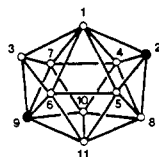


**Table III.** Bond Distances and Total Energy of 2,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> from Geometry-Optimized ab Initio SCF MO Calculations at the STO-3G Level<sup>a</sup>2,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub><sup>b</sup>  
point group C<sub>s</sub>

C <sub>2</sub> B <sub>1</sub>	1.639	B <sub>1</sub> B <sub>6</sub>	2.010	C <sub>2</sub> H	1.077
C <sub>2</sub> B <sub>4</sub>	1.568	B <sub>3</sub> B <sub>6</sub>	1.646	C <sub>9</sub> H	1.080
C <sub>2</sub> B <sub>8</sub>	1.694	B <sub>4</sub> B <sub>7</sub>	1.836	B <sub>1</sub> H	1.154
C <sub>9</sub> B <sub>3</sub>	1.687	B <sub>4</sub> B <sub>8</sub>	1.807	B <sub>3</sub> H	1.146
C <sub>9</sub> B <sub>6</sub>	1.723	B <sub>4</sub> B <sub>10</sub>	1.764	B <sub>4</sub> H	1.150
C <sub>9</sub> B <sub>10</sub>	1.692	B <sub>6</sub> B <sub>11</sub>	1.788	B <sub>6</sub> H	1.149
B <sub>1</sub> B <sub>3</sub>	1.706	B <sub>8</sub> B <sub>10</sub>	1.754	B <sub>8</sub> H	1.147
B <sub>1</sub> B <sub>4</sub>	2.065	B <sub>10</sub> B <sub>11</sub>	1.857	B <sub>10</sub> H	1.148

<sup>a</sup>All bond distances are in Å. <sup>b</sup>Total energy is -300.6324 au.initial and final C<sub>2v</sub> structures **19** and **21**.The rule of topological charge stabilization<sup>20</sup> predicts the following order for the four most stable isomers of C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>:

$$\begin{matrix} 2,3 > 2,10 > 2,6 > 2,9 \\ 0 & 25.4 & 20.4 \end{matrix}$$

Again, numbers appearing below the isomer designations in the sequence are energies (in kcal/mol) relative to the lowest energy 2,3-isomer. The energies were obtained from ab initio SCF MO calculations with the STO-3G basis set. We reported total energies and optimized structures of the 2,3- and 2,10-isomers in our earlier study. Table III contains the corresponding information for the 2,9-isomer. The qualitative ordering sequence is not completely consistent with calculated energies. The isomers 2,3, 2,6, and 2,10 are linked together near the center of Figure 2. The relatively low-energy 2,9-isomer appears at a terminal position at the top of the diagram. Calculation of geometry-optimized energies of many or all of the remaining 17 isomers of C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> might reveal metastable isomers protected from rearrangement by higher energy isomers as we predict for C<sub>2</sub>B<sub>6</sub>H<sub>8</sub> and C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>. Such a project, even at the STO-3G level, would require more computer time than we expect to have available to us in the near future.

### Conclusions

We have used reaction pathways connecting carborane isomers through DSD framework reorganizations and estimates of relative

stabilities of isomers based on minimal basis set but geometry-optimized ab initio SCF MO calculations to rationalize the existence of particular isomers and experimental observations of the rearrangements of C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>, C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>, and C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> and to predict the metastability of an isomer that has not yet been reported. It should be possible to isolate 1,2-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub> because it is separated from the minimum energy 1,7-isomer by energy barriers that result from the interposition of higher energy isomers along the reaction pathway. We report total energies and geometry-optimized structures at the STO-3G level for 2,7-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>, 2,4-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>, and 2,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>. These results supplement our earlier set of molecular structure calculations at the same level of theory for *closo*-carboranes and boranes. We found the energy of unknown 2,7-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> to be slightly lower than that of one of the known isomers of this carborane. However, we do not expect 2,7-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> to be isolated because it is an intermediate on the reaction pathway between two lower energy isomers.

The results of our calculations and our examination of reaction graphs based on DSD framework reorganizations combine with the experimental work of others to support the proposal of DSD rearrangements for the 8-, 10-, and 11-atom boranes and carboranes. But the proof of any mechanistic proposal must be infinitely difficult. Indeed, other mechanisms have been suggested for these rearrangements. Johnson<sup>37</sup> has proposed a single-edge cleavage process as a general mechanism for polyhedral rearrangements, and this mechanism merits serious study, particularly for the five- and six-atom cages. Finally, the framework reorganizations of the *closo*-boranes and carboranes are examples of degenerate cage rearrangements or pseudorotations, processes known to occur in other species such as the bullvalenes<sup>38,39</sup> and the P<sub>7</sub><sup>3-</sup> ion.<sup>40</sup> Although the mechanisms of the various rearrangements differ in detail, they constitute a larger class of processes of importance to both organic and inorganic chemistry.

**Acknowledgment.** J.J.O. is grateful to the University of South Carolina for a summer research fellowship funded by the Committee on Research and Productive Scholarship. B.M.G. acknowledges correspondence and a helpful discussion with Professor R. B. King of the University of Georgia concerning polyhedral cage rearrangements.

- (37) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1986**, 27-30.  
 (38) Doering, W. v. E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715-737.  
 (39) Schröder, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 481-482.  
 Schröder, G.; Merenyi, R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 752-761.  
 (40) Baudler, M.; Ternberger, H.; Faber, W.; Hahn, J. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34b*, 1690-1697.

## Characterizing the 2-Norbornyl Cation in the Gas Phase

Marcia C. Blanchette, John L. Holmes,\* and F. P. Lossing

Contribution from the Chemistry Department, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4. Received August 4, 1986

**Abstract:** The gas-phase heat of formation,  $\Delta H_f^\circ$ , of the 2-norbornyl cation has been reassessed as  $767 \pm 5$  kJ mol<sup>-1</sup> by considering all available experimental data. This ion can be distinguished in the gas phase from isomeric [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> species by its collisional activation mass spectrum which, unlike all other [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> ions studied, contained a significant peak at *m/z* 66, [C<sub>5</sub>H<sub>6</sub>]<sup>+</sup>. Its charge stripping mass spectrum was similarly structure-diagnostic in that it alone lacked peaks corresponding to [C<sub>7</sub>H<sub>10</sub>]<sup>2+</sup> and [C<sub>7</sub>H<sub>11</sub>]<sup>2+</sup>.

The solution chemistry of the 2-norbornyl cation has been a topic of interest and controversy since 1949 when Winstein and Trifan<sup>1</sup> first proposed that the ion has a nonclassical bridged structure. Indeed, a recent issue of *Accounts of Chemical Research*<sup>2</sup> contained a series of articles about the structure and

chemistry of this celebrated species.

Although a number of mass spectral investigations of [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> ions derived from 2-norbornyl compounds have been reported,<sup>3</sup>

(1) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953.

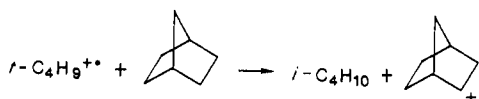
(2) (a) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. (b) Brown, H. C. *Ibid.* **1983**, *16*, 432. (c) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Ibid.* **1983**, *16*, 440. (d) Walling, C. *Ibid.* **1983**, *16*, 448.

Table I. Heats of Formation of  $C_7H_{11}^+$  Ions

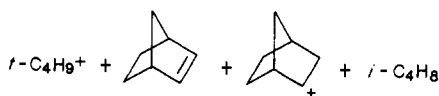
precursor molecule (M)	neutral fragment <sup>a</sup>	$\Delta H_f^\circ$ [M], kJ mol <sup>-1</sup>	appearance energy, <i>m/z</i> 95, eV <sup>b</sup>	$\Delta H_f^\circ[C_7H_{11}^+]$ , kJ mol <sup>-1</sup>
2,4-octadiene	CH <sub>3</sub> <sup>•</sup>	18 <sup>c</sup>	9.72	809
2,6-octadiene	CH <sub>3</sub> <sup>•</sup>	20 <sup>c</sup>	9.02	744
3,6-dimethylcyclohexene	CH <sub>3</sub> <sup>•</sup>	-60 <sup>c</sup>	9.78	736
1-methylcyclohexene	H <sup>•</sup>	-43 <sup>d</sup>	≤11.4	≤837
norbornane	H <sup>•</sup>	-57 <sup>c</sup>	10.78	765
3-ethylcyclopentene	H <sup>•</sup>	-13 <sup>c</sup>	10.50	782
vinylcyclopentane	H <sup>•</sup>	-0.2 <sup>c</sup>	≤12.0	≤936
ethylidenecyclopentane	H <sup>•</sup>	-18 <sup>c</sup>	≤11.4	≤866
2-bromonorbornane	Br <sup>•</sup>			768 ± 5 kJ mol
2-iodonorbornane	I <sup>•</sup>			ref 6 and see Discussion

<sup>a</sup>  $\Delta H_f^\circ[H] = 218$  kJ mol<sup>-1</sup>; <sup>17</sup>  $\Delta H_f^\circ[CH_3^\bullet] = 147$  kJ mol<sup>-1</sup>. <sup>18</sup> <sup>b</sup> See Experimental Section; estimated error ±0.05 eV. <sup>c</sup> By additivity, ref 19. <sup>d</sup> Reference 9.

none have produced direct evidence which would permit the unequivocal structural identification of the 2-norbornyl cation in the gas phase. It has, for example, clearly been shown from metastable ion studies that, in isotopically labeled  $[C_7H_{11}]^+$  ions produced by electron impact from simple 2-norbornyl derivatives,<sup>3b</sup> the carbon and hydrogen atoms lose all positional identity before fragmentation by the reactions of lowest energy requirement, losses of C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>. Clearly, if such dissociations generate 2-norbornyl cations, they will be found among lower energy  $[C_7H_{11}]^+$  species. The heat of formation of the (supposed) 2-norbornyl cation has been measured via several techniques. Solomon and Field<sup>4</sup> obtained -6 kJ mol<sup>-1</sup> for  $\Delta H$  for the reaction



and Saluja and Kebarle<sup>5</sup> measured  $\Delta H = -18$  kJ mol<sup>-1</sup> for the reaction



Appearance energies (AE) of  $[C_7H_{11}]^+$  ions from *exo*-2-norbornyl bromide and iodide, measured using energy selected electrons,<sup>6</sup> gave values of 766 and 767 kJ mol<sup>-1</sup> with the major uncertainty, ±5 kJ mol<sup>-1</sup>, lying in the neutral precursor enthalpies.

The above information, however, contains no evidence directly indicative of the norbornyl cation structure being generated in either the equilibrium experiments or the dissociative ionizations of norbornyl halides. In particular, the latter reactions could in principle be preceded by rearrangement in the molecular ion yielding an isomeric  $[C_7H_{11}]^+$  cation with a similar heat of formation. For example, the 3-ethylcyclopentenyl cation (substituent at the end of the delocalized  $\pi$  system) has an estimated  $\Delta H_f^\circ \approx 775$  kJ mol<sup>-1</sup> ( $\Delta H_f^\circ$ [methylcyclopentenyl<sup>+</sup>] is 795 kJ mol<sup>-1</sup>).<sup>6</sup> In view of the great versatility of collision-induced fragmentation studies in aiding the assignment of structure to gas-phase ions,<sup>7</sup> it was decided to subject selected  $[C_7H_{11}]^+$  ions to such experimental investigations in the hope that some clear criteria would emerge to assist in the unequivocal identification of the 2-norbornyl cation.

## Results and Discussion

(1) **Thermochemistry.** First it is useful to review the thermochemistry from the ion-molecule reactions<sup>4,5</sup> quoted above. Now  $\Delta H_f^\circ[t-C_4H_9]^+$  seems reasonably secure at 694 kJ mol<sup>-1</sup>,<sup>8</sup> and -134.5<sup>9</sup> and -17 kJ mol<sup>-1</sup><sup>9</sup> are well-established values for

$\Delta H_f^\circ[i-C_4H_{10}]$  and  $\Delta H_f^\circ[i-C_4H_8]$ , respectively. However,  $\Delta H_f^\circ$ [norbornane] and  $\Delta H_f^\circ$ [norbornene] are less secure with values of -52<sup>9</sup> and -62 kJ mol<sup>-1</sup><sup>10</sup> reported for the former and 70<sup>9</sup> and 91 kJ mol<sup>-1</sup><sup>10</sup> for the latter. The values of -52 and 70 kJ mol<sup>-1</sup> from ref 9 for  $\Delta H_f^\circ$  of norbornane and norbornene, respectively, appear to be the more reliable. The enthalpy change for single to double bond is 122 kJ mol<sup>-1</sup>, in keeping with such changes for both strained and unstrained ring compounds, e.g., for cyclobutane to cyclobutene, 128 kJ mol<sup>-2</sup>,<sup>9</sup> and cyclopentane to cyclopentene, 111 kJ mol<sup>-1</sup>.<sup>9</sup> From ref 10 the corresponding enthalpy change for norbornane to norbornene, 153 kJ mol<sup>-1</sup>, is excessive, even for ring-strained species. Thus, from these equilibrium measurements, recalculated enthalpies of 771 and 763 kJ mol<sup>-1</sup> are to be preferred, giving a mean  $\Delta H_f^\circ[C_7H_{11}^+]$  of 767 kJ mol<sup>-1</sup>. This is in excellent agreement with the results from appearance energies.<sup>6</sup>

The losses of halogen from *exo*-2-norbornyl bromide and iodide molecular ions were accompanied by weak metastable peaks. That for *exo*-2-norbornyl bromide was very weak (ca.  $5 \times 10^{-6}$  of the base peak, *m/z* 67) but was flat-topped, and the kinetic energy release calculated from the peak width at half-height,  $T_{0.5}$ , was  $8.7 \pm 2$  kJ mol<sup>-1</sup>. The metastable peak for loss of I<sup>•</sup> from the iodo compound was more intense (ca.  $5 \times 10^{-5}$  of the base peak) with a  $T_{0.5}$  of  $0.36 \pm 0.02$  kJ mol<sup>-1</sup>.

Corrections to appearance energy measurements for kinetic energy release cannot properly be made at the present state of knowledge. AE measurements give threshold energies for ions fragmenting with a mean first-order rate constant of ca.  $750$  s<sup>-1</sup>, significantly smaller than that for ions decomposing metastably, ca.  $10^4$  s<sup>-1</sup>.<sup>11</sup> The internal energies and corresponding kinetic energy releases ( $T$ ) for the metastable ions will be larger than for the former, but the quantitative relationship between  $T$  values and different internal energies is not known. Furthermore, there is also a lack of knowledge concerning the quantitative partitioning of the excess internal energy of a fragmenting ion among the translational degrees of freedom of the products. Thus  $T$  values cannot be simply related to the corresponding ion internal energy.<sup>7</sup> The result for the iodo compound indicates that any such correction is small, and, moreover, AE values for the loss of I<sup>•</sup> from a variety of iodo compounds have provided reliable  $\Delta H_f^\circ$  values for a number of carbocations; the low ionization energy of iodo compounds (i.e., charge located at the I atom) and the weak C-I bond appear to contribute to a marked lack of rearrangement in the molecular ions prior to I<sup>•</sup> loss.<sup>12-15</sup>

(9) Pedley, J. B.; Rylance, J. *Computer-Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, Sussex, England, 1977.

(10) Steele, W. Y. *Chem. Thermodyn.* **1978**, *10*, 919.

(11) Burgers, P. C.; Holmes, J. L. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 15.

(12) Holmes, J. L.; Lossing, F. P. *Can. J. Chem.* **1979**, *57*, 249.

(13) Burgers, P. C.; Holmes, J. L.; Lossing, F. P.; Povel, F. R.; Terlouw, J. K. *Org. Mass Spectrom.* **1983**, *18*, 335.

(14) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Szulejko, J. E. *Org. Mass Spectrom.* **1983**, *18*, 596.

(15) Blanchette, M. C.; Holmes, J. L.; Hop, C. E. C. A.; Lossing, F. P.; Postma, R.; Ruttink, P. J. A.; Terlouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 7589.

(3) (a) DeJongh, D.; Shrader, S. R. *J. Am. Chem. Soc.* **1966**, *88*, 3881.  
(b) Holmes, J. L.; McGillivray, D. L.; Isaacs, N. S. *Can. J. Chem.* **1970**, *48*, 2791; *Org. Mass Spectrom.* **1974**, *9*, 510.

(4) Solomon, J. J.; Field, F. H. *J. Am. Chem. Soc.* **1976**, *98*, 1567.

(5) Saluja, P. P. S.; Kebarle, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 1084.

(6) Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917.

(7) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(8) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647.

**Table II.** Collisional Activation Mass Spectra of  $C_7H_{11}^+$  Ions<sup>a</sup>

precursor molecule	<i>m/z</i>																							
	27	28	29	39	41	43	50	51	52	53	55	63	65	66	(67) <sup>b</sup>	77	78	79	80	89	91	92	(93) <sup>b</sup>	94
2,6-octadiene	15	1	6	41	35	2	9	22	11	35	54	8	22	120	86	16	115	22	1	50	3	130	78	
3,6-dimethylcyclohexene	14	1	5	46	33	2	12	26	13	37	60	9	25	290	93	20	120	22	2	50	3	335	63	
1-methylcyclohexene	20	2	10	55	42	2	12	30	15	47	82	10	30	430	105	22	135	c	2	50	5	455	c	
norbornane	23	1	10	57	44	3	12	29	15	45	75	10	57	260	98	21	125	c	2	50	4	420	c	
3-ethylcyclopentene	27	1	13	78	61	5	16	37	16	58	115	13	65	895	98	21	120	44	2	50	5	630	97	
vinylcyclopentane	16	2	6	52	35	2	12	28	13	40	67	11	110	395	96	21	120	54	2	50	3	435	65	
ethylidenecyclopentane	17	2	8	54	37	2	14	28	13	42	81	12	31	780	93	21	115	40	2	50	5	905	100	
norbornene + H <sup>+</sup> <sup>d</sup>	26	1	8	75	62	2	11	28	15	42	49	11	40	50	180	87	23	115	18	2	50	9	67	33
2-bromonorbornane	10	2	4	41	32	1	10	21	10	32	55	10	32	40	450	88	18	110	21	1	50	4	460	40
2-iodonorbornane	11	2	4	46	37	1	11	23	11	35	58	10	35	51	555	87	18	98	29	2	50	5	685	135

<sup>a</sup> See Experimental Section for details. Abundances normalized to  $m/z$  91 = 50. <sup>b</sup> Peaks partially of unimolecular origin. <sup>c</sup> Artifact peak interference. <sup>d</sup> Abundances corrected for contributions from  $^{13}C_6H_{10}^{+}$ .

**Table III.** Charge-Stripping Mass Spectra<sup>a</sup> of  $C_7H_{11}^+$  Ions

precursor molecule	peak abundances, <i>m/z</i>						
	44.5	45	45.5	46	46.5	47	47.5
2,4-octadiene	1	22	30	16	20	1	10
2,6-octadiene	1	13	17	16	45	1	8
3,6-dimethylcyclohexene	1	16	21	15	40	<1	7
1-methylcyclohexene	1	19	26	14	34	<1	7
norbornane	1	19	25	16	34	<1	7
3-ethylcyclopentene	1	26	33	17	16	1	5
vinylcyclopentane	1	24	34	18	21	<1	2
ethylidenecyclopentane	1	26	35	17	19	<1	1.5
norbornene + H <sup>+</sup>	1	22	28	27	20	<1	<1
2-bromonorbornane	1	23	34	26	16	<0.5	<0.2
2-iodonorbornane	1	20	30	25	15	<i>b</i>	<i>b</i>

<sup>a</sup> For experimental details see ref 27. <sup>b</sup> Artifact peak interference.

In the absence of any further evidence, the above differences between the thermochemical data from ion-molecule reactions and from AE measurements are reconciled, and we propose that the overall mean  $\Delta H_f^\circ$  of  $767 \pm 5$  kJ mol<sup>-1</sup> is that for the 2-norbornyl cation. This value relates to a classical - nonclassical energy difference of +45 kJ mol<sup>-1</sup>, in fair agreement with the +60 kJ mol<sup>-1</sup> from ab initio molecular orbital theory calculations.<sup>16</sup>

The AE of  $[C_7H_{11}]^+$ ,  $m/z$  95, from a variety of  $C_8H_{14}$  and  $C_7H_{12}$  isomers was measured using energy selected electrons. The results are shown in Table I. Some of the  $[C_7H_{11}]^+$  product ions have  $\Delta H_f^\circ$  within ca. 40 kJ mol<sup>-1</sup> of the proposed  $\Delta H_f^\circ$  [2-norbornyl<sup>+</sup>]. All fragment by loss of  $C_2H_4$  producing composite metastable peaks indistinguishable from those for the norbornyl halides, showing that all  $[C_7H_{11}]^+$  ions, irrespective of their origin, have common reaction channels for this fragmentation.

**(2) Collisional Activation (CA) Mass Spectra.** Although in general CA mass spectra have not proved to be strongly structure-diagnostic for isomeric hydrocarbon ions, minor differences in singly or doubly charged daughter ion abundances have provided valuable information, e.g., for the  $[C_7H_7]^+$  and  $[C_3H_5]^{2+}$  isomers.<sup>20,21</sup> If the proposed identity of the above  $[C_7H_{11}]^+$  is indeed correct, then certainly  $[C_7H_{11}]^+$  so generated and having low internal energy should have common, characteristic CA and charge-stripping (CS) mass spectra.

The CA and CS mass spectra are given in Tables II and III, respectively. Despite the wide variations in precursor molecule structures, the CA mass spectra of all  $[C_7H_{11}]^+$  ions are very closely similar. However, the  $m/z$  95 species derived from the bromide and iodide have one characteristically different peak,  $m/z$  66, essentially absent in the CA mass spectra of all other  $[C_7H_{11}]^+$

ions. These CA mass spectra are from  $[C_7H_{11}]^+$  ions which have excess internal energies from nil (their generation threshold) up to that required for fragmentation to  $[C_5H_7]^+ + C_2H_4$ , ca. 120 kJ mol<sup>-1</sup> ( $\Delta H_f^\circ[C_5H_7^+] = 833$  kJ mol<sup>-1</sup>,<sup>22</sup>  $\Delta H_f^\circ[C_2H_4] = 52$  kJ mol<sup>-1</sup>). Because all atom positional identity is lost prior to this fragmentation,<sup>3b</sup> the higher internal energy ions will be a mixture of structures, so that it is clearly desirable to examine ions of low internal energy. The protonation of norbornene using methylpropane under chemical ionization conditions generates such ions, although in the present apparatus a small fraction contained sufficient energy to decompose unimolecularly. The first field-free region metastable peaks for  $[C_7H_{11}]^+$  generation from the bromide and iodide were too weak (see above) to be selectively transmitted through the magnet (apparent masses  $m/z$  51.9 (51.3) and 40.7, respectively) and then subjected to collision-induced dissociation. The resulting weak CA mass spectra of these low internal energy species contained too many artifact peaks for meaningful analysis. Inspection of  $[C_7H_{11}]^+$  ions of lowest attainable internal energy was achieved by lowering the ionizing electron energy for the bromide and iodide fragmentations to the point at which  $m/z$  67 daughter ions, generated via the metastable fragmentation of  $C_7H_{11}^+$  ions, had virtually disappeared. The CA mass spectra of these  $[C_7H_{11}]^+$  ions still contained  $m/z$  66 and were otherwise closely similar to those shown in Table II. It seems clear, therefore, that the peak at  $m/z$  66 is characteristic of the norbornyl cation.

Note that the H atom loss from ionized norbornane does not produce a  $[C_7H_{11}]^+$  ion which displays  $m/z$  66 in its CA mass spectrum which is closely similar to that of the ion derived from 1-methylcyclohexene. The molecular ion may well ring open prior to H atom loss, a process of greater energy requirement than loss of a halogen atom.

Because the CA mass spectra contained only one structure-diagnostic peak, the charge-stripping (CS) mass spectra were also examined, but using O<sub>2</sub> as collision gas, a target molecule which has proved to be more sensitive in CS studies to structural differences than He.<sup>21</sup> The results are shown in Table III. The doubly charged ions  $m/z$  44.5-47.5 do not overlap with any singly charged fragments. There is again a significant difference between the norbornyl ions and  $m/z$  95 species from the other precursor molecules, namely, that the former show no  $[C_7H_{10}]^{2+}$  or  $[C_7H_{11}]^{2+}$  ions, whereas all others either do so, or have notably different abundances among the  $m/z$  45-46.5 peaks. The norbornane [M - H]<sup>+</sup> ion is again clearly not the norbornyl cation and has the same CS mass spectra as the [M - H]<sup>+</sup> ion from 1-methylcyclohexene.

A number of additional experiments, although unsuccessful, should be mentioned. Precursor molecules were sought, which upon dissociative ionization might be expected to generate norbornyl radicals. For example, 2-norbornylmethylamine has  $m/z$  30 ( $CH_2N^+H_2$ ) as base peak in its normal mass spectrum, but this fragmentation does not take place unimolecularly in the metastable time frame. Had it done so, the collision-induced dissociative ionization mass spectrum<sup>23</sup> of the norbornyl radical

(16) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. *J. Am. Chem. Soc.* **1983**, *105*, 5915.

(17) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data*, **1977**, *6*, Suppl. 1.

(18) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(19) Benson, S. W. *Thermochemical kinetics*; Wiley-Interscience: New York, 1976.

(20) Proctor, C. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1983**, *18*, 193.

(21) McLafferty, F. W.; Barbalas, M. P.; Turecek, F. *J. Am. Chem. Soc.* **1983**, *105*, 1.

(22) Wolkoff, P.; Holmes, J. L.; Lossing, F. P. *Can. J. Chem.* **1980**, *58*, 251.

would have been recorded and compared with the CA and CS mass spectra described above. It was also attempted to make the 2-norbornyl anion, by dissociative electron detachment or by reaction of various norbornyl derivatives with OH<sup>-</sup> in the mass spectrometer's ion source. Had a significant flux of [C<sub>7</sub>H<sub>11</sub>]<sup>-</sup> ions been produced, then their collision-induced charge reversal mass spectrum<sup>24</sup> would have been investigated. Finally, the neutralization-reionization mass spectra<sup>25</sup> of the various [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> ions were recorded, using Xe as the charge exchange gas and He as reionization gas.<sup>26</sup> All [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> produced intermediate free radicals of sufficient stability to be collisionally reionized, but the mass spectra proved to contain no clear structural distinctions.

### Experimental Section

Unimolecular ion fragmentations and the various collision-induced events were observed using a VG Analytical ZAB-2F mass spectrometer

(23) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Szulejko, J. E.; Terlouw, J. K. *Org. Mass Spectrom.* **1984**, *19*, 442.

(24) Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959.

(25) Danis, P. O.; Wesdemiotis, C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 7454.

(26) Terlouw, J. K.; Kieskamp, W. M.; Holmes, J. L.; Mommers, A. A.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *64*, 245.

under conditions referenced in the text or as described elsewhere.<sup>27</sup> Appearance energies were measured using an apparatus comprising an electrostatic electron monochromator<sup>28</sup> together with a quadrupole mass analyzer and minicomputer data system.<sup>29</sup> Compounds were of research grade and used without further purification. *exo*-2-Norbornyl iodide was prepared by treating norbornene with HI at -78 °C.

**Acknowledgment.** M.C.B. acknowledges a Graduate Studentship from the Province of Ontario, and J.L.H. thanks the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

**Registry No.** 2-Norbornyl cation, 24321-81-1; 2,4-octadiene, 13643-08-8; 2,6-octadiene, 4974-27-0; 3,6-dimethylcyclohexene, 19550-40-4; 1-methylcyclohexene, 591-49-1; norbornane, 279-23-2; 3-ethylcyclopentene, 694-35-9; vinylcyclopentane, 3742-34-5; ethylenecyclopentane, 2146-37-4; *exo*-2-norbornyl bromide, 2534-77-2; *exo*-2-norbornyl iodide, 30983-85-8; norbornene, 498-66-8.

(27) Burgers, P. C.; Holmes, J. L.; Szulejko, J. E.; Mommers, A. A.; Terlouw, J. K. *Org. Mass Spectrom.* **1983**, *18*, 254.

(28) Maeda, J.; Semeluk, G. P.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 395.

(29) Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 9.

## Dynamic Processes in Crystals Examined through Difference Displacement Parameters $\Delta U$ : Pseudo-Jahn-Teller Distortion in *cis*-Cu<sup>II</sup>N<sub>4</sub>O<sub>2</sub> Coordination Octahedra

M. Stebler and H. B. Bürgi\*

Contribution from the Laboratorium für Chemische und Mineralogische Kristallographie der Universität, CH-3012 Bern, Switzerland. Received April 28, 1986

**Abstract:** Anisotropic displacement parameters ("temperature factors") obtained from routine single-crystal diffraction experiments contain chemically useful information. This is shown for [Cu<sup>II</sup>(LL)<sub>2</sub>OXO] complexes (LL is phenanthroline, bipyridine, or bipyridylamine, OXO is NO<sub>2</sub><sup>-</sup>, HCOO<sup>-</sup>, or CH<sub>3</sub>COO<sup>-</sup>) which undergo static or dynamic pseudo-Jahn-Teller deformation. Observed displacement parameters reflect this deformation: they agree well with results from model calculations based on a simplified potential energy curve for the deformation.

The primary results from single-crystal diffraction experiments are long lists of atomic positional and displacement ("thermal") parameters. It is generally accepted that positional parameters are a reliable source of information on molecular structure. The attitude of chemists and crystallographers toward the information contained in displacement parameters is ambiguous and may be characterized as one of negligent pessimism which is changing only slowly toward cautious optimism.

Several recent studies justify this change: The rigid body model of molecular motion in crystals as derived from displacement parameters<sup>1</sup> has been generalized to allow treatment of molecules with internal flexibility.<sup>2-5</sup> The chemical or physical significance

of motional characteristics derived from displacement parameters has been tested by comparing results from diffraction experiments with results from other methods.<sup>5,6</sup> The comparisons indicate that significant information on internal molecular motion may be obtained even from routine structure determinations. Here this conclusion is exemplified by analyzing literature data for [Cu<sup>II</sup>(LL)<sub>2</sub>OXO] complexes, some of which undergo automerization in the solid state (Figure 1). It will be shown how the structural changes occurring during this process may be obtained from observed harmonic, anisotropic displacement parameters.

Crystal and molecular structures have been published for several compounds of general composition [Cu<sup>II</sup>(LL)<sub>2</sub>OXO]Y (Table I and V). LL is one of the bidentate ligands 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), or 2,2'-bipyridylamine (bipyam). OXO is bidentate nitrite (ONO<sup>-</sup>), nitrate (ONO<sub>2</sub><sup>-</sup>), acetate (CH<sub>3</sub>COO<sup>-</sup>), or formate (HCOO<sup>-</sup>). Y is a noncoordinating anion (NO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>). The complex cations show a wide spectrum of octahedral coordination geometries. Cu-N distances trans to each other are between 1.97 and 2.01 Å (Cu-N3, Cu-N4) and Cu-N distances trans to O's between 2.02 and 2.18 Å (Cu-N1,

(1) (a) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 63. (b) Crüickshank, D. W. J. *Acta Crystallogr.* **1956**, *9*, 754-756.

(2) Johnson, C. K. In *Crystallographic Computing*; Ahmed, F. R. Ed.; Munksgaard, Copenhagen, 1970.

(3) (a) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1984**, *A40*, C-339. (b) Dunitz, J. D.; White, D. N. J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1973**, *A29*, 93. (c) Trueblood, K. N.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Sci.* **1983**, *B39*, 120.

(4) He, X. M.; Craven, B. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1985**, *A41*, 244.

(5) (a) Bürgi, H. B. *Trans. Am. Crystallogr. Assoc.* **1984**, *20*, 61. (b) Ammeter, J. H.; Bürgi, H. B.; Gamp, E.; Meyer-Sandrin, V.; Jensen, W. P. *Inorg. Chem.* **1979**, *18*, 733. (c) Chandrasekhar, K.; Bürgi, H. B. *Acta Crystallogr., Sect. B: Struct. Sci.* **1984**, *B40*, 387-397.

(6) (a) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2218. (b) Bonadeo, H.; Bürgi, H. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1982**, *A38*, 29. (c) Gramaccioni, C. M.; Filippini, G. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 784.