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Structure and Intramolecular Motions in Bicyclo[2.2.2]octane as Studied by Gas Electron Diffraction

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A least-squares analysis of the electron-diffraction intensities for bicyclo[2.2.2]octane in gas phase measured at 28°C has given the following structural parameters: r_g(C–C) (average) = 1.542 ±0.004Å, r_g(C–H) (average) = 1.107±0.009Å, $r_g(C_1\text{–}C_2) = 1.53_8 \pm 0.01_5$Å, $r_g(C_2\text{–}C_3) = 1.55_2 \pm 0.02_9$Å, $\angle C_1\text{–}C_2\text{–}C_3 = 109.7° \pm 0.7°$, and $\angle \text{H–C–H} = 110._1° \pm 5._6°$, where the uncertainties represent estimated limits of error. The potential function for the twisting motion around the D_{3h} symmetry axis is found to have a broad minimum; in terms of the dihedral angle of torsion about the C_2–C_3 axis, ϕ, the potential has an rms angle of 12.0°±1.5° and a "classical turning point" of 21.5°±0.5° (7.2° and 12.8°, respectively, in terms of the dihedral angle of twist, τ). Best fit to the observed intensities has been achieved when a quartic function, $V(\phi) = k_2\phi^2 + k_4\phi^4$ with $k_2 = -4.0$ kcal/mol and $k_4 = 54.2$ kcal/mol, is assumed. The potential function probably has a hump of the order of 100 cal/mol at the D_{3h} conformation. Hence, this molecule may be regarded as having a "quasi-D_{3h} structure". The above features are consistent with those for the derivatives of this molecule in crystal phase studied by Dunitz and Ermer by X-ray diffraction, and also with semiempirical estimates based on the calculations of the intramolecular strain energy.

Bicylco[2.2.2]octane (BO) has three cyclohexane rings fused together at the carbon atoms 1 and 4 (Fig. 1). In the structure with the highest symmetry, D_{3h}, the rings are locked in a boat form, one of the unstable conformations of cyclohexane.[1] As the rings are twisted about the three-fold axis, the symmetry is lowered to D_3.

There have been controversial reports in the literature as to the symmetry of this molecule. Turner *et al.*[2] concluded from the relatively large heats of hydrogenation of bicyclo[2.2.2]octane and octadiene that BO should have a D_3 symmetry. They thought that such a twisted structure should relieve some of the torsional strain in the system, since for D_{3h} the atoms are in eclipsed positions about the C_2–C_3 axes. This structure was supported by Hendrickson,[3] who calculated the strain energy and found that it favored a structure twisted slightly around the C_3 axis. On the other hand, Gleicher and Schleyer[4] preferred a D_{3h} structure based on results from a similar calculation.

The infrared and Raman spectra of BO by MacFarlane and Ross[5] were consistent with those predicted on the assumption that the molecular symmetry was D_{3h}; the twsiting, if present, was thought to be slight. The microwave studies of 1-chloro and 1-bromo derivatives by Nethercot and Javan[6] also estimated the twist angle[*1] to be essentially

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[1] M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).

[2] R. B. Turner, W. R. Weador and R. E. Winkler, *J. Amer. Chem. Soc.*, **79**, 4116 (1957).

[3] J. B. Hendrickson, *Chem. Eng. News*, **39**, 40 (1961).

[4] G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

[5] J. J. MacFarlane and I. G. Ross, *J. Chem. Soc.*, **1960**, 4169.

[6] A. H. Nethercot and A. Javan, *J. Chem. Phys.*, **21**, 363 (1953).

[*1] See Analysis section for the definition of the "twist" angle and the "torsional" angle.

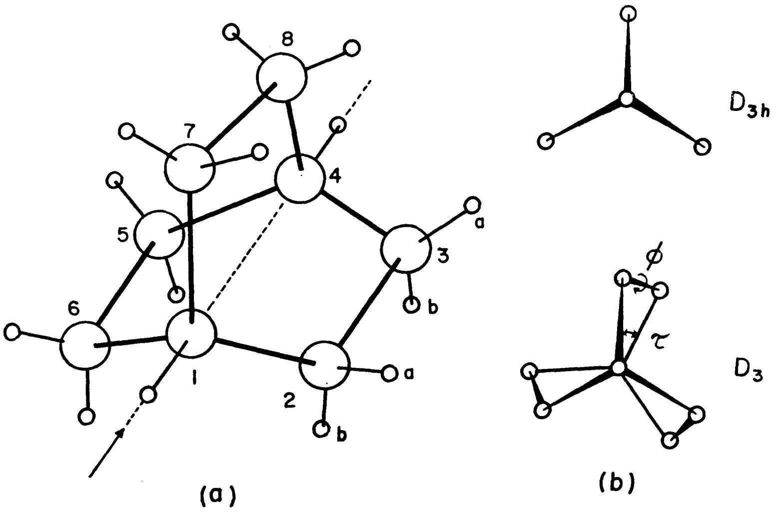

Fig. 1. a) Bicyclo[2.2.2]octane. b) Carbon skeletons as viewed from the C_1–C_4 axis.

zero (0°±4°). As for the crystal structures of BO derivatives, Cameron *et al.*7) estimated the twist angle to be about 3°, whereas Ermer and Dunitz8) found no significant deviation from D_{3h} symmetry in the carbon skeleton; an rms amplitude of the half-twist angle (upper limit) of 5.9°±0.2° was derived from the analysis of their anisotropic thermal ellipsoids.

From all the above studies no conclusive structure of the free BO molecule is yet known. The potential function for the twist motion may have a broad minimum near the D_{3h} conformation, where a hump may or may not exist. In this connection, a recent semiempirical calculation of Ermer and Dunitz8,9) predicted the potential to have a small hump of only about 100 cal/mol with an rms torsional angle[*1] of 13.8°. Under these circumstances, the structure of unsubstituted BO has been investigated by means of gas-phase electron diffraction with the aim of obtaining information on the twisting potential function.

Experimental

Purified sample of BO was kindly provided by Dr. Hiroshi Tanida of Shionogi Research Laboratory. Diffraction photographs were taken at 28°C on Fuji Process Hard Plates with an apparatus equipped with an r^3-sector.10) The accelerating voltage (about 40 kV) was stabilized within 0.01% during exposure, 17—20 min for a camera length of 107.79 mm and about 7 min for 243.24 mm. The beam current was 0.31 μA, and the vacuum was kept under 5×10^{-5} Torr while the sample gas was introduced into the chamber through a nozzle of 0.2 mm diameter. The wavelength of the electron beam was calibrated to within 0.07% with reference to the r_a(C–O) bond length of carbon dioxide,10) 1.1646 Å.

The photographs were developed at 20°C for 5 min with FD-131 developer diluted twice. Four plates for each camera length were used for density measurements. The optical densities (0.19 to 0.41) were recorded digitally at intervals of integral q values11) (from 20 to 140 and from 8 to 65 for the short and long camera lengths, respectively); they were assumed to be proportional to the electron intensities.12)

The intensity curve obtained above was corrected for sector imperfection and divided by a theoretical background function, which took account of elastic and inelastic atomic scattering.13) In addition, extraneous scattering observed at large q values (15% at q=80 and 45% at 120) was subtracted so as to make the background nearly flat for all the scattering angles. This procedure seemed justified because an intensity measurement of carbon dioxide, after a similar background correction, gave experimental mean amplitudes in good agreement with their theoretical values. This procedure, however, had a significant influence on the measurement of the C_1–C_2 and C_2–C_3 bond distances, since they are so closely spaced that their mean amplitudes correlate strongly with the bond distances (see next section).[*2]

As illustrated in Fig. 2, the observed molecular in-

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7) A. F. Cameron, G. Ferguson and D. G. Morris, *Chem. Commun.*, **1968**, 316.

8) O. Ermer and J. D. Dunitz, *ibid.*, **1968**, 567; *Helv. Chim. Acta*, **52**, 1861 (1969).

9) J. D. Dunitz and O. Ermer, *Acta Cryst.*, **A25**, S126 (1969).

10) Y. Murata, K. Kuchitsu and M. Kimura, *Japan. J. Appl. Phys.*, **9**, 591 (1970).

11) Y. Morino, K. Kuchitsu and T. Fukuyama, This Bulletin, **40**, 423 (1967).

12) Y. Morino and T. Iijima, *ibid.*, **35**, 1661 (1962); R. C. Valentine, "The Response of Photographic Emulsions to Electrons," Advances in Optical and Electron Microscopy, Vol. 1, ed. by R. Baerer and V. E. Coslett, Academic Press, New York, N. Y. (1965), p. 180.

13) T. G. Strand and R. A. Bonham, *J. Chem. Phys.*, **40**, 1686 (1964); C. Tavard, D. Nicolas and M. Rouault, *J. Chim. Phys.*, **64**, 540 (1967).

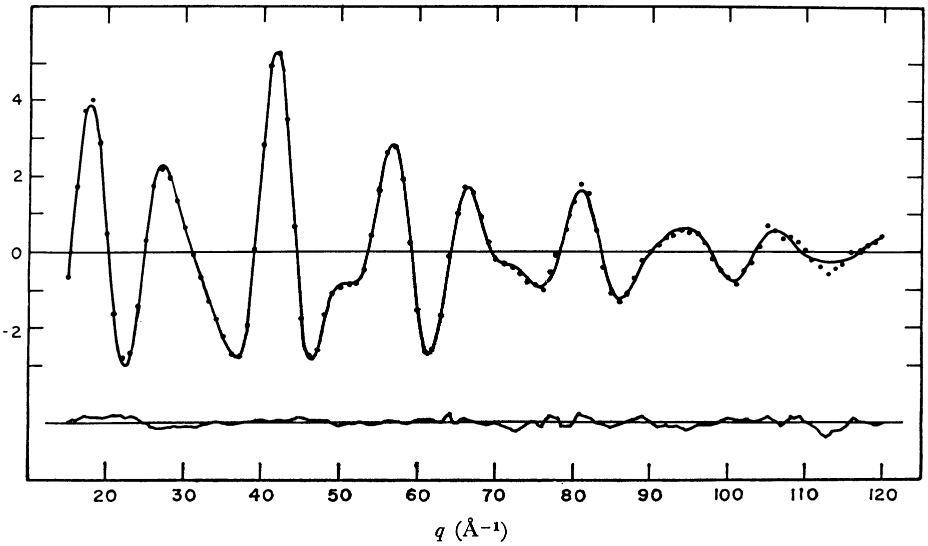

Fig. 2. Molecular intensity curves for bicyclo[2.2.2]octane. Upper solid curve: experimental; dots: best-fit theoretical; lower curve: experimental minus theoretical.

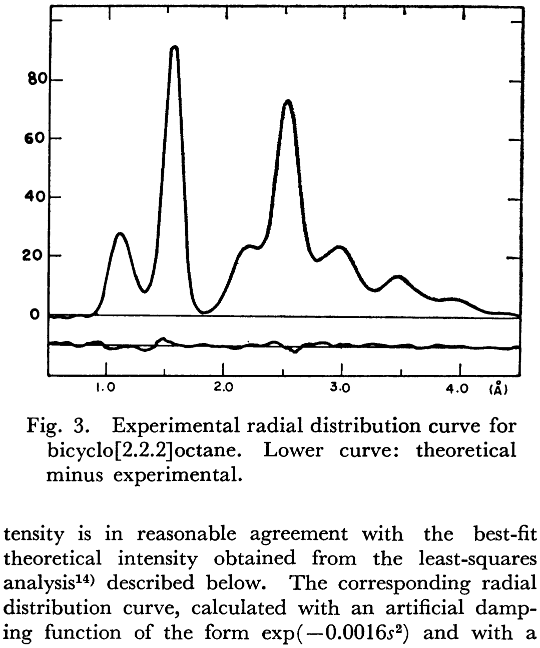

Fig. 3. Experimental radial distribution curve for bicyclo[2.2.2]octane. Lower curve: theoretical minus experimental.

tensity is in reasonable agreement with the best-fit theoretical intensity obtained from the least-squares analysis[14] described below. The corresponding radial distribution curve, calculated with an artificial damping function of the form $\exp(-0.0016s^2)$ and with a correction for nonnuclear scattering,[15] is shown in Fig. 3. Most of the computations were carried out by a HITAC-5020E computer in the Computer Centre of the University of Tokyo.

Analysis

Definition of Dihedral Angles. As shown in Fig. 1, the dihedral angle between the C_1–C_2–C_4 and C_1–C_3–C_4 planes is called the "twist angle" τ about the C_3 axis, while the dihedral angle between the C_1–C_2–C_3 and C_2–C_3–C_4 planes is called the "torsional angle" ϕ about the C_2–C_3 bond. They are related by

$$\tan(\tau/2) = r_2[(r_2-2r_1\cos\alpha)^2 + 4r_1^2\sin^2\alpha\sin^2(\phi/2)]^{-1/2}\tan(\phi/2) \quad (1)$$

where the C_1–C_2 (r_1) and C_2–C_3 (r_2) distances and the C_1–C_2–C_3 angle (α) are assumed to be constant. For small ϕ, τ is equal to 0.605ϕ. In the following analysis the ϕ angle is taken instead of τ as a parameter representing the twist motion.

Choice of Independent Parameters. The number of independent parameters sufficient to describe the D_{3h} structure is seven, while for the D_3 structure, in general four additional parameters are required. In order to facilitate the analysis, the following assumptions were made:

a) The C_1–H and C_2–H bond lengths are equal. Since a weighted average, $[r_g(C_1\text{–H})\times 2/14+r_g(C_2\text{–H})\times 12/14]$, is obtained from the analysis for r_g(C–H), it is likely that r_g(C–H) represents the C_2–H bond length.

b) The angles C_1–C_2–C_3, C_2–C_3–H and H–C_2–H do not depend on the torsional angle.

c) The plane H–C_2–H is perpendicular to the C_1–C_2–C_3 plane and bisects the C_1–C_2–C_3 angle (α), and *vice versa.*

Thus for D_3 symmetry the following six independent parameters were taken: the C_1–C_2 and C_2–C_3

[*2] Numerical experimental data of the levelled total intensity have been filed with the Chemical Society of Japan. A copy may be secured upon request to the Society.

14) Y. Morino, K. Kuchitsu and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).

15) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

distances, the angles α, the equilibrium torsional angle ϕ_e, the weighted mean C–H distance, and the H–C_2–H angle.

Calculation of Mean Amplitudes. The mean amplitudes and the vibrational corrections on internuclear distances, $r_a - r_\alpha$, were calculated by the method discussed in a previous paper[16] with a set of the Urey-Bradley force constants for a D_{3h} structure. The force constants, given in Table 1, were transferred mainly from those for cyclohexane.[17] The vibrational frequencies obtained from this calculation are compared in Table 2 with the observed values of Brüesch and Günthard.[18] The agreement is fair, although their assignments are still far from complete.

TABLE 1. UREY-BRADLEY FORCE CONSTANTS FOR BICYCLO[2.2.2]OCTANE[a] (in md/Å)

K(C-C)	2.30	F(C-C)	0.20
K(C-H)	4.10	F(C-H)	0.41
H(C-C-C)	0.32	F(H-H)	0.18
H(C-C-H)	0.225	Y[b]	0.11
H(H-C-H)	0.40		

a) Estimated from the force constants for cyclohexane.[17]

b) Defined in Eq. (3); in md·Å units.

As for the twisting mode, the symmetry coordinate is given by the equation

$$S_4(A_1'') = \frac{1}{\sqrt{3}}(\phi_{23}+\phi_{56}+\phi_{78}) \tag{2}$$

where ϕ_{ij}, the torsional coordinate about the C_i–C_j axis defined by Miyazawa and Fukushima,[19] is practically synonymous with the ϕ coordinate defined here according to the assumption (b) made above. The force constant Y for this torsional motion is defined by[*3]

$$V(\text{torsion}) = \frac{1}{2}Y(\phi_{23}^2+\phi_{56}^2+\phi_{78}^2) \tag{3}$$

Since the corresponding normal mode has the lowest frequency, Y has a strong influence on some of the calculated mean amplitudes. Accordingly, the mean amplitudes were calculated by the use of several different Y values. While analogous force constants for torsion about the *gauche* conformation (Y_{gauche}) have been reported for normal hydrocarbons[20] and cycloalkanes,[17] no comparable Y_{cis} constant for the *cis* conformation (possibly negative) is known. A semiempirical estimate of the potential function in terms of intramolecular strain energy (see Discussion) shows that the Y constant for this molecule (Eq. (3)) originates essentially from the positive Y_{gauche} about the C_1–C_2, C_3–C_4, ··· axes balanced by the negative Y_{cis} about the C_2–C_3, C_5–C_6, and C_7–C_8 axes. Thus the Y constant should be appreciably smaller than the Y_{gauche} given in the literature, ~0.11 md·Å, and may even be negative. For the present purpose,

TABLE 2. VIBRATIONAL FREQUENCIES OF BICYCLO[2.2.2]OCTANE

	Calcd[a]	Obsd[b]		Calcd	Obsd		Calcd	Obsd		Calcd	Obsd
A_1'	2918	—	A_1''	2881	—	E'	2894	2918	E''	2900	—
	2889	—		1186	—		2888	2863		2883	—
	1483	1439		934	—		1480	1456		1476	—
	1282	1235		134[c]	—		1327	1348		1340	
	1028	1018	A_2''	2919	2905		1234	1266		1284	1315
	740	790		2898	2888		1164	1100		1182	1221
	537	677		1477	1453		1056	1055		1077	1131
A_2'	2892	—		1346	1340		864	866		922	955
	1173	—		864	986		735	817		523	603
	732	760		781	796		359	371		253	—

a) Calculated with the use of the force constants listed in Table 1; in cm^{-1} units.

b) Observed values[18b] in the solid or CS_2 and CCl_4 solutions.

c) The value calculated in Ref. 18a, 65 cm^{-1}, seems to be in error because of the confusion of the torsional force constant Y defined in Eq. (3) (corresponding to $3H_\tau$) with H_τ defined in Ref. 20a. See text.

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[16] K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966).

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

[18] a) P. Brüesch, *Spectrochim. Acta*, **22**, 867 (1966). b) P. Brüesch and Hs. H. Günthard, *ibid.*, **22**, 877 (1966).

[19] T. Miyazawa and K. Fukushima, *J. Mol. Spectry.*, **15**, 308 (1965).

[*3] On the assumption (b), the force constant Y corresponds to three times the constant H_τ defined by Schachtschneider and Snyder[20] provided their definition of the torsional coordinate in regard to the *trans* conformation is translated into that in the *cis* conformation.

[20] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, a) **19**, 117 (1963); b) **21**, 169 (1965).

it is sufficient to assume Y to be positive and quadratic with the above upper limit. For the Y values of 0.11, 0.08, 0.05, and 0.025 md·Å, the corresponding frequencies of the twisting motion are 134, 116, 92, and 66 cm^{-1}, respectively, whereas all the other frequencies are insensitive to Y. This indicates that this normal mode is almost completely separable from other modes. In fact, the S_4 coordinate contributes more than 95% of the potential energy distribution[21] to the lowest A_1'' mode. Calculated mean amplitudes (listed in Table 3) and vibrational corrections were used in the subsequent least-squares analyses as fixed constants so as to facilitate convergence.

Least-squares Analysis of Molecular Intensity. The experimental molecular intensity was analyzed by a standard least-squares method[14] with the sets of mean amplitudes II through V based on the above choice of the Y constant. The analysis based on Set II converged to a D_3 structure with the ϕ_e angle of 12.2°±0.7°, where the uncertainty represents standard error. For the other sets of Y, all the parameters were essentially unchanged except for ϕ_e, which decreased with the decrease in Y. For Set V, where Y=0.025, ϕ_e was essentially zero, apparently giving a D_{3h} structure. Accordingly, the shape of the potential function as derived from the above analysis depends significantly on the assumption about Y. Nevertheless, it is clear from the analysis that this molecule has a floppy structure in thermal equilibrium as regards the twisting motion. The potential function for this motion is studied in more detail in later sections.

Estimation of Uncertainties. The structural

TABLE 3. CALCULATED MEAN AMPLITUDES FOR BICYCLO[2.2.2]OCTANE[a)]

C_1-C_2	533	C-H	789	$C_7\cdots H_4$	1025
C_2-C_3	528	$C_7\cdots H_1$	1066	$C_7\cdots H_{2b}$	1055
$C_1\cdots C_4$	664	$C_1\cdots H_7$	1075	$C_1\cdots H_4$	977
$C_1\cdots C_8$	654	$C_2\cdots H_{3a}$	1077		

set[b)]	I	II	III	IV	V
$C_2\cdots C_7$	729	729	732	737	742
$C_3\cdots C_7$	766	886	924	1000	1176
$C_7\cdots H_{2a}$	1557	1580	1609	1655	1740
$C_7\cdots H_{3a}$	1506	1914	2052	2318	2894
$C_1\cdots H_8$	1202	1281	1316	1384	1542
$C_7\cdots H_{3b}$	1083	1090	1092	1097	1107

a) Calculated by using the force constants given in Table 1; in 10^{-4} Å units.

b) Sets I through V correspond to the force constants for torsion defined in Eq. (3), assumed to be ∞, 0.11, 0.08, 0.05, and 0.025 md·Å, respectively. Values listed in the upper section do not depend on the choice of Y.

TABLE 4. STRUCTURAL PARAMETERS FOR BICYCLO[2.2.2]OCTANE

	Exp.[a)]	X.D.[b)]	Calcd.[c)]
C-$C_{av.}$[d)]	1.542 ± 0.004	1.541	1.543
C_1-C_2	$1.53_8 \pm 0.01_5$	1.540	1.542
C_2-C_3	$1.55_2 \pm 0.02_9$	1.543	1.544
∠C_1-C_2-C_3	109.7°±0.7°	109.9°	110.0°
$C_1\cdots C_4$	$2.59_2 \pm 0.02$	2.592	2.597
C-$H_{av.}$[d)]	1.107 ± 0.009	—	—
∠H-C-H	$110._1° \pm 5._6°$	—	—
k[e)]	0.96 ± 0.03	—	—

a) Experimental r_g distances in Å and r_α angles determined in the present study with estimated limits of error.

b) Crystal data for bicyclo[2.2.2]octane-1,4-dicarboxylic acid observed by Ermer and Dunitz[8] by X-ray diffraction.

c) Estimates from a strain-minimization calculation by Gleicher and Schleyer.[4]

d) Weighted mean values of bond distances; see text.

e) Index of resolution.

TABLE 5. ERROR MATRIX[a)]

	C_1-C_2	C_2-C_3	C-H	∠$C_1C_2C_3$	∠HCH	ϕ_e	k
C_1-C_2	0.0050	−0.0074	0.0016	0.0020	−0.0095	0.0044	−0.0040
C_2-C_3		0.0111	−0.0024	−0.0032	0.0143	−0.0062	0.0060
C-H			0.0035	0.0011	0.0056	0.0011	0.0028
∠$C_1C_2C_3$				0.0034	−0.0036	−0.0031	0.0025
∠HCH					0.0332	−0.0079	0.0095
ϕ_e						0.0138	−0.0013
k							0.0118

a) Error matrix for fixed mean amplitudes. Units for the distances are Å, those for the angles are rad., and the index of resolution k is dimensionless. Elements of the matrix are given by $\sigma_{ij} = \mathrm{sgn}[(B^{-1})_{ij}][|(B^{-1})_{ij}| V^*PV/(n-m)]^{1/2}$, where the notations follow Ref. 14. The diagonal element σ_{ii} represents the random standard error for the parameter i.

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21) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1952).

22) K. Hedberg and M. Iwasaki, *Acta Cryst.*, **17**, 529 (1964).

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

parameters determined are listed in Table 4. The limits of error were estimated as 2.5 times the random standard errors derived from the least-squares analysis,[14] which are included in the error matrix[22] given in Table 5 as diagonal elements, plus systematic errors. Principal sources of systematic errors are as follows: a) uncertainty in the scale factor, b) sector imperfections, c) extraneous scattering, and d) the use of theoretical mean amplitudes in the analysis. The errors due to sources a) and b) are estimated to be 0.07% and 0.05% of the corresponding distances, respectively.[23] The uncertainties due to c) and d) for all the distance and angle parameters, except for the bonded C–C distances, are at most of the order of their random standard errors, since the systematic error in the estimation of extraneous scattering causes uncertainties in the mean amplitudes and the index of resolution,[14] and since all the parameters (except for the C_1–C_2 and C_2–C_3 distances) are practically uncorrelated with the mean amplitudes and the index of resolution, as confirmed by a test analysis with systematic variations of the mean amplitudes used in the analysis.

As for the C_1–C_2 and C_2–C_3 distances, their difference derived from the analysis is contingent on their estimated amplitudes. Therefore, a systematic error due to the uncertainties in the C–C bond-stretching force constants used for calculating the mean amplitudes were taken into account as well as the uncertainty in the estimation of extraneous scattering. The total systematic errors in the C–C amplitudes are thus estimated to be 0.002 Å for C_1–C_2 and 0.005 Å for C_2–C_3, resulting in the final estimates of the uncertainties in their distances given in Table 4. Thus the C_1–C_2 and C_2–C_3 distances are hardly distinguishable in the present analysis, although the most probable value of the latter distance appears to be appreciably longer than the former.[*4,24,25] The weighted mean value of the r_g(C–C) distances, on the other hand, has been determined with much higher precision.

Large-amplitude Analysis. In order to further investigate the potential function $V(\phi)$ for the twisting motion as represented in terms of ϕ, the following "large-amplitude" analysis was undertaken. Since the S_4 coordinate is separable from other coordinates to a good approximation, the twisting motion can be described in terms of a single coordinate ϕ. The molecular intensity for such a nonrigid molecule may be given by a classical weighted average of the intensity in regard to the torsional angle,[26]

$$qM(q) = k\sum_{i\neq j} A_{ij}\mu_{ij}(q)\exp\left[-\frac{1}{2}(\pi l_{ij}q/10)^2\right] \int_{-\pi}^{\pi} w(\phi)\left\{\sin\left[\frac{\pi}{10}qr_{ij}(\phi)\right]\Big/r_{ij}(\phi)\right\}\mathrm{d}\phi \tag{4}$$

where k is the index of resolution, A_{ij} is a constant proportional to the atomic numbers of i and j, μ_{ij} is a known function[15] of q related to the elastic and inelastic scattering factors for i and j, and l_{ij} is the mean amplitude of the i-j pair due to the framework vibrations (*i.e.*, those apart from the twisting motion); the calculated mean amplitudes listed in Table 3 [Set I for $Y=\infty$], which were assumed to be independent of ϕ, were used for l_{ij}. The weight function w is given by Boltzmann statistics as

$$w(\phi) = \exp[-V(\phi)/\boldsymbol{k}T]\Big/\int_{-\pi}^{\pi}\exp[-V(\phi)/\boldsymbol{k}T]\mathrm{d}\phi \tag{5}$$

It is sometimes more convenient to work on the corresponding radial distribution function,[27]

$$f(r) = k\sum_{i\neq j}\frac{1}{2}A_{ij}(\pi H_{ij})^{1/2} \int_{-\pi}^{\pi}\left(w(\phi)\exp\{-H_{ij}[r-r_{ij}(\phi)]^2\}/r_{ij}(\phi)\right)\mathrm{d}\phi \tag{6}$$

where H_{ij} is defined in terms of the artificial damping coefficient b by

$$H_{ij} = (4b+2l_{ij}^2)^{-1} \tag{7}$$

In order to estimate the potential function from the present experimental data, the various functions for V, *viz.*,

(a) Square well: $V(\phi)=0$ for $\phi<\beta$ and ∞ for $\phi\geq\beta$
(b) Double parabola: $V(\phi)=a(|\phi|-b)^2$
(c) Quadratic: $V(\phi)=c\phi^2$
(d) Quadratic-quartic: $V(\phi)=k_2\phi^2+k_4\phi^4$

were applied to Eqs. (5) and (6).

A best-fit set of parameters for each potential function was searched for by a trial-and-error comparison of the observed and theoretical $qM(q)$ and $f(r)$ curves. The ranges of the experimental data most sensitive to $V(\phi)$ are $q=45$—60 Å^{-1} for the molecular intensity, and $r=2.7$—3.5 Å for the radial distribution curve. Typical examples are shown in Fig. 4.

For case (a), the limit angle β is found to be 22°± 4°. The coefficients a and b for case (b) are about 17 kcal/mol and 11°, respectively, corresponding to a potential cusp $V(0)$ of about 500 cal/mol, while for case (c) the constant c is 4.3 kcal/mol. For case (d) the set of parameters thus obtained was further refined by a least-squares analysis.

[*4] Our recent electron-diffraction study of triethylenediamine (1,4-diazabicyclo[2.2.2]octane)[24] has shown that the $r_g(C_2$–$C_3)$ distance is about 0.02 Å longer than that of the C–C distance in cyclohexane.[25]

24) A. Yokozeki and K. Kuchitsu, This Bulletin, to be published.

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

26) Y. Morino and E. Hirota, *J. Chem. Phys.*, **28**, 185 (1958).

27) J. Karle, *ibid.*, **15**, 202 (1947).

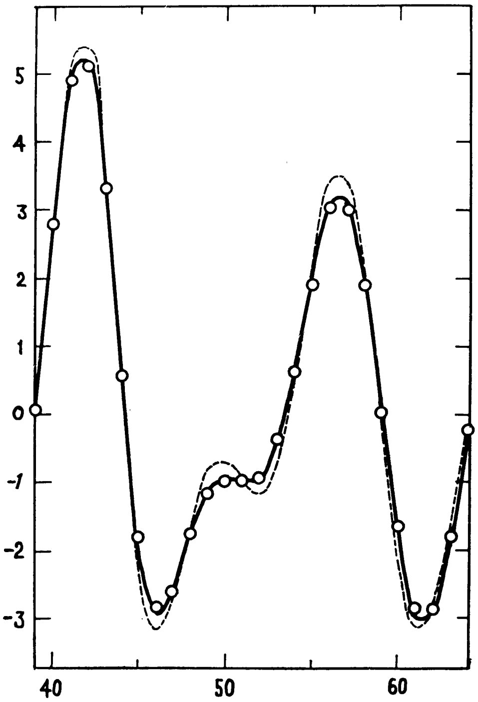

Fig. 4. (a)

The most probable set is $k_2=-4.0\pm3.3$ and $k_4=54.2\pm34.5$ (kcal/mol).

With the above adjustment of parameters, the experimental curves agree with the theoretical curves based on any one of the functions of (a) through (d) to a similar degree of consistency. As shown in Fig. 5, all the best-fit functions given above yielded a nearly equal rms angle, $\langle\phi^2\rangle^{1/2}$, of about 12° and a nearly equal "classical turning point" (the angle where the potential energy is comparable with the thermal energy at room temperature), $\phi_t\sim21°$. Since the intensity curve is sensitive to $\langle\phi^2\rangle^{1/2}$ and ϕ_t, they are the parameters readily determinable from the diffraction experiment irrespective of the type of the potential function assumed in the analysis.

On a physical basis, the function of (d) seems to be more realistic than the other functions. The most probable set of the k_2 and k_4 parameters has a potential hump of 75±100 cal/mol at the D_{3h} position and a broad double minimum at about 11°; the standard error given above has been estimated by taking into account the correlation between the k_2 and k_4 parameters.[28]

Discussion

Structure. The weighted mean value of the r_g(C–C) distances, $[(2/3)r_g(C_1–C_2)+(1/3)r_g(C_2–C_3)]$

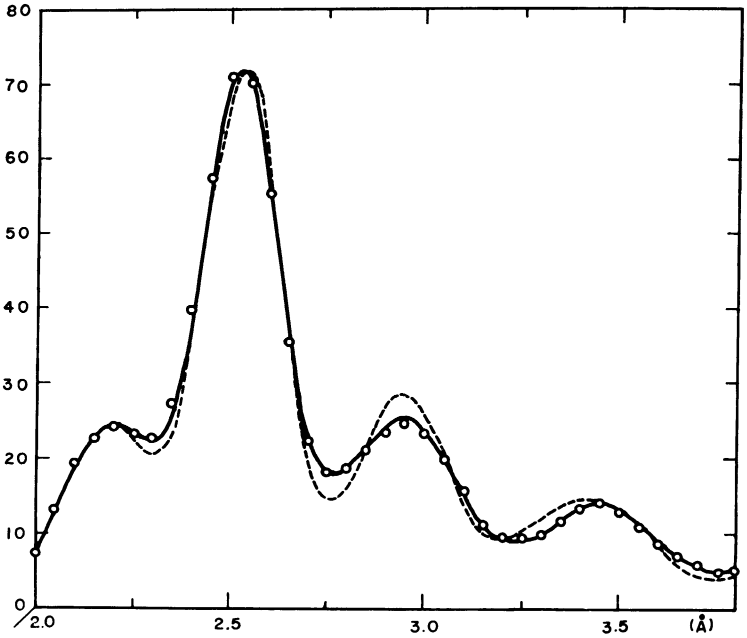

Fig. 4. (b)

Fig. 4. Dependence of the molecular intensity (a) and the radial distribution curve (b) on the potential function for twisting motion. Circles, experimental values representing their estimated uncertainties; solid curve, case (d) (quartic) potential function with the parameters given in the text; broken curve, case (c) (quadratic) potential function with $c=17$ kcal/mol corresponding to the force constant for torsion, $Y=0.08$ md·Å.

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[28] Y. Morino and T. Nakagawa, *J. Mol. Spectry.*, **26**, 496 (1968).

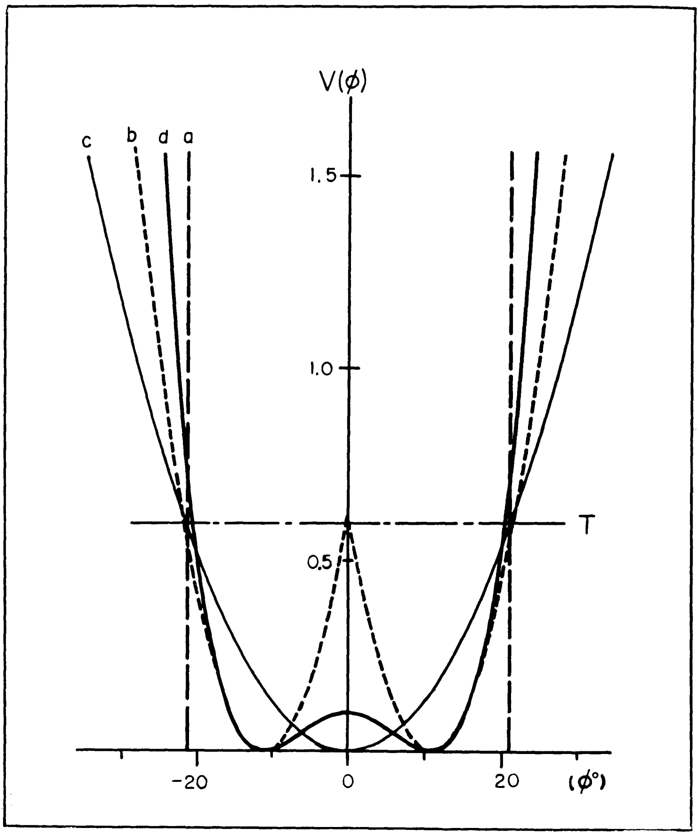

Fig. 5. Best-fit estimates of the potential functions for torsion (in kcal/mol), a—d, corresponding to the cases (a)—(d) discussed in the text. Line T denotes the thermal energy at room temperature, where the experiment was made.

$=1.542\pm0.004$ Å, is not significantly different from the r_g(C–C) distance in cyclohexane,[25] $1.540_4\pm0.001_0$ Å, indicating little overall influence of intramolecular strain on the C–C bond distances. The thermal-average C–C–C bond angle is similar to the tetrahedral angle. This structure appears to be consistent with the corresponding structures in crystalline BO derivatives determined by X-ray diffraction[8] (Table 4), although one should note that the latter parameters are based on a different definition and may also be subject to a crystal-field effect. The parameters for a free molecule estimated by a strain-minimization calculation[4] are also compatible with the present experimental values. The hydrogen parameters for the methylene group are analogous to those in cyclohexane[25] within their experimental uncertainties.

Twisting Motion. The present analysis has shown that the twisting motion has a large amplitude; the potential has a classical turning point of 21.5°±0.5° for the C–C torsional angle and an rms angle of 12.0°±1.5°, which correspond to 12.8°±0.3° and 7.2°±0.9°, respectively, in terms of the twist angle τ. The potential probably has a hump at the D_{3h} position much lower in height than the thermal energy at room temperature. Hence, the BO molecule may be said to have a "quasi-D_{3h} structure".

Semiempirical Calculation of the Potential Function It seems of interest in this connection to investigate whether the potential function derived above can be accounted for by a semiempirical model.[29] The strain energy of this molecule may be given as a function of the torsional angle by

$$E(\phi)=\frac{1}{2}H\sum_i[\alpha_i(\phi)-\alpha_0]^2+\frac{1}{2}f\sum_j(1+\cos 3\phi_j)+\sum V_{\mathrm{nb}}(\phi) \qquad (8)$$

where the bending and torsional force constants, H and f respectively, are estimated to be 98.5 kcal/mol (a bending force constant of the Urey-Bradley type for alkanes[20b,29]) and 2.93 kcal/mol (the torsional barrier for ethane[30]). The reference

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

[30] K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959); S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

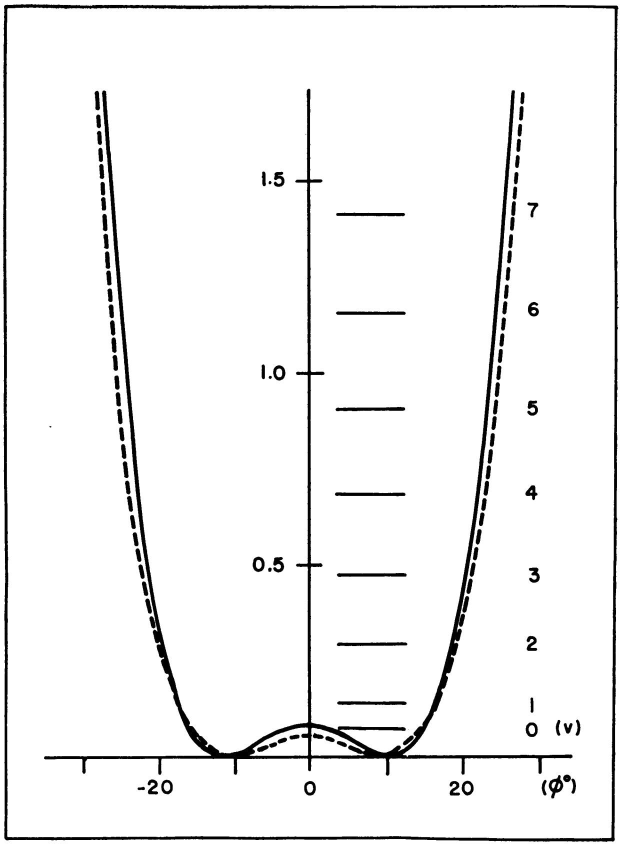

Fig. 6. Estimated potential functions for torsion (in kcal/mol).

Solid curve, best-fit function for case (d) given in the text; broken curve, a model function estimated by Eq. (8). The energy levels are estimated by the use of the d function.

for the CCC bond angle, α_0, is taken as the tetrahedral angle. In addition to the three assumptions made in the analysis section, the bond distances are assumed to be constant. The nonbonded interactions assumed for C–C, C–H, and H–H pairs (in kcal/mol) are

$$\left.\begin{aligned} V_{\mathrm{nb}}(\mathrm{C}\cdot\cdot\mathrm{C}) &= 1.66\times10^4\exp(-3.63r)-325/r^6 \\ V_{\mathrm{nb}}(\mathrm{C}\cdot\cdot\mathrm{H}) &= 1.29\times10^4\exp(-4.12r)-125/r^6 \\ V_{\mathrm{nb}}(\mathrm{H}\cdot\cdot\mathrm{H}) &= 1.00\times10^4\exp(-4.60r)-49.2/r^6 \end{aligned}\right\} \quad (9)$$

as taken from Hendrickson's paper.[31)]

The resulting function $E(\phi)$ has a broad minimum around $\phi=10°$, as illustrated in Fig. 6, with a small hump of about 50 cal/mol at $\phi=0°$. The turning point ϕ_t is estimated to be about 23°, in good agreement with the experimental result given above. The general feature of the curve for $\phi \gtrsim 15°$ rests on the contributions from the first and third terms in Eq. 8; as the molecule is twisted from the D_{3h} conformation, the distortion of the bridgehead-carbon valence angles and the increasing interactions among the nonbonded C–C pairs contribute nearly equally to the steep rise in the potential, outweighing a slight decrease in the interactions among the nonbonded C–H and H–H pairs. For smaller torsional angles ($\phi<10°$), on the other hand, the sum of the first and third terms makes a nearly flat curve, and the potential shape is sensitive to the second term in Eq. 8. This term causes a small hump at the D_{3h} conformation, and the height and the minimum position depend on a competitive sum of six *gauche* terms (about the C_1–C_2 axis, *etc.*), which favor the D_{3h} conformation, and three *cis* terms (about the C_2–C_3 axis, *etc.*), which work in the opposite direction.

A recent calculation of this potential by Ermer and Dunitz[8,9)] using a range of semiempirical functions has reached essentially the same conclusion, with a predicted minimum of about 100 cal/mol and an rms torsional angle of 13.8°.

Estimation of Energy levels. The energy levels for this twisting motion were calculated from

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[31)] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961).

the Hamiltonian,[32,33]

$$H = P_\phi^2/2M(\phi) + V(\phi) \qquad (10)$$

where $V(\phi)$ is the quartic function estimated above, and P_ϕ is the angular momentum conjugate to ϕ. The reduced mass $M(\phi)$ was estimated with a semirigid framework,[32],[*5] where, besides the assumptions (a)—(c) made in the analysis section, all the bond distances were assumed to be constant in the twisting motion. The resulting $M(\phi)$ depends only slightly on ϕ:

$$M(\phi) = 29.08 - 5.29\phi^2 + 6.54\phi^4 \text{ (amu)}$$

for ϕ (in rad.) $\lesssim 40°$. Thus the reduced mass was assumed to be constant (28.9 amu); the error due to the use of this effective mass is less than 1% of the energy levels estimated. A computer program written by Ueda and Shimanouchi[32] was used for calculating the levels listed in Table 6. Since the energy values, particularly those of lower levels, depend critically on the detailed shape of the potential, the listed values are only semiquantitative. Nevertheless, the presence of several levels under the thermal energy at room temperature is clearly demonstrated. Comparable energy values were obtained from the model potential function (8). Ermer and Dunitz[8,9] have estimated the energy differences between higher levels to be about 60 cm^{-1} by the use of their semiempirical potential functions. Though the fundamental transitions are infrared inactive, a direct measurement of the levels by some spectroscopic means, such as an analysis of combined transitions appearing in near-infrared band progressions,[34] could supply further information on this potential function.

TABLE 6. ESTIMATED ENERGY LEVELS OF THE TWISTING MOTION FOR BICYCLO[2.2.2]OCTANE[a] (in cm^{-1} units)

v	E_v	v	E_v	v	E_v
0	24.0	3	165.8	6	403.4
1	48.4	4	237.9	7	495.0
2	103.4	5	317.5	8	591.7

a) Semiquantitative estimates based on the experimental potential function (d) given in the text.

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[*5] The method of high-frequency splitting developed by Thorson and Nakagawa[33] gave 29.14 amu for $M(0)$.

32) T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, **47**, 4042 (1967).

33) W. R. Thorson and I. Nakagawa, *ibid.*, **33**, 994 (1960).

34) T. Ueda and T. Shimanouchi, *ibid.*, **47**, 5018 (1967).