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Structures of Bicyclo[2.2.2]octene and Bicyclo[2.2.2]octadiene as Studied by Gas Electron Diffraction

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Bicyclo[2.2.2]oct-2-ene and bicyclo[2.2.2]octa-2,5-diene have been investigated by gas electron diffraction. They are found to have C_{2v} symmetry in respect of the thermal-average nuclear positions. The structural parameters with estimated limits of error (the r_g bond lengths and the angles difined in the r_α structure) determined by a least-squares analysis on the molecular intensities are as follows for octene and octadiene, respectively: $C(sp^3)$–$C(sp^3)$ (weighted average of the C_1–C_7 and C_7–C_8 bonds) $=1.549\pm0.008$ and 1.553 ± 0.017 Å, $C(sp^2)$–$C(sp^3)=1.509\pm0.015$ and 1.521 ± 0.008 Å, $C(sp^2)$–$C(sp^2)=1.341\pm0.008$ and 1.339 ± 0.005 Å, $C(sp^3)$–H (average) $=1.112\pm0.008$ and 1.105 ± 0.012 Å, $\angle$C–C=C$=114.2\pm0.6°$ and $113.5\pm0.5°$, the dihedral angle θ between the C_1–C_2–C_3–C_4 and C_1–C_6–C_5–C_4 planes$=121.2\pm2.1°$ and $123.4\pm2.2°$, $\angle$C=C–H$=122.4\pm6.0°$ and $125.5\pm4.0°$, $\angle$H–C–H$=109.2\pm4.0°$ and $111.3\pm7.0°$. A conformational analysis based on an empirical prescription of strain energies, similar to that of Jacob *et al.*, and a molecular-orbital analysis (CNDO/2) have accounted for the observed bond angles given above to within 1.5°.

A previous paper has reported on the structure and intramolecular motions of bicyclo[2.2.2]octane (BO) in the gas phase.1) The weighted average of the C_1–C_2 and C_2–C_3 bond distances (r_g(average)$=1.542\pm0.004$ Å) is similar to the C–C bond distance in cyclohexane,2) and the C–C–C bond angles ($\angle C_1$–C_2–$C_3=109.7°\pm0.7°$ and $\angle C_2$–C_1–$C_6=108.9°\pm0.6°$ in terms of the r_α structure3)) are close to the tetrahedral angle. The potential function for the twisting motion around the D_{3h} symmetry axis has a broad minimum and probably has a hump of the order of 0.1 kcal/mol at the D_{3h} conformation.4)

In connection with the above investigation, bicyclo[2.2.2]octene (BE) and bicyclo[2.2.2]octadiene (BD), in which the ethylene bridges in BO are partly replaced by vinylene bridges, are of interest in view of the influence of the double bonds on structural parameters. The observed heats of hydrogenation for these compounds,5) which are larger than those expected from that for cyclohexene, indicate that the rings are appreciably strained. To our knowledge, however, no study of the structures of BE and BD has been reported, and even the symmetry of the molecules is uncertain.5) Therefore, their structures have been investigated by means of gas electron diffraction.

Since these molecules have unequivalent pairs of closely-spaced C–C bond distances (C_1–C_2, C_1–C_7, and

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1) A. Yokozeki, K. Kuchitsu, and Y. Morino, This Bulletin, **43**, 2017 (1970).

2) H. Kambara, K. Kuchitsu, and Y. Morino, *ibid.*, to be published.

3) K. Kuchitsu, T. Fukuyama, and Y. Morino *J. Mol. Structure*, **1**, 463 (1968).

4) E. Hirota, *J. Mol. Spectrosc.*, **38**, 367 (1971).

5) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

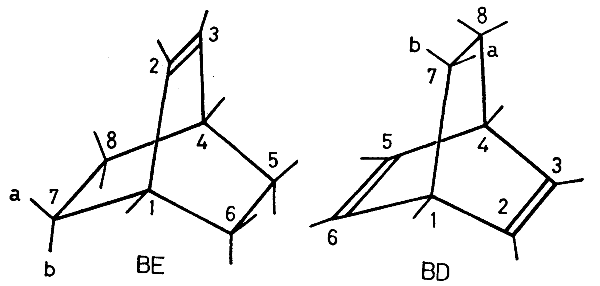

Fig. 1. The numbering of bicyclo[2.2.2]octene (BE) and bicyclo[2.2.2]octadiene (BD).

C_7–C_8), a separation of those pairs[6,7] was a serious problem in the present analysis. In order to elude the trouble, all the C(sp^3)–C(sp^3) bond distances were assumed to be equal, and the weighted average value ($\frac{1}{3}[2r_g(C_1–C_7)+r_g(C_7–C_8)]$), instead of the individual bond distances, was determined.

Experimental

Purified samples of BE and BD were supplied by courtesy of Dr. Hiroshi Tanida of Shionogi Research Laboratory. Diffraction photographs were taken at 20°C on Fuji Process Hard plates with an apparatus equipped with an r^3-sector[8]; the accelerating voltage (stabilized within 0.01%) and the bean current were about 40 kV and 0.35 μA, respectively. The pressures of the samples maintained in thermal equilibrium with their solid states were about 4 Torr for BE and 7 Torr for BD. Typical experimental conditions are listed in Table 1. Other experimental and interpretational procedures have been described in a previous paper.[1] Reduced molecular intensity and radial distribution curves are shown in Figs. 2 and 3.[9] The calculations were carried out by using the HITAC-5020E at the Computer Centre of the University of Tokyo.

TABLE 1. TYPICAL EXPERIMENTAL CONDITIONS

	Camera length (mm)	Exposure time (min)	Range of densities	Range of q values[a]
BE[b]	107.77	15	0.18—0.46	25—130
	243.24	3.5	0.11—0.35	8—60
BD[c]	107.77	10	0.16—0.51	25—130
	243.24	2.5	0.23—0.55	8—60

a) Ranges of the intensity data used for the analysis in the interval of $q=1$.
b) Bicyclo[2.2.2]octene.
c) Bicyclo[2.2.2]octadiene.

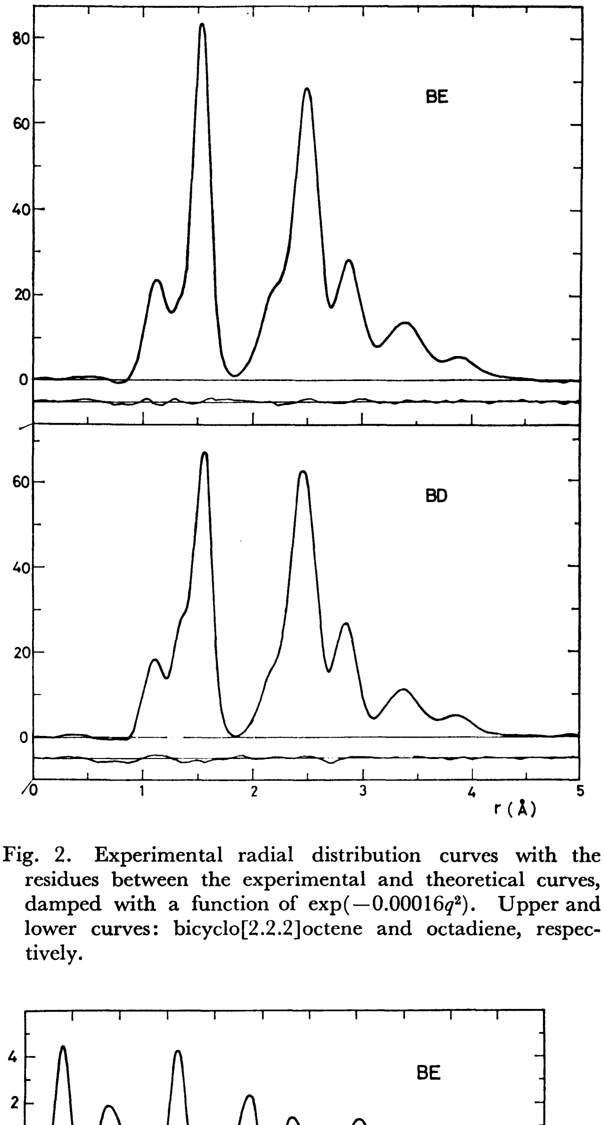

Fig. 2. Experimental radial distribution curves with the residues between the experimental and theoretical curves, damped with a function of $\exp(-0.00016q^2)$. Upper and lower curves: bicyclo[2.2.2]octene and octadiene, respectively.

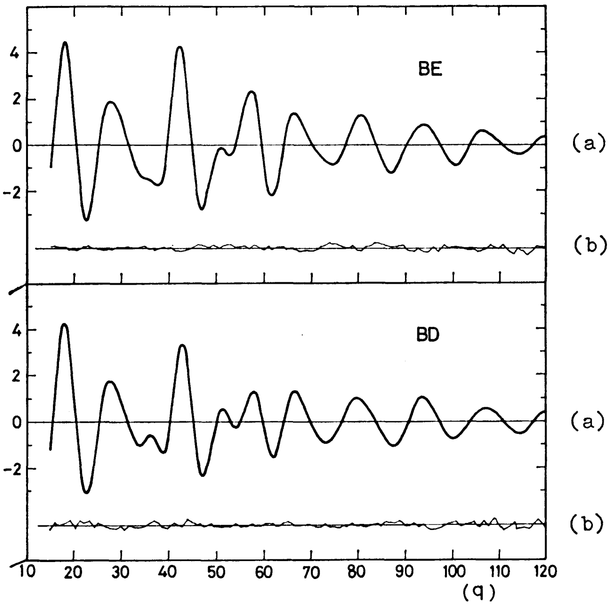

Fig. 3. Molecular intensity curves for bicyclo[2.2.2]octene (upper) and octadiene (lower). (a): best-fit theoretical, (b): experimental minus theoretical.

Analysis

Structural Parameters. The point-group symmetry of these molecules in equilibrium was not clear at the

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[6] Y. Morino, K. Kuchitsu, and A. Yokozeki. This Bulletin. **40**, 1552 (1967); *ibid.*, **44**, (1971), in press.

[7] G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.*, **87**, 795, 805 (1968); J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

[8] Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **9**, 591 (1970).

[9] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7109). A copy may be secured by citing the document number and by remitting, in advance, ¥400 for photoprints. Payment by check or money order payable to: the Chemical Society of Japan, 5, 1-Chome, Kanda-Surugadai, Chiyodaku, Tokyo.

initial stage of the present analysis. Even though a flexible quasi-C_{2v} structure (like that observed in BO) or a rigid C_2 structure seemed to be improbable because of the presence of vinylene bridges, the C_{2v} symmetry had to be proved experimentally. If they have C_{2v} symmetry, the numbers of independent parameters sufficient to describe the geometrical arrangements are 16 and 14 for BE and BD, respectively. In this symmetry, the ethylene bridges ($-CH_2-CH_2-$) is borne to have a *cis* conformation around the C–C axis. For a C_2 symmetry with twisted conformations, the numbers of independent parameters are 28 and 25 for BE and BD, respectively. In order to facilitate the analysis and to limit the variable parameters to a reasonable number, the following assumptions about the parameters (in regard to the r_a structure[1,3]) were made.

1) All the $C(sp^3)-H$ bond distances are equal.

2) The $C(sp^3)-H$ bond distances are equal to that of ethylene[10] ($r_a=1.0896$ Å).

3) The vinylene group ($C-CH=CH-C$) is planar.

4) The $H-C_j-H$ plane of the methylene group is perpendicular to the $C_i-C_j-C_k$ plane and bisects the $C_i-C_j-C_k$ angle, and *vice versa*.

5) The C–C–H angles at the bridgehead are equal; *i.e.*, $\angle C_2-C_1-H=\angle C_6-C_1-H=\angle C_7-C_1-H$.

Besides the above assumptions, the following constraint was introduced.

6) All the $C(sp^3)-C(sp^3)$ bond distances are equal.

As mentioned in the introduction, this assumption was almost imperative for the present analysis. The influence of this constraint on the results is discussed in later sections. The above assumptions reduce the independent parameters for C_{2v} symmetry to eight for either molecule, while for C_2 symmetry one additional parameter is required. For either molecule the parameters to be determined are: four bond distances (weighted-average $C(sp^3)-C(sp^3)$ and $C(sp^3)-H$, $C(sp^2)-C(sp^3)$, and C=C), three bond angles ($\angle C-C=C$, $\angle C=C-H$, $\angle H-C-H$), the angle θ defined by the two straight lines connecting the center of the $C_1\cdots C_4$ with those of the C_2-C_3 and C_5-C_6 distances, and the torsional angle ϕ (the dihedral angle between the $C_1-C_7-C_8$ and $C_4-C_8-C_7$ planes). The parameter ϕ is a measure of whether the molecule has C_{2v} or C_2 symmetry in regard to the thermal-average nuclear positions.

TABLE 2. ESTIMATED FORCE CONSTANTS FOR BICYCLO [2.2.2] OCTENE AND OCTADIENE[a)]

K(C–C)	2.30	K(C–H)	4.23
K(=C–C)	3.24	K(=C–H)	4.39
K(C=C)	7.42	W(=C–H)	0.36
H(C–C–C)	0.32	F(C–C–C)	0.20
H(C=C–C)	0.29	F(C=C–C)	0.40
H(C–C–H)	0.22	F(C–C–H)	0.48
H(C=C–H)	0.16	F(C=C–H)	0.45
H(H–C–H)	0.43	F(H–C–H)	0.07
Y(C–C)	0.11	Y(C=C)	0.48

a) The estimated force constants taken from cyclohexane[12] and several olefins (butene, pentene, *etc.*).[13] The torsional (Y) and wagging (W) force constants are in md·Å units, while the others are in md/Å units.

Calculation of Mean Amplitudes and Shrinkage Corrections. The root-mean-square vibrational amplitudes and shrinkage corrections[11] for all the atom pairs in BE and BD were calculated from a normal-coordinate analysis by using the Urey-Bradley force constants (listed in Table 2) transferred from those for cyclohexane[12] and normal olefins (butene, pentene, *etc.*).[13] The procedures have been described elsewhere.[11]

Since the force constant Y characterizing the torsional motion[1] is not known for a *cis* conformation about a C–C single bond, Y was assumed to be equal to that for the *gauche* conformation (0.11 md·Å for cyclohexane,[12] as discussed in a previous paper.[1]) The lowest twisting frequencies calculated from the above Y value for BE and BD are higher than for BO, and they depend less sensitively on Y. A change in Y from 0.11 to 0.025 md·Å leads to that in the lowest twisting frequency from 163 to 120 cm^{-1} for BE and from 203 to 170 cm^{-1} for BD, while for BO the change is from 134 to 66 cm^{-1}. Therefore, the uncertainty in the calculated mean amplitudes due to that in Y is much less than that for BO, and the ϕ parameters determined in the following analysis is essentially free from the assumption about the Y value. The uncertainties in the assumed force constants were estimated to be 10—20%, *i.e.*, three times the random standard errors quoted in the force constants determined by the Urey-Bradley analysis.[12-14] In that event, the errors in the calculated mean amplitudes caused by the above-mentioned uncertainties in the force constants were at most ±5% for bonded atom pairs and less than ±10% for nonbonded pairs. These

TABLE 3. MEAN AMPLITUDES AND SHRINKAGE CORRECTIONS[a)]

	l_{ij}	d_{ij}		l_{ij}	d_{ij}		l_{ij}	d_{ij}
$C_2=C_3$	424	32	C_7-H	798	132	$C_7\cdots H_2$	1237	25
C_1-C_2	502	11	C_1-H	794	83	$C_1\cdots H_8$	1239	22
C_1-C_7	532	14	$C_2\cdots H_3$	971	79	$C_2\cdots H_{7b}$	1035	47
C_7-C_8	523	33	$C_1\cdots H_7$	1058	69	$C_3\cdots H_1$	991	20
$C_2\cdots C_7$	723	1	$C_7\cdots H_8$	1060	89	$C_1\cdots H_3$	956	45
$C_1\cdots C_3$	586	3	$C_7\cdots H_1$	1074	29	$C_8\cdots H_1$	1024	15
$C_1\cdots C_8$	644	0	$C_1\cdots H_2$	1003	60	$C_3\cdots H_{7b}$	1056	32
$C_3\cdots C_7$	812	−9	$C_2\cdots H_1$	1044	27	$C_7\cdots H_3$	1226	17
$C_1\cdots C_4$	629	−6	$C_2\cdots H_{7a}$	1565	−10	$C_1\cdots H_4$	958	17
$C_2\cdots H$	781	126	$C_3\cdots H_{7a}$	1746	−39			
$C_6\cdots C_7$	727	8	$C_6\cdots H_{7b}$	1559	3	$C_6\cdots H_{7a}$	1049	55
$C_8\cdots C_6$	876	−12	$C_5\cdots H_{7b}$	1862	−50	$C_5\cdots H_{7a}$	1081	29
$C_2\cdots C_6$	687	1	$C_2\cdots H_6$	1169	28			
$C_2\cdots C_5$	739	−4	$C_2\cdots H_5$	1140	25			

a) Calculated mean amplitudes (l_{ij}) and shrinkage corrections (d_{ij}) in 10^{-4} Å units. The first section is common to bicyclo[2.2.2] octene and octadiene, and the second and last sections correspond to the pairs in octene and octadiene, respectively. The H···H pairs are not listed.

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[10] K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966).

[11] K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

[12] H. Takahashi and T. Shimanouchi, *J. Mol. Spectrosc.*, **13**, 43 (1964).

[13] T. Shimanouchi, Y. Abe, and Y. Alaki, *Polymer J.*, **2**, 199 (1971). The authors are indebted to Professor Takehiko Shimanouchi and the other authors for giving their experimental results before publication.

[14] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

uncertainties were of the order of the experimental errors, which were estimated for analogous molecules (*e.g.*, triethylenediamine[15]). Therefore, the calculated values listed in Table 3 were used as constant parameters for the subsequent analysis, and the systematic errors in the structural parameters due to this procedure were estimated to be less than their random standard errors.

Least-Squares Analysis. Initial values of the structural parameters were taken from a preliminary analysis of the radial distribution curves: C=C=1.34 Å, C(sp^2)–C(sp^3)=1.51 Å, C(sp^3)–C(sp^3) (average)=1.55 Å, ∠C–C=C=114°, $\angle\theta=120°$. C_{2v} structures ($\phi\sim0°$) were suggested at this stage. The nine parameters mentioned above were determined for either molecule by a least-squares analysis on the molecular intensities with a preset weight function[16] and with the estimated mean amplitudes and shrinkage corrections. The most probable values and their error matrices[17] are listed in Tables 4 and 5, respectively. As a result of the above analyses, the ϕ parameters, started from 10°, converged to zero. If the molecules had double-minimum potentials in terms of ϕ, similar to that in BO, the ϕ parameters should have converged to significantly nonzero values when the above-mentioned Y values were used. (In fact, this has been observed in the case of BO, where the ϕ parameter depended on Y.) In order to further examine this problem, the dependence of the ϕ parameters on Y was investigated by the use of different sets of the mean amplitudes. Essentially zero ϕ parameters were obtained from any set used in the analysis.

In order to estimate the systematic error due to the assumption 6, the constraint 6 was released in the least-squares analysis. Strong correlation between the C_1–C_7 and C_7–C_8 distances was observed in the error matrices, and as a result, they were determined only with standard errors of about 0.014 Å, and their weighted averages deviated from those given in Table 4 by about 0.003 Å for BE and 0.005 Å for BD. At the same time, the C_1–C_2 (C(sp^2)–C(sp^3)) distances changed from those listed in Table 4 by about 0.01 Å for BE and 0.004 Å for BD, respectively. Other parameters changed only within their random standard errors. Therefore, the systematic errors from this source were taken into account in the C(sp^3)–C(sp^3) (average) and C(sp^2)–C(sp^3) parameters.

TABLE 4. STRUCTURAL PARAMETERS[a)]

	BE	BD
C–C[b)]	1.549 ± 0.008	1.553 ± 0.017
=C–C	1.509 ± 0.015	1.521 ± 0.008
C=C	1.341 ± 0.008	1.339 ± 0.005
C–H[b)]	1.112 ± 0.008	1.105 ± 0.012
∠C=C–C	114.2° ± 0.6°	113.5° ± 0.5°
θ	121.2° ± 2.1°	123.4° ± 2.2°
ϕ	0.4° ± 0.5°	0.1° ± 0.3°
∠C=C–H	122.4° ± 6.0°	125.5° ± 4.0°
∠H–C–H	109.2° ± 4.0°	111.3° ± 7.0°
k	1.00 ± 0.02	0.93 ± 0.03

a) The most probable values of the structural parameters (see text) for bicyclo [2.2.2] octene (BE) and octadiene (BD). The distance parameters (r_g) are in Å units and the angles are represented by the r_α structure. The index of resolution k is dimensionless. The uncertainties represent the estimated limits of error (see text).

b) Weighted average of the C (sp^3)–C(sp^3) bond distances and that of the C(sp^3)–H bond distances.

TABLE 5. ERROR MATRIX[a)]

	C–C	=C–C	C=C	C–H	∠C=C–C	θ	ϕ	∠C=C–H	∠H–C–H	k
	11	−14	10	−2	3	−22	−21	−22	26	25
C–C	43									
		24	17	6	8	32	9	26	−43	39
=C–C	−9	8								
			26	11	8	32	14	17	−34	−28
C=C	−11	3	13							
				24	7	−5	−30	−18	42	6
C–H	−6	3	8	42						
					18	−30	−15	37	25	4
∠C=C–C	14	6	−3	5	16					
						106	32	−84	−87	−41
θ	−26	12	18	15	−1	131				
							34	28	32	−16
ϕ	−16	9	10	−8	−11	25	17			
								356	217	−39
∠C=C–H	36	10	11	−28	21	−66	42	221		
									95	84
∠H–C–H	80	−26	−20	87	29	115	48	−34	486	
										96
k	64	−15	−15	8	22	−22	−13	74	146	119

a) Error matrix ($\times10^{-4}$) for the independent parameters (see text). The upper and lower triangles represent the elements for bicyclo [2.2.2] octene and octadiene, respectively. Units for the distances are Å, those for the angles are rad., and the index of resolution k is dimensionless.

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15) A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 72 (1971).

16) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

17) K. Hedberg and M. Iwasaki, *ibid.*, **17**, 529 (1964).

TABLE 6. COMPARISON OF THE STRUCTURES OF BICYCLO [2.2.2]-COMPOUNDS[a)]

	BO		BE		BD	
	Obsd[b)]	Calcd[c)]	Obsd[d)]	Calcd[e)]	Obsd[d)]	Calcd[e)]
C–C[f)]	1.542	1.541	1.549		1.553	
=C–C	——		1.509		1.521	
C=C	——		1.341		1.339	
$\angle C_1$–C_2=C_3	——		114.2°	114.5°	113.5°	114.0°
$\angle C_1$–C_7–C_8	109.7°	109.9°	109.3°	109.7°	108.3°	109.6°
$\angle C_2$–C_1–C_6	108.9°	109.0°	108.0°	107.7°	106.8°	106.0°
$\angle C_2$–C_1–C_7					107.7°	106.5°
$\angle C_6$–C_1–C_7			107.6°	107.3°		
θ	(120°)	(120°)	121.2°	121.2°	123.4°	122.6°
C–H[f)]	1.107		1.112		1.105	
$\angle$C=C–H	——		122.4°		125.5°	
$\angle$H–C–H	110.1°		109.2°		111.3°	

a) Molecular structures of bicyclo [2.2.2] octane (BO), octene (BE), and octadiene (BD) by gas electron diffraction. The distances are represented by r_g in Å units and the angles by an r_α representation.

b) Ref. 1.

c) Ref. 21 (calculated values).

d) The present work.

e) Calculated values based on a strain-relief mechanism (see text).

f) Weighted average of the C(sp^3)–C(sp^3) bond distances and that of the C(sp^3)–H bond distances.

The limits of error in the most probable values of the structural parameters, quoted in Table 4, were estimated to be 2.5 times the random standard errors listed in Table 5 as diagonal elements plus systematic errors [those mentioned above and the experimental systematic errors (0.12% for the distance parameters due to sector imperfection, uncertainty in the electron wavelength, *etc.*[3)])].

Discussion

Molecular Symmetry. The ϕ parameters determined from the analysis are essentially zero, regardless of the torsional force constant (Y) assumed in the analysis. This implies that these molecules have C_{2v} conformations in respect of the thermal-average nuclear positions and that the potentials of torsion in BE and BD have relatively sharp minima around the C_{2v} positions ($\phi=0°$). In these molecules, unlike BO, the torsional motion couples with a twist around the double bond (C_2–C_3), which demands a high cost of energy.

Bond Distances. The structural parameters determined above are compared with BO in Table 6. The weighted-average values of the C(sp^3)–C(sp^3) bond lengths are 1.542±0.004 (which is similar to that in cyclohexane[2)]), 1.549±0.008 and 1.553±0.017 Å for BO, BE, and BD, respectively. The corresponding values for norbornane and norbornadiene[5)] are 1.549±0.003 and 1.573±0.014 Å. The C(sp^2)–C(sp^3) bond distances are 1.509±0.015 Å for BE (analogous to that in propylene, $r_s=1.501\pm0.004$ Å[18)]), 1.521±0.008 Å for BD and 1.535±0.007 Å for norbornadiene. The above systematic differences in the C–C single bond distances, notwithstanding their relatively large limits of error, may be regarded as the influence of intramolecular strain. The double bond distances in such bicyclic compounds, on the contrary, are nearly equal to those in normal olefins (*e.g.*, 1.337 Å for ethylene[10)]). This can be explained by considering that the stretching force constant for double bonds is, in general, several fold larger than that for single bonds, so that the former distance is hardly influenced by the intramolecular strain.

Bond Angles. The effect of angle strain in these bicyclic compounds is also exhibited. The deviation in the C–C–C bond angles from the tetrahedral angle increases in the sequence of BO, BE, and BD. The C=C–C bond angles are about 6° smaller than the trigonal angle, while the corresponding deformation in norbornadiene is about 12°. The C_1–C_4 distances in the three molecules are nearly equal, 2.59, 2.57, and 2.56 Å for BO, BE, and BD, respectively. On the other hand, the dihedral angle θ appears to increase as the molecules have more vinylene groups. A similar trend has been observed in norbornane and norbornadiene.

The above observation can be predicted semiquantitatively, as listed in Table 6, by a strain-relief mechanism similar to that of Jacob *et al.*[19)] In the present calculation the strain energy in the molecule was constructed only in terms of angle deformations and nonbonded interactions. The force constants for the deformations of the C–C–C and C–C=C bond angles were assumed to be equal to each other, 0.687 md·Å, as estimated from the Urey-Bradley force fields for saturated hydrocarbons reported by Schachtschneider and Snyder.[14)] Standard values for the C–C–C and C–C=C angle were chosen to be the tetrahedral and trigonal angles, respectively. All the nonbonded interactions among the C–C, C–H, and H–H pairs were

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[18)] D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

[19)] E. J. Jacob, H. B. Thompson, and L. S. Bartell, *ibid.*, **47**, 3736 (1967).

calculated by use of the functions reported by Hendrickson[20] and by Jacob *et al.*[18] The latter functions are much harder than the former, so that the latter appears to overestimate the steric interactions. In fact, a minimization of the total energy showed that the energy for BD was about 30 kcal/mol *smaller* than that for BE according to the latter function, whereas the energy for BD was about 10 kcal/mol *larger* than that for BE according to the former. In spite of the above discrepancies, the conformational analyses for bond angles were in good agreement with each other (within 0.5°). In addition, the model used in the present study gave bond angles in BO similar to those based on a more elaborate scheme by Gleicher and Schleyer[21] (within 1°).

For the purpose of comparison, another conformational analysis was made by means of a quantum-mechanical scheme known as SCF CNDO/2.[22] A program written by Segal[23] was used in the calculations. The energy was minimized by varying two independent parameters (∠C–C=C and θ) systematically in step of 0.5°, while other parameters were assumed to be constant and equal to the observed values listed in Table 4. The ∠C–C=C and θ parameters were predicted to be 114.5° and 121.0° for BE and 115.0° and 122.5° for BD, respectively, in essential agreement with the corresponding values (Table 6) derived from the above-mentioned classical method.

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