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# Structural determination of carvone, a component of spearmint, by means of gas electron diffraction augmented by theoretical calculations

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## Abstract

The molecular structure and conformation of carvone, a compound with a minty odor, were investigated by means of gas electron diffraction supported by theoretical calculations. Electron diffraction patterns were recorded by heating the nozzle up to 128 °C to obtain enough scattering intensity. The infrared spectrum was also measured by using an absorption cell with a path length of 10 m. The obtained molecular scattering intensities were analyzed with the aid of theoretical calculations and infrared spectroscopy. It was revealed that the experimental data are well reproduced by assuming that carvone consists of a mixture of three conformers that have the isopropenyl group in the equatorial position and mutually differ in the torsional angle around the single bond connecting the ring and the isopropenyl group. It was also found that the puckering amplitude of the ring of carvone is close to those of menthol and isomenthol, a minty compound and its nonminty isomer. The determined structural parameters ( $r_g$  and  $\angle_\alpha$ ) of the most abundant conformer of carvone are as follows:  $\langle r(\text{C}-\text{C}) \rangle = 1.520(3) \text{ \AA}$ ;  $\langle r(\text{C}=\text{C}) \rangle = 1.360(5) \text{ \AA}$ ;  $r(\text{C}=\text{O}) = 1.225(5) \text{ \AA}$ ;  $\langle r(\text{C}-\text{H}) \rangle = 1.104(4) \text{ \AA}$ ;  $\langle \angle \text{C}=\text{C}-\text{C} \rangle = 121.1(5)^\circ$ ;  $\langle \angle \text{C}-\text{C}-\text{C} \rangle = 110.4(5)^\circ$ ;  $\angle \text{C}-\text{CO}-\text{C} = 117.1(14)^\circ$ ;  $\langle \angle \text{C}-\text{C}-\text{H} \rangle = 111.1(13)^\circ$ . Angle brackets denote average values and parenthesized values are the estimated limits of error ( $3\sigma$ ) referring to the last significant digit.

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**Keywords:** Carvone; Molecular structure; Gas electron diffraction; MP2 calculations; DFT calculations

## 1. Introduction

Recently, we have determined the vapor-phase structures of menthol and isomenthol, which are a minty compound and its nonminty isomer by

means of gas electron diffraction, and we have found that menthol has essentially only one conformer while isomenthol has two stable conformers in the gas phase [1]. The relationship between the molecular structure and the minty odor has so far been studied only on the basis of the computationally obtained geometry [2], and the experimental determination of various compounds is essential for further quantitative discussions. In

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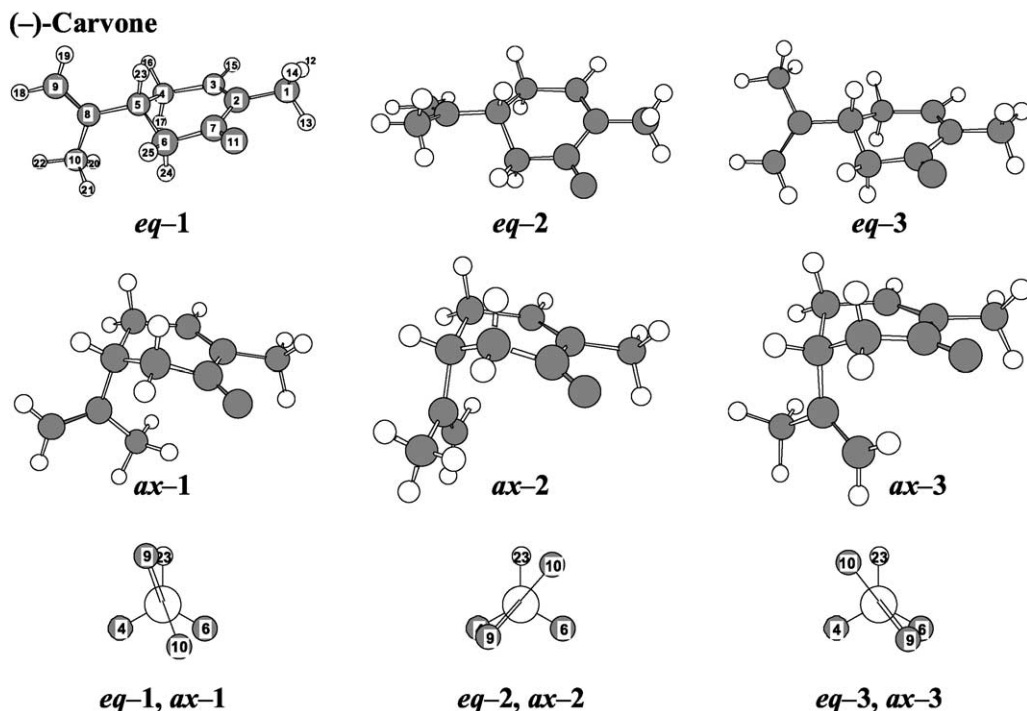


Fig. 1. Molecular models and atom numbering for some possible conformers of carvone. Newman projections are viewed from the direction of  $C_8$  to  $C_5$ .

the present study, the geometrical structure and conformational property of carvone (Fig. 1) have been determined. Carvone is known as a component of spearmint. Contrary to isomenthol that has quite different odor from menthol despite being an isomer of it, carvone's spearmint odor is similar to the peppermint odor of menthol although its chemical composition is rather different from those of menthol and isomenthol. Therefore it is expected that the structural study of carvone will provide further information about the structure–odor relationship. As in the preceding study [1], infrared spectroscopy and theoretical calculations by sophisticated methods, MP2 and DFT, have been used in this study to provide supporting information.

## 2. Experimental

The commercial sample of (*R*)-(-)-carvone (Tokyo Chemical Industry Co., Ltd) with purity

better than 99% was used without further purification. Electron diffraction pattern was recorded on  $8 \times 8$  in. Kodak projector slide plates with an apparatus equipped with an  $r^3$ -sector [3]. The camera distance was 244.2 mm to cover  $s$ -range ( $4.7$ – $33.8 \text{ \AA}^{-1}$ ) sufficient for the molecule of this size. Despite its obvious minty odor, the sample of carvone has insufficient vapor pressure for the electron diffraction experiment at room temperature. Therefore the sample was heated by using the nozzle reported in Ref. [4] and the temperature of the nozzle tip was kept at  $128^\circ\text{C}$ . The accelerating voltage of incident electrons was about 37 kV and the wavelength of the electron was  $0.06333 \text{ \AA}$ , which was calibrated to the  $r_a(\text{C}=\text{S})$  distance of  $\text{CS}_2$  ( $1.5570 \text{ \AA}$ ) [5]. The photometry process was described in detail elsewhere [6]. Other experimental conditions are as follows: beam current was  $1.4 \mu\text{A}$ ; background pressure during exposure was  $4.6$ – $4.8 \times 10^{-6}$  Torr; uncertainty in the scale factor was 0.04%; exposure time was 76–100 s; number

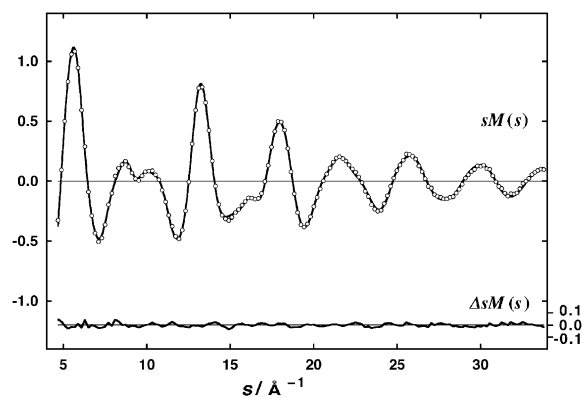


Fig. 2. Experimental (open circles) and theoretical (solid curve) molecular scattering intensities of carvone;  $\Delta sM(s) = sM(s)^{\text{obs}} - sM(s)^{\text{calc}}$ . The theoretical curve was calculated from the best-fit parameters.

of plates used was 4. The experimental intensities and backgrounds are available as supplementary information (Table S1).

Elastic atomic scattering factors were calculated as described in Ref. [7], and inelastic ones were taken from Ref. [8]. The experimental molecular scattering intensities are shown in Fig. 2 with the final calculated ones. A diagonal weight matrix was used in the least-squares analysis on the molecular scattering intensities.

A gas-phase FTIR spectrum of carvone was measured at room temperature on a Bomem DA3.16 spectrometer with a resolution of  $0.5 \text{ cm}^{-1}$ . An absorption cell with a path length of 10 m was used. The sample pressures were about 50 mTorr.

### 3. Theoretical calculations

**Possible conformers.** As the six-membered ring of carvone has three  $\text{sp}^2$  carbon atoms,  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_7$ , these atoms and  $\text{C}_4$  and  $\text{C}_6$  carbons are almost coplanar. Therefore, the ring has two possible forms that are labeled *eq* and *ax* according to the position, equatorial and axial, of the  $\text{C}_8$  carbon, respectively. These forms are further classified according to the orientation of the isopropenyl group caused by the internal rotation around the  $\text{C}_5\text{--C}_8$  single bond, such as *eq-1*, *ax-2*, and so on. See Fig. 1 for the illustration.

**MP2 and B3LYP calculations.** At first, geometrical optimizations of all the conformers shown in Fig. 1 were carried out by means of MP2 and B3LYP theoretical calculations with the 6-31G\*\* basis set. Program GAUSSIAN 98 [9] was used. The obtained relative energies for these methods are listed in Table 1. As mentioned below, our final conclusion is that there is no significant amount of the *ax* conformers in the gas phase. The structural parameters for only the *eq* conformers are listed in Table 2, and those for the *ax* conformers are given in Table S2 of supplementary information.

The Gibbs free-energy differences,  $\Delta G$ , at  $128^\circ\text{C}$  were estimated from the energy differences,  $\Delta E$ , listed in Table 1, rotational constants calculated from the structural parameters listed in Tables 2 and S2, and the vibrational frequencies. The vibrational frequencies used were obtained from the B3LYP/6-31G\*\* calculations and the scaling method as described below. The obtained  $\Delta G$  values as well as the relative abundance at  $128^\circ\text{C}$  estimated from these free energy differences are listed in Table 1.

According to the MP2 method, the free energy differences between the *eq* and the *ax* conformers are  $1.6 \text{ kcal mol}^{-1}$  or less, and the abundance of the *ax* conformers is not negligible (28% in total).

Table 1

Relative energies and estimated abundance for the possible conformers of carvone obtained from the MP2/6-31G\*\* and B3LYP/6-31G\*\* calculations (in  $\text{kcal mol}^{-1}$  and %)

Conformers <sup>a</sup>	MP2/6-31G**			B3LYP/6-31G**		
	$\Delta E^b$	$\Delta G^c$	Abundance <sup>d</sup>	$\Delta E^b$	$\Delta G^c$	Abundance <sup>d</sup>
<i>eq-1</i>	0.00	0.00	39.5	0.00	0.00	44.8
<i>eq-2</i>	0.62	0.81	14.4	0.30	0.49	24.2
<i>eq-3</i>	0.40	0.62	18.1	0.26	0.48	24.6
<i>ax-1</i>	1.03	1.59	5.4	2.12	2.67	1.6
<i>ax-2</i>	0.80	1.16	9.2	2.05	2.38	2.3
<i>ax-3</i>	0.37	0.86	13.4	1.81	2.26	2.6

<sup>a</sup> See Fig. 1 for the definitions of the conformers.

<sup>b</sup> The total energy for the *eq-1* conformer is  $-463.246772E_h$ .

<sup>c</sup> Estimated from the  $\Delta E$ , rotational constants and vibrational frequencies (see text).

<sup>d</sup> Estimated from the  $\Delta G$  assuming the temperature of 401 K.

<sup>e</sup> The total energy for the *eq-1* conformer is  $-464.715421E_h$ .

Table 2

Geometrical parameters of the *eq* conformers of carvone obtained from the MP2/6-31G\*\* and B3LYP/6-31G\*\* calculations

Parameters	MP2/6-31G**			B3LYP/6-31G**		
	<i>eq</i> -1	<i>eq</i> -2	<i>eq</i> -3	<i>eq</i> -1	<i>eq</i> -2	<i>eq</i> -3
<i>Bond lengths (Å)</i>						
C <sub>1</sub> –C <sub>2</sub>	1.4991	1.4989	1.4989	1.5044	1.5041	1.5040
C <sub>2</sub> =C <sub>3</sub>	1.3511	1.3509	1.3504	1.3472	1.3470	1.3465
C <sub>3</sub> –C <sub>4</sub>	1.5011	1.5012	1.5011	1.5042	1.5047	1.5045
C <sub>4</sub> –C <sub>5</sub>	1.5327	1.5264	1.5354	1.5433	1.5354	1.5463
C <sub>5</sub> –C <sub>6</sub>	1.5313	1.5347	1.5260	1.5412	1.5447	1.5343
C <sub>6</sub> –C <sub>7</sub>	1.5151	1.5165	1.5143	1.5239	1.5248	1.5231
C <sub>2</sub> –C <sub>7</sub>	1.4844	1.4834	1.4839	1.4894	1.4883	1.4894
C <sub>5</sub> –C <sub>8</sub>	1.5090	1.5114	1.5114	1.5201	1.5216	1.5217
C <sub>8</sub> =C <sub>9</sub>	1.3420	1.3420	1.3418	1.3373	1.3372	1.3370
C <sub>8</sub> –C <sub>10</sub>	1.5051	1.5057	1.5060	1.5108	1.5114	1.5114
C <sub>7</sub> =O <sub>11</sub>	1.2335	1.2337	1.2336	1.2232	1.2233	1.2232
C <sub>1</sub> –H <sub>12</sub>	1.0886	1.0886	1.0886	1.0931	1.0931	1.0931
C <sub>1</sub> –H <sub>13</sub>	1.0896	1.0895	1.0896	1.0950	1.0950	1.0950
C <sub>1</sub> –H <sub>14</sub>	1.0893	1.0893	1.0893	1.0948	1.0948	1.0948
C <sub>3</sub> –H <sub>15</sub>	1.0865	1.0864	1.0866	1.0899	1.0898	1.0900
C <sub>4</sub> –H <sub>16</sub>	1.0929	1.0923	1.0920	1.0967	1.0962	1.0959
C <sub>4</sub> –H <sub>17</sub>	1.0963	1.0962	1.0972	1.1011	1.1011	1.1016
C <sub>9</sub> –H <sub>18</sub>	1.0818	1.0817	1.0817	1.0865	1.0862	1.0862
C <sub>9</sub> –H <sub>19</sub>	1.0819	1.0798	1.0798	1.0866	1.0844	1.0845
C <sub>10</sub> –H <sub>20</sub>	1.0911	1.0907	1.0917	1.0968	1.0964	1.0975
C <sub>10</sub> –H <sub>21</sub>	1.0910	1.0917	1.0910	1.0967	1.0975	1.0968
C <sub>10</sub> –H <sub>22</sub>	1.0888	1.0887	1.0887	1.0928	1.0928	1.0928
C <sub>5</sub> –H <sub>23</sub>	1.0958	1.0983	1.0985	1.0978	1.1015	1.1017
C <sub>6</sub> –H <sub>24</sub>	1.0956	1.0962	1.0960	1.1000	1.1001	1.1004
C <sub>6</sub> –H <sub>25</sub>	1.0906	1.0895	1.0898	1.0935	1.0924	1.0930
<i>Bond angles (deg)</i>						
C <sub>1</sub> –C <sub>2</sub> =C <sub>3</sub>	123.68	123.78	123.79	123.73	123.85	123.86
C <sub>1</sub> –C <sub>2</sub> –C <sub>7</sub>	116.46	116.54	116.56	116.47	116.59	116.56
C <sub>3</sub> =C <sub>2</sub> –C <sub>7</sub>	119.86	119.68	119.65	119.79	119.56	119.58
C <sub>2</sub> =C <sub>3</sub> –C <sub>4</sub>	124.09	124.00	124.15	124.76	124.74	124.77
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	111.57	111.37	112.03	112.19	112.16	112.49
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	108.61	108.15	108.55	108.94	108.53	108.78
C <sub>5</sub> –C <sub>6</sub> –C <sub>7</sub>	111.22	111.70	111.47	112.45	112.74	112.63
C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub>	116.97	117.23	117.05	117.33	117.44	117.36
C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub>	112.73	115.13	111.64	113.07	115.27	112.14
C <sub>6</sub> –C <sub>5</sub> –C <sub>8</sub>	113.00	111.89	114.73	113.37	112.30	114.98
C <sub>5</sub> –C <sub>8</sub> =C <sub>9</sub>	120.31	123.31	123.08	120.44	123.69	123.40
C <sub>5</sub> –C <sub>8</sub> –C <sub>10</sub>	118.12	115.54	115.72	118.36	115.45	115.62
C <sub>9</sub> =C <sub>8</sub> –C <sub>10</sub>	121.57	121.15	121.19	121.20	120.85	120.98
C <sub>2</sub> –C <sub>7</sub> =O <sub>11</sub>	121.07	121.10	121.06	121.24	121.32	121.20
C <sub>6</sub> –C <sub>7</sub> =O <sub>11</sub>	121.92	121.65	121.85	121.39	121.20	121.38
C <sub>2</sub> –C <sub>1</sub> –H <sub>12</sub>	110.94	110.93	110.95	111.33	111.34	111.36
C <sub>2</sub> –C <sub>1</sub> –H <sub>13</sub>	110.60	110.55	110.59	110.85	110.80	110.83
C <sub>2</sub> –C <sub>1</sub> –H <sub>14</sub>	110.38	110.43	110.36	110.65	110.70	110.63
H <sub>12</sub> –C <sub>1</sub> –H <sub>13</sub>	109.06	109.07	109.07	108.90	108.89	108.90
H <sub>12</sub> –C <sub>1</sub> –H <sub>14</sub>	109.01	109.00	109.02	108.82	108.80	108.81
H <sub>13</sub> –C <sub>1</sub> –H <sub>14</sub>	106.74	106.75	106.74	106.14	106.15	106.14
C <sub>2</sub> =C <sub>3</sub> –H <sub>15</sub>	118.73	118.74	118.75	118.72	118.73	118.77
C <sub>4</sub> –C <sub>3</sub> –H <sub>15</sub>	117.19	117.25	117.09	116.52	116.52	116.47
C <sub>3</sub> –C <sub>4</sub> –H <sub>16</sub>	109.81	110.02	108.99	109.77	109.87	109.01
C <sub>5</sub> –C <sub>4</sub> –H <sub>16</sub>	109.69	110.28	110.62	109.89	110.38	110.75

Table 2 (continued)

Parameters	MP2/6-31G**			B3LYP/6-31G**		
	eq-1	eq-2	eq-3	eq-1	eq-2	eq-3
C <sub>3</sub> –C <sub>4</sub> –H <sub>17</sub>	109.43	109.04	110.07	108.89	108.48	109.51
C <sub>5</sub> –C <sub>4</sub> –H <sub>17</sub>	109.99	109.66	108.76	110.32	110.04	109.24
H <sub>16</sub> –C <sub>4</sub> –H <sub>17</sub>	106.22	106.33	106.20	105.57	105.69	105.61
C <sub>8</sub> –C <sub>9</sub> –H <sub>18</sub>	121.57	120.69	120.73	121.71	120.92	120.99
C <sub>8</sub> –C <sub>9</sub> –H <sub>19</sub>	121.33	122.74	122.60	121.73	123.02	122.83
H <sub>18</sub> –C <sub>9</sub> –H <sub>19</sub>	117.09	116.57	116.67	116.55	116.06	116.18
C <sub>8</sub> –C <sub>10</sub> –H <sub>20</sub>	111.73	111.63	110.70	111.98	111.94	110.98
C <sub>8</sub> –C <sub>10</sub> –H <sub>21</sub>	111.23	110.55	111.64	111.58	110.91	111.94
C <sub>8</sub> –C <sub>10</sub> –H <sub>22</sub>	110.68	111.12	111.04	111.00	111.40	111.38
H <sub>20</sub> –C <sub>10</sub> –H <sub>21</sub>	107.14	107.06	107.15	106.54	106.51	106.56
H <sub>20</sub> –C <sub>10</sub> –H <sub>22</sub>	107.96	107.98	108.31	107.75	107.75	108.10
H <sub>21</sub> –C <sub>10</sub> –H <sub>22</sub>	107.93	108.33	107.84	107.75	108.11	107.65
C <sub>4</sub> –C <sub>5</sub> –H <sub>23</sub>	106.87	106.92	106.69	106.60	106.79	106.25
C <sub>6</sub> –C <sub>5</sub> –H <sub>23</sub>	107.56	107.12	107.48	107.20	106.65	107.29
C <sub>8</sub> –C <sub>5</sub> –H <sub>23</sub>	107.77	107.23	107.37	107.27	106.81	106.91
C <sub>5</sub> –C <sub>6</sub> –H <sub>24</sub>	109.66	108.56	109.41	110.00	108.92	109.70
C <sub>7</sub> –C <sub>6</sub> –H <sub>24</sub>	107.49	108.29	107.52	106.91	107.71	106.87
C <sub>5</sub> –C <sub>6</sub> –H <sub>25</sub>	112.22	113.08	112.33	112.04	112.90	112.26
C <sub>7</sub> –C <sub>6</sub> –H <sub>25</sub>	108.27	107.49	108.14	108.10	107.34	108.00
H <sub>24</sub> –C <sub>6</sub> –H <sub>25</sub>	107.80	107.55	107.78	107.05	106.95	107.09
<i>Dihedral angles (deg)</i>						
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	–177.99	–178.78	–177.71	–178.35	–179.03	–178.19
C <sub>1</sub> –C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub>	–174.29	–176.29	–173.64	–175.25	–176.21	–174.68
C <sub>7</sub> –C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	2.33	1.78	2.79	2.51	1.91	2.78
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	21.71	24.45	20.42	21.23	23.14	20.36
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	–51.17	–52.97	–49.97	–48.81	–49.99	–48.12
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub> –C <sub>7</sub>	59.12	58.40	58.75	55.59	55.31	55.60
C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub> –C <sub>5</sub>	–36.72	–34.03	–37.42	–33.89	–32.51	–34.67
C <sub>3</sub> –C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub>	5.42	3.19	5.89	3.96	2.92	4.42
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub>	–177.19	–178.92	–177.40	–175.82	–176.91	–176.43
C <sub>8</sub> –C <sub>5</sub> –C <sub>6</sub> –C <sub>7</sub>	–175.02	–173.77	–175.60	–177.57	–176.08	–177.70
C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub> –C <sub>9</sub>	–110.37	15.25	112.67	–113.21	13.43	113.44
C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub> –C <sub>10</sub>	69.69	–164.82	–66.58	66.90	–165.77	–67.07
C <sub>6</sub> –C <sub>5</sub> –C <sub>8</sub> –C <sub>9</sub>	126.01	–108.76	–11.35	122.15	–111.56	–11.53
C <sub>6</sub> –C <sub>5</sub> –C <sub>8</sub> –C <sub>10</sub>	–53.93	71.17	169.40	–57.73	69.25	167.96
C <sub>1</sub> –C <sub>2</sub> –C <sub>7</sub> –O <sub>11</sub>	3.76	2.17	4.12	2.49	1.78	2.77
C <sub>3</sub> –C <sub>2</sub> –C <sub>7</sub> –O <sub>11</sub>	–176.53	–178.35	–176.35	–178.30	–179.09	–178.13
C <sub>5</sub> –C <sub>6</sub> –C <sub>7</sub> –O <sub>11</sub>	145.24	147.52	144.84	148.38	149.50	147.88
C <sub>3</sub> –C <sub>2</sub> –C <sub>1</sub> –H <sub>12</sub>	–0.19	0.03	–0.10	0.01	0.28	0.25
C <sub>3</sub> –C <sub>2</sub> –C <sub>1</sub> –H <sub>13</sub>	–121.35	–121.11	–121.27	–121.38	–121.06	–121.14
C <sub>3</sub> –C <sub>2</sub> –C <sub>1</sub> –H <sub>14</sub>	120.75	120.99	120.85	121.15	121.44	121.39
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub> –H <sub>15</sub>	1.85	1.75	1.89	1.57	1.56	1.68
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub> –H <sub>16</sub>	143.54	147.05	143.18	143.72	146.31	143.60
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub> –H <sub>17</sub>	–100.24	–96.70	–100.72	–101.16	–98.61	–101.31
C <sub>5</sub> –C <sub>8</sub> –C <sub>9</sub> –H <sub>18</sub>	179.31	179.68	–179.63	179.71	–179.91	179.93
C <sub>5</sub> –C <sub>8</sub> –C <sub>9</sub> –H <sub>19</sub>	–0.82	–0.93	1.00	–0.47	–0.04	0.24
C <sub>5</sub> –C <sub>8</sub> –C <sub>10</sub> –H <sub>20</sub>	–55.42	–61.18	–53.47	–57.43	–61.19	–55.89
C <sub>5</sub> –C <sub>8</sub> –C <sub>10</sub> –H <sub>21</sub>	64.26	57.88	65.80	61.90	57.62	63.03
C <sub>5</sub> –C <sub>8</sub> –C <sub>10</sub> –H <sub>22</sub>	–175.76	178.21	–173.82	–177.90	178.09	–176.39
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub> –H <sub>23</sub>	64.60	62.10	65.58	66.57	64.64	67.10
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub> –H <sub>24</sub>	–59.64	–60.93	–60.04	–63.45	–64.18	–63.30
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub> –H <sub>25</sub>	–179.42	179.82	–179.69	177.59	177.18	177.76

See Fig. 1 for the atom numbering and the definitions of the conformers.

Table 3  
Structural constraints and independent parameters of carvone

Parameters	<i>eq</i> -1	<i>eq</i> -2	<i>eq</i> -3	<i>ax</i> -1	<i>ax</i> -2	<i>ax</i> -3
<i>Bond lengths (Å)</i>						
C <sub>1</sub> –C <sub>2</sub>	$r_1 + 0.0002$	$r_1 - 0.0001$	$r_1 - 0.0002$	$r_1 + 0.0002$	$r_1 - 0.0002$	$r_1 - 0.0002$
C <sub>1</sub> –H <sub>12</sub>	$r_4$	$r_4 + 0.0001$	$r_4 + 0.0001$	$r_4 - 0.0001$	$r_4 + 0.0001$	$r_4 + 0.0002$
C <sub>1</sub> –H <sub>13</sub>	$r_4$	$r_4 + 0.0001$	$r_4 + 0.0001$	$r_4 - 0.0001$	$r_4 + 0.0001$	$r_4 + 0.0002$
C <sub>1</sub> –H <sub>14</sub>	$r_4$	$r_4 + 0.0001$	$r_4 + 0.0001$	$r_4 - 0.0001$	$r_4 + 0.0001$	$r_4 + 0.0002$
C <sub>2</sub> =C <sub>3</sub>	$r_2$	$r_2 - 0.0002$	$r_2 - 0.0007$	$r_2 - 0.0005$	$r_2 - 0.0008$	$r_2 - 0.0008$
C <sub>2</sub> –C <sub>7</sub>	$r_1 - 0.0148$	$r_1 - 0.0159$	$r_1 - 0.0148$	$r_1 - 0.0166$	$r_1 - 0.0164$	$r_1 - 0.0162$
C <sub>3</sub> –C <sub>4</sub>	$r_1$	$r_1 + 0.0005$	$r_1 + 0.0003$	$r_1 - 0.0010$	$r_1 + 0.0011$	$r_1 + 0.0004$
C <sub>3</sub> –H <sub>15</sub>	$r_4 - 0.0072$	$r_4 - 0.0081$	$r_4 - 0.0080$	$r_4 - 0.0070$	$r_4 - 0.0080$	$r_4 - 0.0080$
C <sub>4</sub> –C <sub>5</sub>	$r_1 + 0.0391$	$r_1 + 0.0312$	$r_1 + 0.0421$	$r_1 + 0.0463$	$r_1 + 0.0369$	$r_1 + 0.0468$
C <sub>4</sub> –H <sub>16</sub>	$r_4 + 0.0030$	$r_4 + 0.0034$	$r_4 + 0.0036$	$r_4 + 0.0026$	$r_4 + 0.0028$	$r_4 + 0.0029$
C <sub>4</sub> –H <sub>17</sub>	$r_4 + 0.0030$	$r_4 + 0.0034$	$r_4 + 0.0036$	$r_4 + 0.0026$	$r_4 + 0.0028$	$r_4 + 0.0029$
C <sub>5</sub> –C <sub>6</sub>	$r_1 + 0.0370$	$r_1 + 0.0405$	$r_1 + 0.0301$	$r_1 + 0.0423$	$r_1 + 0.0441$	$r_1 + 0.0325$
C <sub>5</sub> –C <sub>8</sub>	$r_1 + 0.0159$	$r_1 + 0.0174$	$r_1 + 0.0175$	$r_1 + 0.0203$	$r_1 + 0.0228$	$r_1 + 0.0219$
C <sub>5</sub> –H <sub>23</sub>	$r_4 + 0.0030$	$r_4 + 0.0034$	$r_4 + 0.0036$	$r_4 + 0.0026$	$r_4 + 0.0028$	$r_4 + 0.0029$
C <sub>6</sub> –C <sub>7</sub>	$r_1 + 0.0197$	$r_1 + 0.0206$	$r_1 + 0.0189$	$r_1 + 0.0182$	$r_1 + 0.0190$	$r_1 + 0.0204$
C <sub>6</sub> –H <sub>24</sub>	$r_4 + 0.0030$	$r_4 + 0.0034$	$r_4 + 0.0036$	$r_4 + 0.0026$	$r_4 + 0.0028$	$r_4 + 0.0029$
C <sub>6</sub> –H <sub>25</sub>	$r_4 + 0.0030$	$r_4 + 0.0034$	$r_4 + 0.0036$	$r_4 + 0.0026$	$r_4 + 0.0028$	$r_4 + 0.0029$
C <sub>7</sub> =O <sub>11</sub>	$r_3$	$r_3 + 0.0001$	$r_3 + 0.0000$	$r_3 + 0.0010$	$r_3 + 0.0000$	$r_3 + 0.0008$
C <sub>8</sub> =C <sub>9</sub>	$r_2 - 0.0099$	$r_2 - 0.0100$	$r_2 - 0.0102$	$r_2 - 0.0093$	$r_2 - 0.0105$	$r_2 - 0.0097$
C <sub>8</sub> –C <sub>10</sub>	$r_1 + 0.0066$	$r_1 + 0.0072$	$r_1 + 0.0072$	$r_1 + 0.0058$	$r_1 + 0.0074$	$r_1 + 0.0080$
C <sub>9</sub> –H <sub>18</sub>	$r_4 - 0.0072$	$r_4 - 0.0081$	$r_4 - 0.0080$	$r_4 - 0.0070$	$r_4 - 0.0080$	$r_4 - 0.0080$
C <sub>9</sub> –H <sub>19</sub>	$r_4 - 0.0072$	$r_4 - 0.0081$	$r_4 - 0.0080$	$r_4 - 0.0070$	$r_4 - 0.0080$	$r_4 - 0.0080$
C <sub>10</sub> –H <sub>20</sub>	$r_4$	$r_4 + 0.0001$	$r_4 + 0.0001$	$r_4 - 0.0001$	$r_4 + 0.0001$	$r_4 + 0.0002$
C <sub>10</sub> –H <sub>21</sub>	$r_4$	$r_4 + 0.0001$	$r_4 + 0.0001$	$r_4 - 0.0001$	$r_4 + 0.0001$	$r_4 + 0.0002$
C <sub>10</sub> –H <sub>22</sub>	$r_4$	$r_4 + 0.0001$	$r_4 + 0.0001$	$r_4 - 0.0001$	$r_4 + 0.0001$	$r_4 + 0.0002$
<i>Bond angles (deg)</i>						
C <sub>2</sub> –C <sub>1</sub> –H <sub>12</sub>	$\theta_4$	$\theta_4 + 0.01$	$\theta_4 + 0.03$	$\theta_4 - 0.02$	$\theta_4 + 0.01$	$\theta_4 - 0.03$
C <sub>2</sub> –C <sub>1</sub> –H <sub>13</sub>	$\theta_4 - 0.48$	$\theta_4 - 0.52$	$\theta_4 - 0.50$	$\theta_4 - 0.68$	$\theta_4 - 0.77$	$\theta_4 - 0.70$
C <sub>2</sub> –C <sub>1</sub> –H <sub>14</sub>	$\theta_4 - 0.68$	$\theta_4 - 0.63$	$\theta_4 - 0.70$	$\theta_4 - 0.44$	$\theta_4 - 0.41$	$\theta_4 - 0.47$
C <sub>1</sub> –C <sub>2</sub> =C <sub>3</sub>	$\theta_1 - 1.02$	$\theta_1 - 0.91$	$\theta_1 - 0.90$	$\theta_1 - 1.02$	$\theta_1 - 0.88$	$\theta_1 - 0.92$
C <sub>3</sub> =C <sub>2</sub> –C <sub>7</sub>	$\theta_1 - 4.97$	$\theta_1 - 5.20$	$\theta_1 - 5.17$	$\theta_1 - 5.12$	$\theta_1 - 5.27$	$\theta_1 - 5.22$
C <sub>2</sub> =C <sub>3</sub> –C <sub>4</sub>	$\theta_1$	$\theta_1 - 0.01$	$\theta_1 + 0.01$	$\theta_1 + 0.66$	$\theta_1 + 0.19$	$\theta_1 - 0.02$
C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub>	$\theta_3$	$\theta_3 + 0.12$	$\theta_3 + 0.04$	$\theta_3 + 0.07$	$\theta_3 - 0.12$	$\theta_3 + 0.02$
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	$\theta_2$	$\theta_2 - 0.02$	$\theta_2 + 0.30$	$\theta_2 + 2.73$	$\theta_2 + 1.78$	$\theta_2 + 0.93$
C <sub>3</sub> –C <sub>4</sub> –H <sub>16</sub>	$\theta_4 - 1.55$	$\theta_4 - 1.46$	$\theta_4 - 2.32$	$\theta_4 - 3.31$	$\theta_4 - 3.04$	$\theta_4 - 2.62$
C <sub>3</sub> –C <sub>4</sub> –H <sub>17</sub>	$\theta_4 - 2.44$	$\theta_4 - 2.85$	$\theta_4 - 1.82$	$\theta_4 - 1.72$	$\theta_4 - 1.58$	$\theta_4 - 1.71$
C <sub>5</sub> –C <sub>4</sub> –H <sub>16</sub>	$\theta_4 - 1.43$	$\theta_4 - 0.95$	$\theta_4 - 0.58$	$\theta_4 - 2.49$	$\theta_4 - 2.56$	$\theta_4 - 2.62$
C <sub>5</sub> –C <sub>4</sub> –H <sub>17</sub>	$\theta_4 - 1.01$	$\theta_4 - 1.29$	$\theta_4 - 2.09$	$\theta_4 - 1.43$	$\theta_4 - 1.02$	$\theta_4 - 0.14$
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	$\theta_2 - 3.24$	$\theta_2 - 3.66$	$\theta_2 - 3.40$	$\theta_2 - 2.63$	$\theta_2 - 3.73$	$\theta_2 - 4.20$
C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub>	$\theta_2 + 0.88$	$\theta_2 + 3.09$	$\theta_2 + 0.05$	$\theta_2 + 1.23$	$\theta_2 + 3.01$	$\theta_2 + 0.81$
C <sub>4</sub> –C <sub>5</sub> –H <sub>23</sub>	$\theta_4 - 4.73$	$\theta_4 - 4.54$	$\theta_4 - 5.08$	$\theta_4 - 4.22$	$\theta_4 - 3.66$	$\theta_4 - 4.49$
C <sub>6</sub> –C <sub>5</sub> –C <sub>8</sub>	$\theta_2 + 1.18$	$\theta_2 + 0.11$	$\theta_2 + 2.79$	$\theta_2 + 1.12$	$\theta_2 - 0.24$	$\theta_2 + 2.43$
C <sub>6</sub> –C <sub>5</sub> –H <sub>23</sub>	$\theta_4 - 4.13$	$\theta_4 - 4.68$	$\theta_4 - 4.04$	$\theta_4 - 4.22$	$\theta_4 - 4.29$	$\theta_4 - 3.37$
C <sub>5</sub> –C <sub>6</sub> –C <sub>7</sub>	$\theta_2 + 0.27$	$\theta_2 + 0.55$	$\theta_2 + 0.45$	$\theta_2 + 2.97$	$\theta_2 + 1.11$	$\theta_2 + 1.62$
C <sub>5</sub> –C <sub>6</sub> –H <sub>24</sub>	$\theta_4 - 1.33$	$\theta_4 - 2.41$	$\theta_4 - 1.63$	$\theta_4 + 0.48$	$\theta_4 + 1.56$	$\theta_4 + 1.27$
C <sub>5</sub> –C <sub>6</sub> –H <sub>25</sub>	$\theta_4 + 0.71$	$\theta_4 + 1.58$	$\theta_4 + 0.93$	$\theta_4 - 3.00$	$\theta_4 - 2.61$	$\theta_4 - 2.98$
C <sub>5</sub> –C <sub>8</sub> =C <sub>9</sub>	$\theta_1 - 4.32$	$\theta_1 - 1.06$	$\theta_1 - 1.35$	$\theta_1 - 5.12$	$\theta_1 - 0.68$	$\theta_1 - 1.00$
C <sub>7</sub> –C <sub>6</sub> –H <sub>24</sub>	$\theta_4 - 4.42$	$\theta_4 - 3.62$	$\theta_4 - 4.46$	$\theta_4 - 3.04$	$\theta_4 - 3.33$	$\theta_4 - 2.95$
C <sub>7</sub> –C <sub>6</sub> –H <sub>25</sub>	$\theta_4 - 3.23$	$\theta_4 - 3.99$	$\theta_4 - 3.33$	$\theta_4 - 5.35$	$\theta_4 - 4.48$	$\theta_4 - 4.87$

Table 3 (continued)

Parameters	<i>eq</i> -1	<i>eq</i> -2	<i>eq</i> -3	<i>ax</i> -1	<i>ax</i> -2	<i>ax</i> -3
C <sub>9</sub> =C <sub>8</sub> –C <sub>10</sub>	$\theta_1 - 3.55$	$\theta_1 - 3.90$	$\theta_1 - 3.78$	$\theta_1 - 3.87$	$\theta_1 - 3.95$	$\theta_1 - 4.17$
C <sub>8</sub> –C <sub>10</sub> –H <sub>20</sub>	$\theta_4 + 0.65$	$\theta_4 + 0.61$	$\theta_4 - 0.34$	$\theta_4 + 0.40$	$\theta_4 - 0.32$	$\theta_4 + 0.79$
C <sub>8</sub> –C <sub>10</sub> –H <sub>21</sub>	$\theta_4 + 0.25$	$\theta_4 - 0.42$	$\theta_4 + 0.61$	$\theta_4 - 0.53$	$\theta_4 - 0.00$	$\theta_4 - 0.14$
C <sub>8</sub> –C <sub>10</sub> –H <sub>22</sub>	$\theta_4 - 0.33$	$\theta_4 + 0.07$	$\theta_4 + 0.05$	$\theta_4 + 0.39$	$\theta_4 + 0.61$	$\theta_4 - 0.13$

See Fig. 1 for the atom numbering and the definitions of the conformers.

On the other hand, B3LYP method predicts that the *ax* conformers are more than 2 kcal mol<sup>−1</sup> higher in free energy than the *eq*-1 conformer and the total abundance of the *ax* conformers is less than 7%.

The vibrational calculations for the six conformers were carried out with the B3LYP method to obtain the vibrational frequencies and the harmonic force field.

#### 4. Analyses

**Normal vibration analysis.** The Cartesian force constants of carvone obtained by the B3LYP/6-31G\*\* calculations were transformed into the force constants,  $f_{ij}$ , for the internal coordinates. As the *eq*-1 conformer was predicted to be the most abundant by both methods, MP2 and B3LYP,  $f_{ij}$ s for the *eq*-1 were modified by the scaling method so as to reproduce the experimental vibrational wavenumbers of the gas-phase FTIR spectrum measured in the present study and the liquid-phase vibrational spectra in Ref. [10]. The linear scaling formula  $f_{ij}(\text{scaled}) = (c_i c_j)^{1/2} f_{ij}(\text{unscaled})$  was used where  $c_i$  is a scale factor [11]. The definitions of internal coordinates with the resultant scale factors are listed in Table S3 of supplementary information. The calculated vibrational wavenumbers and scaled force constants are listed in Tables S4 and S5 of supplementary information, respectively.

**Analysis of electron diffraction data.** The following treatments were adopted based on the results of the B3LYP/6-31G\*\* calculations in order to reduce the number of adjustable parameters: (1) coplanarity was assumed around C<sub>2</sub>, C<sub>7</sub> and C<sub>8</sub> atoms; (2) the differences among the C–C single bonds were set equal to their theoretical values; (3)

the difference between the two C=C double bonds was set equal to the theoretical value; (4) the C–H bond lengths were classified into three groups, C(sp<sup>2</sup>)–H, C(methyl)–H and the rest, and the differences among these groups were set equal to the corresponding theoretical values; (5) the differences among the C=C–C angles were set equal to their theoretical values; (6) the differences among all the C–C–C angles but C<sub>2</sub>–C<sub>7</sub>–C<sub>6</sub> and C<sub>5</sub>–C<sub>8</sub>–C<sub>10</sub> were set equal to their theoretical values; (7) the differences among the C–C–H angles were set equal to their theoretical values; (8) all the C=C–H angles were fixed at their theoretical values; (9) the C<sub>7</sub>=O<sub>11</sub> bond was assumed to bisect the C<sub>2</sub>–C<sub>7</sub>–C<sub>6</sub> angle; (10) the parameter differences among the different conformers were set equal to their theoretical values. The independent parameters and the constraints are summarized in Table 3.

Mean amplitudes,  $l$ , and shrinkage corrections,  $r_a - r_\alpha$  [12], of the *eq*-1 conformer were calculated from the above-mentioned scaled force constants. Those of the other conformers were calculated by using the force constants obtained from the B3LYP/6-31G\* calculations and the same scale factor  $c_i$ s as those of the *eq*-1 conformer. The model of small amplitude vibrations was adopted. The mean amplitudes of the bonded pairs were adjusted in a group. In addition, those of the geminal non-bonded pairs such as C<sub>1</sub>⋯C<sub>3</sub> were adjusted in the second group and those of the vicinal non-bonded pairs such as C<sub>1</sub>⋯C<sub>4</sub> and C<sub>2</sub>⋯C<sub>5</sub> were adjusted as the third group. The differences among mean amplitudes in each group were fixed at the calculated values. The mean amplitudes of other pairs were not varied and were fixed at their calculated values. Table 4 lists the mean amplitudes with the corresponding  $r_a$  distances.



Table 4

$r_a$  Distances and mean amplitudes of the *eq*-1 conformer of carvone (Å)

Atom pair <sup>a</sup>	$r_a$	$l_{\text{calc}}$	$l_{\text{obs}}^b$	Group
C <sub>1</sub> –C <sub>2</sub>	1.507	0.051	0.050(2)	1
C <sub>1</sub> ···C <sub>3</sub>	2.520	0.066	0.074(4)	2
C <sub>1</sub> ···C <sub>4</sub>	3.918	0.071	0.087(5)	3
C <sub>1</sub> ···C <sub>5</sub>	4.374	0.094	0.094	
C <sub>1</sub> ···C <sub>6</sub>	3.927	0.076	0.092	3
C <sub>1</sub> ···C <sub>7</sub>	2.568	0.071	0.079	2
C <sub>1</sub> ···C <sub>8</sub>	5.855	0.090	0.090	
C <sub>1</sub> ···C <sub>9</sub>	6.738	0.151	0.151	
C <sub>1</sub> ···C <sub>10</sub>	6.529	0.141	0.141	
C <sub>1</sub> ···O <sub>11</sub>	2.865	0.107	0.123	3
C <sub>1</sub> –H <sub>12</sub>	1.099	0.078	0.078	1
C <sub>1</sub> –H <sub>13</sub>	1.099	0.079	0.078	1
C <sub>1</sub> –H <sub>14</sub>	1.099	0.079	0.078	1
C <sub>2</sub> =C <sub>3</sub>	1.364	0.043	0.042	1
C <sub>2</sub> ···C <sub>4</sub>	2.526	0.060	0.068	2
C <sub>2</sub> ···C <sub>5</sub>	2.885	0.081	0.097	3
C <sub>2</sub> ···C <sub>6</sub>	2.571	0.066	0.074	2
C <sub>2</sub> –C <sub>7</sub>	1.493	0.051	0.050	1
C <sub>2</sub> ···C <sub>8</sub>	4.361	0.080	0.080	
C <sub>2</sub> ···C <sub>9</sub>	5.281	0.118	0.118	
C <sub>2</sub> ···C <sub>10</sub>	5.068	0.126	0.126	
C <sub>2</sub> ···C <sub>11</sub>	2.372	0.060	0.068	2
C <sub>3</sub> –C <sub>4</sub>	1.509	0.051	0.051	1
C <sub>3</sub> ···C <sub>5</sub>	2.496	0.070	0.078	2
C <sub>3</sub> ···C <sub>6</sub>	2.869	0.077	0.094	3
C <sub>3</sub> ···C <sub>7</sub>	2.459	0.060	0.068	2
C <sub>3</sub> ···C <sub>8</sub>	3.842	0.077	0.093	3
C <sub>3</sub> ···C <sub>9</sub>	4.711	0.168	0.168	
C <sub>3</sub> ···C <sub>10</sub>	4.574	0.161	0.161	
C <sub>3</sub> ···O <sub>11</sub>	3.558	0.061	0.077	3
C <sub>3</sub> –H <sub>15</sub>	1.093	0.078	0.077	1
C <sub>4</sub> –C <sub>5</sub>	1.541	0.053	0.053	1
C <sub>4</sub> ···C <sub>6</sub>	2.485	0.075	0.083	2
C <sub>4</sub> ···C <sub>7</sub>	2.919	0.072	0.088	3
C <sub>4</sub> ···C <sub>8</sub>	2.526	0.082	0.090	2
C <sub>4</sub> ···C <sub>9</sub>	3.444	0.221	0.237	3
C <sub>4</sub> ···C <sub>10</sub>	3.215	0.202	0.218	3
C <sub>4</sub> ···O <sub>11</sub>	4.124	0.073	0.090	3
C <sub>4</sub> –H <sub>16</sub>	1.104	0.079	0.078	1
C <sub>4</sub> –H <sub>17</sub>	1.104	0.080	0.079	1
C <sub>5</sub> –C <sub>6</sub>	1.539	0.053	0.053	1
C <sub>5</sub> ···C <sub>7</sub>	2.501	0.075	0.082	2
C <sub>5</sub> –C <sub>8</sub>	1.517	0.052	0.052	1
C <sub>5</sub> ···C <sub>9</sub>	2.471	0.067	0.075	2
C <sub>5</sub> ···C <sub>10</sub>	2.599	0.074	0.082	2
C <sub>5</sub> ···O <sub>11</sub>	3.553	0.095	0.112	3
C <sub>5</sub> –H <sub>23</sub>	1.104	0.079	0.079	1
C <sub>6</sub> –C <sub>7</sub>	1.523	0.053	0.053	1
C <sub>6</sub> –C <sub>7</sub>	2.527	0.080	0.088	2
C <sub>6</sub> ···C <sub>9</sub>	3.574	0.199	0.215	3
C <sub>6</sub> ···C <sub>10</sub>	3.054	0.213	0.229	3

Table 4 (continued)

Atom pair <sup>a</sup>	$r_a$	$l_{\text{calc}}$	$l_{\text{obs}}^b$	Group
C <sub>6</sub> ···O <sub>11</sub>	2.398	0.063	0.071	2
C <sub>6</sub> –H <sub>24</sub>	1.104	0.079	0.079	1
C <sub>6</sub> –H <sub>25</sub>	1.104	0.078	0.078	1
C <sub>7</sub> ···C <sub>8</sub>	3.851	0.081	0.098	3
C <sub>7</sub> ···C <sub>9</sub>	4.787	0.177	0.177	
C <sub>7</sub> ···C <sub>10</sub>	4.501	0.178	0.178	
C <sub>7</sub> =O <sub>11</sub>	1.224	0.039	0.038	1
C <sub>8</sub> =C <sub>9</sub>	1.355	0.043	0.042	1
C <sub>8</sub> –C <sub>10</sub>	1.513	0.052	0.051	1
C <sub>8</sub> ···O <sub>11</sub>	4.798	0.104	0.104	
C <sub>9</sub> ···C <sub>10</sub>	2.516	0.067	0.075	2
C <sub>9</sub> ···O <sub>11</sub>	5.631	0.269	0.269	
C <sub>9</sub> –H <sub>18</sub>	1.093	0.077	0.076	1
C <sub>9</sub> –H <sub>19</sub>	1.093	0.077	0.076	1
C <sub>10</sub> ···O <sub>11</sub>	5.416	0.235	0.235	
C <sub>10</sub> –H <sub>20</sub>	1.099	0.079	0.078	1
C <sub>10</sub> –H <sub>21</sub>	1.099	0.079	0.078	1
C <sub>10</sub> –H <sub>22</sub>	1.099	0.078	0.078	1

<sup>a</sup> See Fig. 1 for the atom numbering. Non-bonded C···H, O···H and H···H pairs are not listed although they were included in the data analysis.

<sup>b</sup> Numbers in parentheses are estimated error limits (3 $\sigma$ ) referring to the last significant digit.

The anharmonicity parameters,  $\kappa$  [13], for bonded atom pairs were estimated in a diatomic approximation,  $\kappa = (a/6)l^4$  [14], where the Morse parameter,  $a$ , was assumed to be 2.0 Å<sup>−1</sup>. Those for nonbonded atom pairs were assumed to be zero.

## 5. Results and discussion

As mentioned above, the MP2 and B3LYP calculations predicted the conformational composition of carvone inconsistently. According to the MP2 calculations, the abundance of the *ax* conformers is significant. On the other hand, the B3LYP calculations predicted it to be less than 7%. Therefore, preliminary analyses were carried out to find out whether the *ax* conformers should be considered or not. In the MP2 model, all the six conformers in Fig. 1 were mixed with the fixed abundance predicted by the MP2/6-31G\*\* calculations (see Table 1). In the DFT model, only the *eq* conformers were considered with the fixed abundance calculated from the free-energy

difference of the B3LYP/6-31G\*\* calculations (47.8, 25.8 and 26.3% for the *eq*-1, *eq*-2 and *eq*-3 conformers, respectively). In both models, the dihedral angle, C<sub>4</sub>–C<sub>5</sub>–C<sub>8</sub>=C<sub>9</sub>, of each conformer was fixed at the B3LYP value. The obtained *R*-factor<sup>1</sup> was 0.049 for the MP2 model (*eq* and *ax* conformers) and 0.051 for the DFT model (*eq* conformers only). As the inclusion of the *ax* conformers (MP2 model) did not revise the fitting quality significantly, we concluded that the abundance of the *ax* conformers is quite low, or, carvone exists exclusively as the *eq* conformers in the gas phase. Very recently, Shin and Hamada [15] measured a VCD spectrum of (*R*)-(-)-carvone and compared it with the theoretical spectra obtained by B3LYP/6-31G\*\* calculations. They have found that the observed spectrum can be reproduced by assuming the three *eq* conformers. Therefore it is likely that carvone exists exclusively as the *eq* conformers also in the liquid phase. So, further analysis was carried out by assuming the *ex* conformers only in order to refine the abundance of the *eq*-1, *eq*-2 and *eq*-3 conformers. It was possible to determine the abundance of the most stable conformer, *eq*-1, with a good precision, but it was not possible to determine how the rest of the abundance was shared by the minor conformers, *eq*-2 and *eq*-3. So, the final analysis was carried out by fixing the relative abundance of the *eq*-2 and *eq*-3 conformers to the value estimated by the B3LYP/6-31G\*\* calculations (i.e. 25.8/26.3) while the abundance of the *eq*-1 conformer was varied. This treatment is equivalence of assuming the free-energy difference between the *eq*-2 and *eq*-3 conformers to be equal to the B3LYP value. In addition, the determination of the dihedral angle, C<sub>4</sub>–C<sub>5</sub>–C<sub>8</sub>=C<sub>9</sub>, of any of the conformers was not successful. When this dihedral angle of the *eq*-1 conformer was varied, it did not converge and another analysis in which the dihedral angles, C<sub>4</sub>–C<sub>5</sub>–C<sub>8</sub>=C<sub>9</sub>, of the *eq* conformers were bound as one parameter resulted in very large standard deviation of this parameter (13°). Therefore, the dihedral angles, C<sub>4</sub>–C<sub>5</sub>–C<sub>8</sub>=C<sub>9</sub>,

Table 5

Experimental and theoretical molecular structures of the *eq*-1 conformer of carvone

Parameters <sup>a</sup>	ED ( <i>r<sub>g</sub></i> and <i>∠<sub>a</sub></i> ) <sup>b</sup>	MP2/6-31G**	B3LYP/6-31G**
<i>Bond lengths (Å)</i>			
C <sub>1</sub> –C <sub>2</sub>	1.507	1.499	1.504
C <sub>3</sub> –C <sub>4</sub>	1.507	1.501	1.504
C <sub>4</sub> –C <sub>5</sub>	1.546	1.533	1.543
C <sub>5</sub> –C <sub>6</sub>	1.544	1.531	1.541
C <sub>6</sub> –C <sub>7</sub>	1.527	1.515	1.524
C <sub>2</sub> –C <sub>7</sub>	1.492	1.484	1.489
C <sub>5</sub> –C <sub>8</sub>	1.523	1.509	1.520
C <sub>8</sub> –C <sub>10</sub>	1.513	1.505	1.511
⟨C–C⟩	1.520	1.510	1.517
C <sub>2</sub> =C <sub>3</sub>	1.365	1.351	1.347
C <sub>8</sub> =C <sub>9</sub>	1.355	1.342	1.337
⟨C=C⟩	1.360	1.347	1.342
C <sub>7</sub> =O <sub>11</sub>	1.225(5)	1.234	1.223
⟨C–H⟩	1.104(4)	1.090	1.094
<i>Bond angles and dihedral angle (deg)</i>			
C <sub>2</sub> =C <sub>3</sub> –C <sub>4</sub>	123.9	124.1	124.8
C <sub>1</sub> –C <sub>2</sub> =C <sub>3</sub>	122.8	123.7	123.7
C <sub>5</sub> =C <sub>8</sub> –C <sub>7</sub>	118.9	119.9	119.8
C <sub>5</sub> –C <sub>8</sub> =C <sub>9</sub>	119.5	120.3	120.4
C <sub>9</sub> =C <sub>8</sub> –C <sub>10</sub>	120.3	121.6	121.2
⟨C=C–C⟩	121.1	121.9	122.0
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	110.6	111.6	112.2
C <sub>4</sub> –C <sub>5</sub> –C <sub>6</sub>	107.4	108.6	108.9
C <sub>5</sub> –C <sub>6</sub> –C <sub>7</sub>	110.9	111.2	112.5
C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub>	111.5	112.7	113.1
C <sub>6</sub> –C <sub>5</sub> –C <sub>8</sub>	111.8	113.0	113.4
⟨C–C–C⟩	110.4	111.4	112.0
C <sub>2</sub> –C <sub>7</sub> –C <sub>6</sub>	117.1(14)	116.9	117.3
⟨C–C–H⟩	111.1(13)	109.8	109.8
C <sub>4</sub> –C <sub>5</sub> –C <sub>8</sub> =C <sub>9</sub>	–113.2(fixed)	–110.4	–113.2

<sup>a</sup> See Fig. 1 for the atom numbering. Angle brackets denote average values.

<sup>b</sup> Numbers in parentheses are estimated error limits (3σ) referring to the last significant digit. The index of resolution is 0.87(2).

of all the conformers were fixed to their theoretical values obtained by the B3LYP/6-31G\*\* calculations.

Table 5 lists the obtained structural parameters for the *eq*-1 conformer of carvone. Experimental radial distribution curves with residuals are shown in Fig. 3. The *R*-factor of the analysis is 0.051. The final conformational composition of carvone has been determined to be 62 ± 18 vs. 38% for the *eq*-1 and (*eq*-2 + *eq*-3) conformers, respectively. The abundance obtained for the *eq*-1 conformer is

<sup>1</sup> *R*-factor is defined as  $R = \{ \sum_i W_i (\Delta sM(s)_i)^2 / \sum_i W_i (sM(s)_i^{\text{obs}})^2 \}^{1/2}$ , where  $\Delta sM(s)_i = sM(s)_i^{\text{obs}} - sM(s)_i^{\text{calc}}$  and  $W_i$  is a diagonal element of the weight matrix.

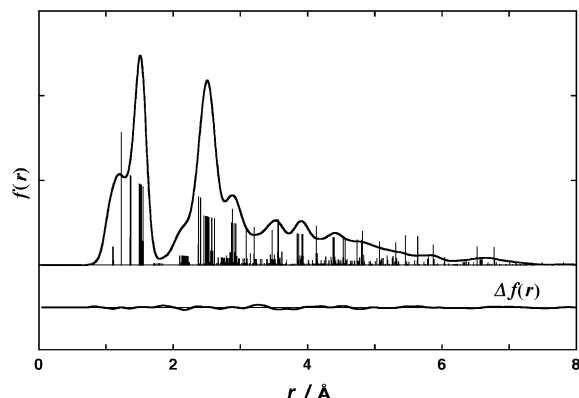


Fig. 3. Experimental radial distribution curves of carvone (62% *eq*-1, 19% *eq*-2 and 19% *eq*-3);  $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$ . Distance distributions are indicated by vertical bars.

consistent with the value predicted by the B3LYP/6-31G\*\* calculations, 47.8%. The correlation matrix is listed in Table S6 of supplementary information.

In Table 5, the structural parameters obtained from the MP2 and B3LYP calculations are compared with the experimental ones. In the two methods, the B3LYP shows slightly better agreements with the experimental results especially for the bond lengths. This is not because the structural constraints are based on the B3LYP structures rather than the MP2 structures. The fitting quality and almost all the fitting parameters were unchanged within their error limits (three times the standard deviations) even by changing the parameter difference values of the constraints from the B3LYP basis to the MP2 basis.

From the  $r_\alpha$  structure of the *eq*-1 conformer obtained in the present study, the puckering parameters of the six-membered ring,  $Q$ ,  $\theta$  and  $\phi$ , defined in Ref. [16] were calculated to be, 0.50 Å, 44.5° and 8.1°, respectively. Those for menthol are, 0.53 Å, 1.0° and 14.6°, respectively, and those for the most abundant conformer of isomenthol are, 0.52 Å, 2.7° and 15.2°, respectively [1]. Obviously, the puckering amplitudes,  $Q$ , of these compounds are close to each other. As illustrated in Fig. 4, small  $\theta$  values of menthol and isomenthol reflect the chair form of their rings. On the other hand, the relatively large  $\theta$  value and small

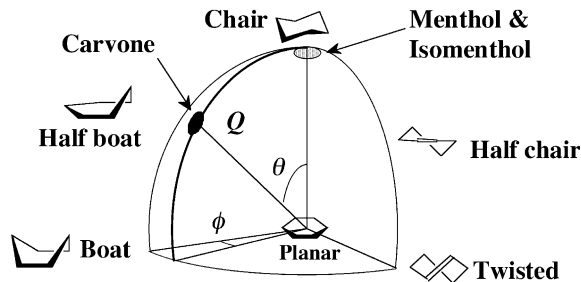


Fig. 4. Illustration of relationship between the puckering parameters of the six-membered ring,  $Q$ ,  $\theta$  and  $\phi$ , and the ring shape.

$\phi$  value of carvone correspond to the half boat form of the ring, in which the C<sub>5</sub> atom that is bonded to the isopropenyl group is out of the plane formed by other ring members. The common feature of these compounds is that, the isopropyl or isopropenyl group is in the equatorial position and one methyl group of the isopropyl or isopropenyl group (C<sub>10</sub> methyl in case of carvone) is oriented perpendicular to the ring. Of course, more detailed discussion of the relationship between the minty odor and the geometrical structure waits for further extensive structural investigation of the related compounds.

## 6. Supplementary material

Tables of the leveled total intensities and the backgrounds, geometrical structures of the *ax* conformers, definitions of the internal coordinates and the corresponding scale factors, vibrational wavenumbers, the scaled harmonic force constants and the correlation matrix are deposited with BLLD as publication No. SUP 26697.

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