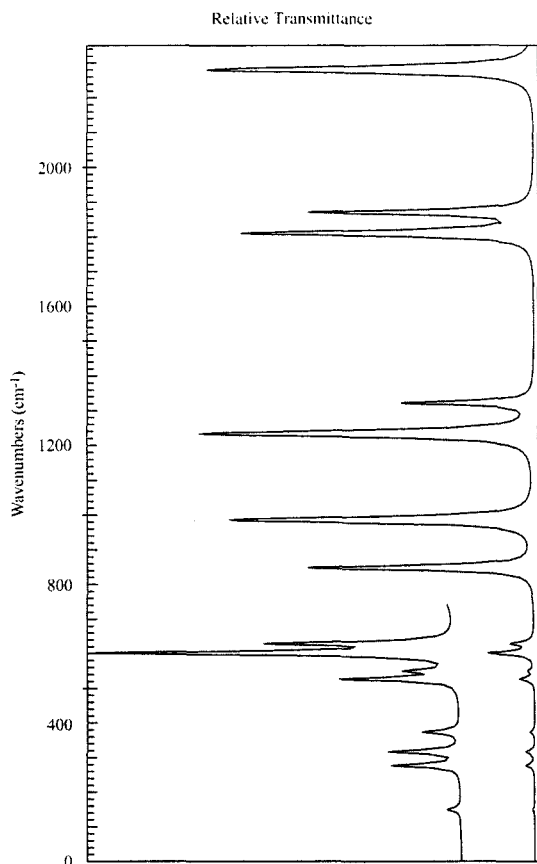
<sup>a</sup> IR intensities and Raman activities are calculated in  $\text{km mol}^{-1}$  and  $\text{\AA}^4 \text{amu}^{-1}$  respectively

<sup>b</sup> Observed wavenumbers for the *trans* conformer of fluorocarbonyl isocyanate from [3]

more stable conformation with the C=O being directed away from the lone-pair on the nitrogen. [39] The *cis-trans* rotational barrier in formyl azide CHO-NNN was predicted to be about  $11 \text{ kcal mol}^{-1}$  [39] as compared to about  $4 \text{ kcal mol}^{-1}$  in formyl isocyanate CHO-NCO. [40] The greater electron-withdrawing effect of the isocyanate NCO group as compared to that of the azide NNN group may increase the partial  $\pi$  character of the C-N bond, and

hence the size of the barrier, as on going from formyl azide [39] to formyl isocyanate. [40]

Similar to formyl azide, the *cis* and the *trans* conformations of halocarbonyl azides were found from full energy optimization in the present work to be the energy minima for the fluoride, chloride and bromide as shown in Fig. 2 and Table 3. From the calculations, the relative stability of the *trans* form (carbonyl C=O and azide NNN groups are in *trans* position to each other) was



**Fig. 7** Calculated vibrational infrared spectrum of bromocarbonyl azide at 300 K by the DFT-B3LYP/6-311++G\*\* calculation

**Fig. 8** Calculated vibrational Raman spectrum of bromocarbonyl azide at 300 K by the DFT-B3LYP/6-311++G\*\* calculation

**Table 9** Calculated vibrational frequencies ( $\text{cm}^{-1}$ ) at B3LYP/6-311++G\*\* level for the *cis* conformer of chlorocarbonylazide

Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act. <sup>a</sup>	Depol. ratio	Obs. <sup>b</sup>	PED <sup>b</sup>
A'	$\nu_1$	2285	403.6	97.7	0.3		87%S <sub>2</sub> , 13%S <sub>4</sub>
	$\nu_2$	1810	383.3	18.9	0.5	1780	95%S <sub>3</sub>
	$\nu_3$	1251	519.6	4.1	0.1		62%S <sub>4</sub> , 24%S <sub>6</sub> , 10%S <sub>2</sub>
	$\nu_4$	1008	366.3	3.1	0.2		48%S <sub>6</sub> , 21%S <sub>4</sub> , 11%S <sub>7</sub> , 11%S <sub>1</sub>
	$\nu_5$	862	174.6	3.7	0.1	789	34%S <sub>7</sub> , 30%S <sub>9</sub> , 12%S <sub>8</sub> , 11%S <sub>1</sub> , 10%S <sub>6</sub>
	$\nu_6$	550	10.6	13.9	0.2		48%S <sub>8</sub> , 28%S <sub>1</sub> , 10%S <sub>9</sub> , 10%S <sub>6</sub>
	$\nu_7$	463	3.8	4.2	0.4	482	42%S <sub>1</sub> , 31%S <sub>7</sub> , 16%S <sub>5</sub>
	$\nu_8$	348	2.7	3.7	0.5	347	68%S <sub>5</sub> , 10%S <sub>1</sub>
	$\nu_9$	161	1.0	4.1	0.5		54%S <sub>9</sub> , 27%S <sub>8</sub> , 13%S <sub>7</sub>
A''	$\nu_{10}$	661	14.5	0.2	0.8		96%S <sub>10</sub>
	$\nu_{11}$	563	4.4	0.4	0.8		89%S <sub>11</sub>
	$\nu_{12}$	112	0.0	1.8	0.8		87%S <sub>12</sub> , 10%S <sub>11</sub>

<sup>a</sup> IR intensities and Raman activities are calculated in  $\text{km mol}^{-1}$  and  $\text{\AA}^4 \text{amu}^{-1}$  respectively

<sup>b</sup> Observed wavenumbers for the *cis* conformer of chlorocarbonyl isocyanate from [9]

predicted to decrease in going from bromide, chloride to the fluoride. This decrease in the relative stability of the *trans* conformer can be explained as a result of the decrease in the steric hindrance between the halogen atom and the lone-pair on the nitrogen of the azide group in going from the bromide, the chloride to the fluoride. This conclusion is supported by the change in the C-X bond length and CNN, XCN and XCO bond angles with the

change in conformation as going from *cis* to *trans* structures of the molecules as shown in Tables 1 and 2.

Furthermore, the two N-N bonds of the azide NNN group were calculated to be of about 1.22 and 1.12 Å as shown in Tables 1 and 2. These calculated distances are consistent with *double* and *triple* bond characters that can only be described on the basis of the following resonance structures:

**Table 10** Calculated vibrational frequencies (cm<sup>-1</sup>) at B3LYP/6-311++G\*\* level for the *trans* conformer of chlorocarbonyl azide

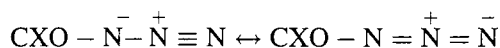
Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act. <sup>a</sup>	Depol. ratio	Obs. <sup>b</sup>	PED <sup>b</sup>
A'	v <sub>1</sub>	2285	358.8	79.1	0.4		88%S <sub>2</sub> , 11%S <sub>4</sub>
	v <sub>2</sub>	1868	672.5	34.5	0.3	1818	94%S <sub>3</sub>
	v <sub>3</sub>	1323	308.5	6.0	0.1		62%S <sub>4</sub> , 28%S <sub>6</sub>
	v <sub>4</sub>	1005	318.1	1.2	0.4	1111	43%S <sub>6</sub> , 23%S <sub>7</sub> , 18%S <sub>4</sub>
	v <sub>5</sub>	645	10.0	9.2	0.4		36%S <sub>9</sub> , 32%S <sub>8</sub> , 13%S <sub>5</sub> , 11%S <sub>6</sub>
	v <sub>6</sub>	631	93.7	13.9	0.1	636	38%S <sub>7</sub> , 29%S <sub>1</sub> , 11%S <sub>8</sub>
	v <sub>7</sub>	429	10.8	7.4	0.4	448	58%S <sub>1</sub> , 19%S <sub>5</sub> , 19%S <sub>7</sub>
	v <sub>8</sub>	646	11.3	0.5	0.7	651	96%S <sub>10</sub>
	v <sub>9</sub>	165	0.4	5.4	0.6		56%S <sub>9</sub> , 21%S <sub>8</sub> , 16%S <sub>5</sub>
A''	v <sub>10</sub>	396	5.3	4.1	0.8	410	45%S <sub>5</sub> , 30%S <sub>8</sub> , 11%S <sub>1</sub>
	v <sub>11</sub>	531	10.1	0.4	0.8		88%S <sub>11</sub>
	v <sub>12</sub>	110	0.2	0.7	0.8		93%S <sub>12</sub>

<sup>a</sup> IR intensities and Raman activities are calculated in km mol<sup>-1</sup> and Å<sup>4</sup> amu<sup>-1</sup> respectively<sup>b</sup> Observed wavenumbers for the *trans* conformer of chlorocarbonyl isocyanate from [9]**Table 11** Calculated vibrational frequencies (cm<sup>-1</sup>) at B3LYP/6-311++G\*\* level for the *cis* conformer of bromocarbonyl azide

Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act. <sup>a</sup>	Depol. ratio	Obs. <sup>b</sup>	PED <sup>b</sup>
A'	v <sub>1</sub>	2280	427.5	117.5	0.3		86%S <sub>2</sub> , 13%S <sub>4</sub>
	v <sub>2</sub>	1810	373.1	17.6	0.6	1778	96%S <sub>3</sub>
	v <sub>3</sub>	1233	542.9	8.3	0.1		64%S <sub>4</sub> , 23%S <sub>6</sub> , 11%S <sub>2</sub>
	v <sub>4</sub>	985	322.0	2.6	0.3		55%S <sub>6</sub> , 22%S <sub>4</sub>
	v <sub>5</sub>	848	224.0	4.3	0.0	775	40%S <sub>7</sub> , 32%S <sub>9</sub> , 13%S <sub>8</sub> , 10%S <sub>1</sub>
	v <sub>6</sub>	526	5.5	10.1	0.2		54%S <sub>8</sub> , 18%S <sub>7</sub> , 12%S <sub>6</sub>
	v <sub>7</sub>	373	3.0	6.9	0.3	382	46%S <sub>1</sub> , 37%S <sub>5</sub> , 14%S <sub>7</sub>
	v <sub>8</sub>	277	5.3	5.6	0.3	284	43%S <sub>5</sub> , 31%S <sub>1</sub>
	v <sub>9</sub>	150	1.1	3.9	0.5		49%S <sub>9</sub> , 25%S <sub>8</sub> , 14%S <sub>7</sub> , 13%S <sub>5</sub>
A''	v <sub>10</sub>	628	12.7	0.2	0.8		92%S <sub>10</sub>
	v <sub>11</sub>	549	3.5	0.7	0.8		88%S <sub>11</sub>
	v <sub>12</sub>	100	0.0	2.5	0.8		89%S <sub>12</sub>

<sup>a</sup> IR intensities and Raman activities are calculated in km mol<sup>-1</sup> and Å<sup>4</sup> amu<sup>-1</sup> respectively<sup>b</sup> Observed wavenumbers for the *cis* conformer of bromocarbonyl isocyanate from [16]**Table 12** Calculated vibrational frequencies (cm<sup>-1</sup>) at B3LYP/6-311++G\*\* level for the *trans* conformer of bromocarbonyl azide<sup>a</sup>

Sym.	No.	Freq.	IR int. <sup>a</sup>	Raman act. <sup>a</sup>	Depol. ratio	Obs. <sup>b</sup>	PED <sup>b</sup>
A'	v <sub>1</sub>	2284	341.8	77.4	0.4		88%S <sub>2</sub> , 11%S <sub>4</sub>
	v <sub>2</sub>	1870	650.5	31.3	0.4	1816	95%S <sub>3</sub>
	v <sub>3</sub>	1322	307.2	7.4	0.1		63%S <sub>4</sub> , 27%S <sub>6</sub>
	v <sub>4</sub>	989	346.5	0.7	0.7	965	48%S <sub>6</sub> , 23%S <sub>7</sub> , 17%S <sub>4</sub>
	v <sub>5</sub>	632	6.6	8.9	0.4		35%S <sub>9</sub> , 32%S <sub>8</sub> , 14%S <sub>6</sub>
	v <sub>6</sub>	601	89.1	16.1	0.1	608	52%S <sub>7</sub> , 17%S <sub>8</sub> , 13%S <sub>1</sub>
	v <sub>7</sub>	363	0.1	2.8	0.1	370	61%S <sub>5</sub> , 26%S <sub>8</sub>
	v <sub>8</sub>	317	16.6	12.9	0.5	344	82%S <sub>1</sub> , 10%S <sub>7</sub>
	v <sub>9</sub>	142	0.1	5.7	0.6		54%S <sub>9</sub> , 24%S <sub>5</sub> , 16%S <sub>8</sub>
A''	v <sub>10</sub>	610	6.8	0.5	0.8	594	89%S <sub>10</sub> , 10%S <sub>11</sub>
	v <sub>11</sub>	527	11.3	0.4	0.8		83%S <sub>11</sub> , 12%S <sub>10</sub>
	v <sub>12</sub>	108	0.1	0.7	0.8		93%S <sub>12</sub>

<sup>a</sup> IR intensities and Raman activities are calculated in km mol<sup>-1</sup> and Å<sup>4</sup> amu<sup>-1</sup> respectively<sup>b</sup> Observed wavenumbers for the *trans* conformer of bromocarbonyl isocyanate from [16]

These structures explain the stability of only the planar *cis* and *trans* conformers and not the non-planar *gauche* form of formyl azide [39] and halocarbonyl azides as a result of noticeable conjugation between the carbonyl C=O and the azide NNN groups, in similar way to halocarbonyl isocyanates CXO-NCO. [40]

We calculated the vibrational wavenumbers of the *cis* and the *trans* conformers of fluoro-, chloro-, and bromocarbonyl azides at the B3LYP/6-311++G\*\* level. Then we carried out normal coordinate calculation to obtain the potential energy distributions PED among the symmetry coordinates of all the normal modes. We made tentative vibrational assignments for the normal modes of the three molecules in their stable conformations based on IR



**Table 13** Halocarbonyl azides determined by ab initio calculations at the B3LYP/6-311++G\*\* level

D. A.	kcal mol <sup>-1</sup> FCO3 B3LYP	kcal mol <sup>-1</sup> ClCO3 B3LYP	kcal mol <sup>-1</sup> BrCO3 B3LYP	Total energy hartree Fluoro B3LYP	Total energy hartree Chloro B3LYP	Total energy hartree Bromo B3LYP
0	0	0	0	-377.4803961	-737.8264562	-2851.746214
15	0.4942896	0.6726907	0.6301455	-377.4796084	-737.8253842	-2851.74521
30	2.3538528	2.4632905	2.3325802	-377.4766645	-737.8225307	-2851.742497
45	4.8675323	4.8541036	4.6197914	-377.4726392	-737.8187207	-2851.738852
60	7.3555467	7.1809107	6.8556095	-377.4686743	-737.8150127	-2851.735289
75	9.1476525	8.7943644	8.3825296	-377.4658184	-737.8124415	-2851.732856
90	9.7882775	9.2729035	8.7750371	-377.4647975	-737.8116789	-2851.73223
105	9.1652856	8.5179462	7.9404488	-377.4657903	-737.812882	-2851.73356
120	7.5399719	6.8340232	6.2201301	-377.4683804	-737.8155655	-2851.736302
135	5.427083	4.7756021	4.1652859	-377.4717475	-737.8188458	-2851.739576
150	3.4381273	2.9083206	2.3232303	-377.4749171	-737.8218215	-2851.742512
165	2.056915	1.6378011	1.0781877	-377.4771182	-737.8238462	-2851.744496
180	1.5668297	1.1807228	0.6421937	-377.4778992	-737.8245746	-2851.745191

relative intensities, Raman activities and calculated PED values and experimental data for fluorocarbonyl isocyanate, [3] chlorocarbonyl isocyanate [9] and bromocarbonyl isocyanate. [16]

Several modes were predicted to be considerably mixed with other vibrations as shown in Tables 7, 8, 9, 10, 11, and 12. However, a comparison between the calculated wavenumbers for the modes that are associated with the CXO group (X is F, Cl and Br) and those observed for halocarbonyl isocyanates [3, 9, 16] shows very reasonable agreement (Tables 7, 8, 9, 10, 11, and 12). The two antisymmetric ( $S_2$ ) and symmetric ( $S_4$ ) NNN and the C=O ( $S_3$ ) stretches in the spectra of the three molecules could be assigned with confidence based on their PED values and infrared intensity. The antisymmetric NNN stretch was predicted to have PED value of about 88%  $S_2$ , while the symmetric one have about 60%  $S_4$  as shown in Tables 7, 8, 9, 10, 11, and 12. The C–N stretch especially in the case of the fluoride and the bromide was predicted to have a high degree of mixing with neighboring vibrations. Finally, in all cases the NNN wagging mode ( $S_{11}$ ) was predicted to slightly mix with the asymmetric torsion ( $S_{12}$ ).

**Acknowledgement** The authors gratefully acknowledge the support of this work by King Fahd University of Petroleum and Minerals.

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