The Molecular Structure of Bicyclo[3.3.0]oct-1,5-ene as Determined by Gas-Phase Electron Diffraction and Molecular Mechanics

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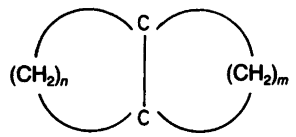
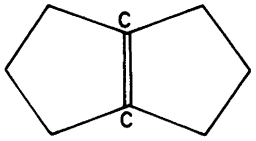
The molecular struture and conformation of the title compound has been studied by gas-phase electron diffraction (GED) and by molecular mechanics calculations, using the MM2 force field. The geometrical parameters (r_a) with 3σ values in parenthesis are: C=C 1.345(5) Å, Csp^2–C 1.498(6) Å, C–C 1.564(6) Å, C–H 1.120(6) Å, ∠C=C–C 112.9(2)°, ∠H–C–H_{AV}. 107.4(2.7)° and the flap angle φ 17(3)°.

Approximately a dozen fused bicyclo[*n.m.*0]alkanes (I) have so far been studied in the gas phase (Refs. 1 and 2 and references therein, as well as Ref. 3). The common, interannular, C–C bond is of particular interest in these systems since the major strain in a molecule of this type normally is associated with the region of the inter-annular bond. The purpose of the present paper is to present the structural results obtained in a study of bicyclo[3.3.0]oct-1,5-ene (BCO, II), a bicyclic system with a common C=C double bond, instead of a single bond as in molecules of type I.



I

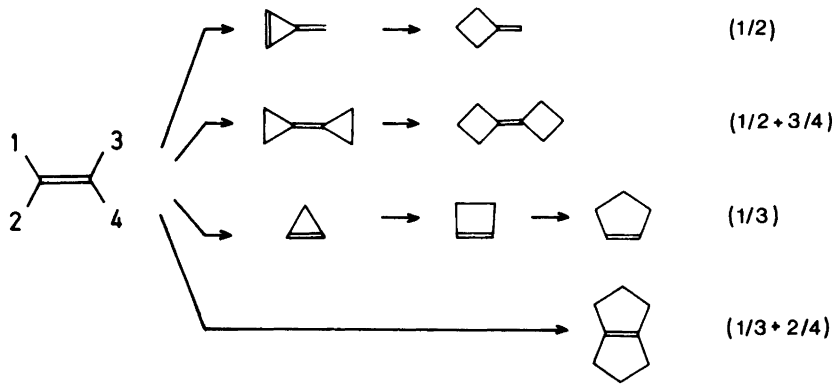


II

The BCO molecule may also be considered as resulting from substitutions at a C=C double bond. In Scheme 1, different types of substitutions are illustrated for molecules whose structures have been studied experimentally. By comparing the structures of strained bicyclic systems with those of "strainless" systems such as ethylene[5] or tetramethylethylene[6] it should be possible to obtain insight into how the induced strain influences the structural parameters.

Experimental and data processing

The sample of BCO used in the present study was prepared by a method described earlier;[7] its purity was 95 % according to gas chromatographic measurements. Electron diffraction diagrams were recorded with the Oslo apparatus[8] at a nozzle temperature of 45 °C. Kodak Electron Image photographic plates were used, and five plates were selected for each of the nozzle-to-photographic plate distances of 476.26 and 196.26 mm. The electron wavelength was 0.06467 Å, as calibrated against diffraction patterns for gaseous benzene, using r_a (C–C) = 1.397 Å as a standard. The estimated standard deviation in the determination of the electron wavelength is 0.1 %. The ranges of the scattering data were 1.375–16.250 and 8.25–38.75 $Å^{-1}$. The experimental data were processed in the usual way,[9] and the



Scheme 1.

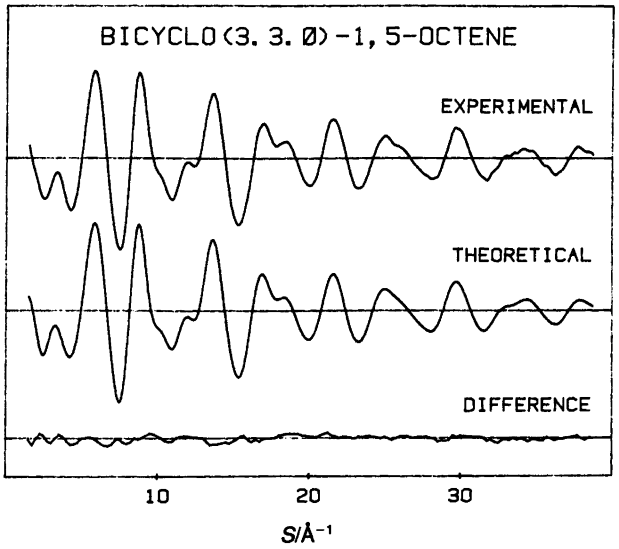


Fig. 1. Experimental and theoretical molecular intensities for bicyclo[3.3.0]oct-1,5-ene.

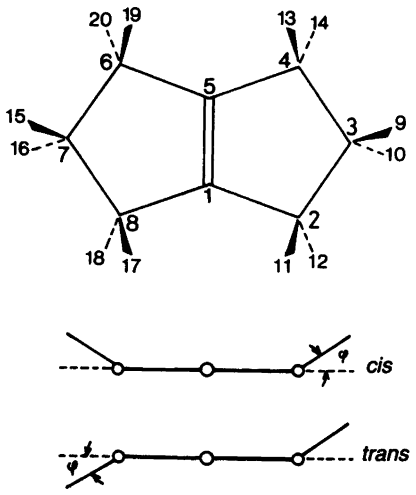


Fig. 3. Molecular model of bicyclo[3.3.0]oct-1,5-ene, showing the numbering of the atoms.

intensities were modified by multiplication with the function $s.f_c^{-2}$. The elastic scattering factors of Schäfer *et al.*[10] and the inelastic scattering factors of Tavard *et al.*[11] were used. Further treatment and structural analysis were carried out in Moscow. The experimental molecular intensity function of BCO is shown in Fig. 1, while the radial distribution curve obtained by Fourier transformation of the intensity values is shown in Fig. 2. The molecular structure was refined by least-squares intensity refinements.[9]

Data analysis

Molecular Mechanics calculations. A molecular model of BCO (C_s symmetry) is shown in Fig. 3. In order to obtain preliminary structural information which might be useful when interpreting the electron diffraction data, molecular mechanics calculations were carried out using Allingers MM2 program.[12] All the required force field parameters were present within the program and were used without any changes.

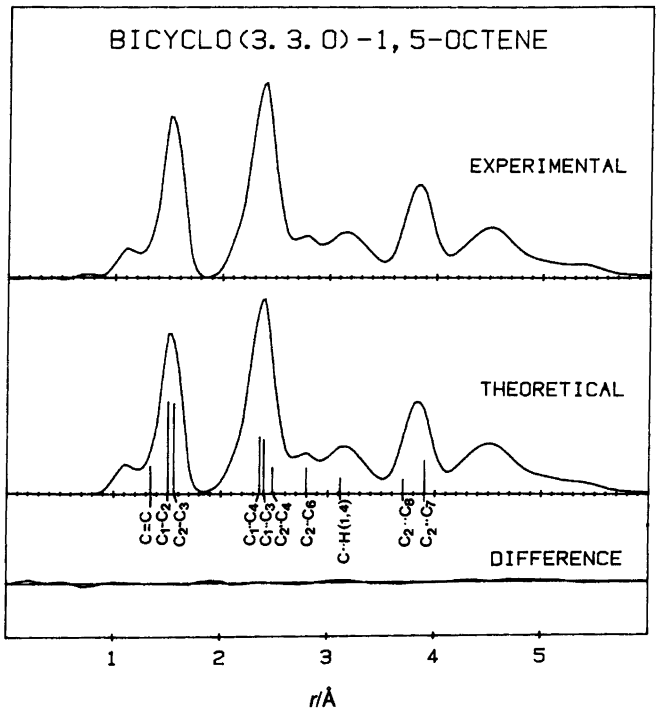


Fig. 2. The experimental RD curve for bicyclo[3.3.0]oct-1,5-ene together with the theoretical RD curve calculated from the parameters in Table 3, and the differences between the two.

Table 1. Results of molecular mechanics (MM2) calculations for *cis* and *trans* conformers of BCO. Distances in Å, angles in degrees, energies in kJ mol^{-1}.

Parameter	*cis*	*trans*
r(C=C)	1.328	1.328
r(C^1–C^2)	1.492	1.492
r(C^2–C^3)	1.552	1.552
r(C^2–H)	1.115	1.115
r(C^3–H)	1.116	1.116
∠C^1–C^2–C^3	100.4	100.3
∠C^2–C^3–C^4	108.7	108.7
∠C=C–C	113.6	113.6
∠H–C^2–H	110.3	110.3
∠H–C^3–H	107.1	107.1
flap angle, φ	19.0	19.1
E_{steric}	82.459	82.422

Since the puckering in the two cyclopentene fragments may be assumed to be roughly independent, the calculations were made for two different conformers, referred to as *cis* and *trans* respectively (see projections in Fig. 3). This was done by restricting the movements of the C^3 and C^7 atoms to the same (*cis*) or to the opposite (*trans*) side of the plane defined by the other carbon atoms. Not surprisingly, the steric energies of both forms were found to be nearly equal, with a difference of 37 J in favour of the *trans* form. The geometrical data resulting from the MM2 calculations of BCO are presented in Table 1.

Structural analysis. Based on the results of the molecular mechanics calculations the following assumptions concerning the BCO structure were introduced:

1. Both forms, *cis* and *trans*, are characterized by the same flap angle, φ, which has opposite signs in the two forms.
2. Since the MM2 calculations showed the two forms to have nearly the same energy, the gas was considered to be an equimolar mixture of *cis* and *trans*.
3. The HCH valence angles were refined under the constraint: ∠H–C$_2$–H = ∠H–C$_3$–H + 3.2°, in accordance with the MM2 data.
4. The *cis* and *trans* forms were assumed to have C_{2v} and C_{2h} symmetry, respectively.
5. Local C_{2v} symmetry at the methylene groups was assumed.

The molecular models of BCO (Fig. 3) may accordingly be described by the following seven parameters: r(C=C), r(C^1–C^2), r(C^2–C^3), r(C–H), ∠C=C–C, ∠H–C–H, and the flap angle φ (the angle between the planes C^2–C^3–C^4 and C^2–C^1–C^5–C^4).

The vibrational amplitudes were calculated by a normal coordinate analysis,[13] using a valence force field taken mainly from the work by Ermer and Lifson[14] (Table 2). The calculation method is based on an expansion of interatomic distances in terms of the cartesian displacement coordinates.[15] The perpendicular amplitude correction coefficients, necessary for determining the structure on a r_α basis, were also calculated, but as the R factor was somewhat higher when the structure was determined for an r_α rather than an r_a geometry, the final results are presented on the basis of an r_a geometry.

The geometrical parameters resulting from the MM2 calculations served as starting values for the analysis. The refinements proceeded rather smoothly, except for the parameters ∠C=C–C and φ, which are also the two parameters that are most highly correlated (corr. factor −0.75). Many refinements were therefore carried out, trying out combinations of these parameters. When φ was set equal to the flap angle observed in cyclopentene,[17] i.e. 28.8°, the fit between experimental and theoretical intensity curves clearly deteriorated, and refinements of φ gave consistently a much smaller value for this parameter. All combinations

Table 2. Valence force constants (in mdyn Å^{-1} or mdyn Å rad^{-1}) used in normal coordinate analysis of BCO.

Type	Valence coordinate	Value	Type	Valence coordinate	Value
Stretch	C=C	9.1	O.o.pl.	C=C(C)C	0.159
	C–C	4.48			
	C–H	4.55	Str./str.	C–C; C–C	0.198
Bend	C=C–C	0.503	Str./bend	C–C; C–C–C	0.418
	C–C–C	0.648		C–C; C–C–H	0.267
	C^2–C^1–C^8	0.725	Bend/bend		
	C–C–H	0.617		C–C–H′; C–C–H″	−0.055
	H–C–H	0.549		C^1–C^2–H; C^1–C^2–C^3	−0.055
				C^1–C^2–C^3; C^2–C^3–H	−0.04
Torsion	–C=C–	0.2634		H–C^2–C^3; C^2–C^3–H	−0.03
	C^1–C^2–	0.0176		C^8–C^1–C^2; C^6–C^5–C^4	0.023
	–C^2–C^3–	0.0190			

Table 3. Final results from least-squares intensity refinements of BCO. Distances (r_a) and amplitudes (u) in Å, angles in degrees, 3σ in parentheses.

Parameter	Distance or Angle	$u_{exp.}$	$u_{calc.}$
r(C=C)	1.345(5)	0.036	0.04407
r(C¹–C²)	1.498(6)	0.047 (6)	0.0499
r(C²–C³)	1.564(6)	0.045	0.0516
r(C–H)	1.120(6)	0.084(5)	0.0793
∠H–C³–H	105.8(27)		
∠C=C–C	112.9(2)		
φ	17(3)		

Dependent distances

	r	$u_{exp.}$		$u_{calc.}$		r	$u_{exp.}$		$u_{calc.}$
C¹···C⁴	2.37	0.059		0.0608	C³···C⁷$_c$	4.54	0.176		0.1021
C¹···C³	2.38	0.063		0.0650	C³···C⁷$_t$	4.58	0.176		0.1021
C²···C⁴	2.51	0.064		0.0664	C⁶···H¹²	4.36	0.210		0.1359
C¹···H¹	2.18	0.106	(3)	0.1080	C³···H¹⁸	4.33	0.216		0.1423
C⁴···H¹⁰	2.24	0.106		0.1082	C³···H¹⁸	4.33	0.216	(33)	0.1423
C³···H¹⁴	2.22	0.109		0.1109	C²···H¹⁵	4.40	0.310		0.2355
C⁴···C⁶	2.76	0.082		0.0679	C⁶···H¹¹	4.45	0.226		0.1522
C¹···H¹⁴	3.08	0.133	(14)	0.1191	C³···H¹⁸	4.46	0.238		0.1638
C⁴···H¹⁹	3.09	0.160		0.1465	C²···H¹⁶	4.73	0.200		0.1257
C⁴···C⁸	3.7	0.066		0.0695					
C⁴···C⁷	3.87	0.074	(11)	0.0772					

of the following set of starting values of ∠C=C–C and φ were finally analyzed in more detail:

∠C=C–C: 111° 112.5° 114°
φ: 10° 13° 17° 20°

According to this study the R factor has only one minimum within the above limits of these parameters.

The anharmonicity constants, a_3, for the C–C and C–H bonds were set equal to 2.0 and 3.0 Å^{-1}, respectively (the electron diffraction asymmetry parameter, $\varkappa_{ij}$, is related to the Morse anharmonicity constant, a_3, and to the vibrational amplitude, u_{ij}, by $\varkappa_{ij} = a_3 u_{ij}^4/6$; Ref. 9). The vibrational amplitudes that could be refined together with the geometrical parameters (Table 3) were found to be close to the values calculated in the normal coordinate analysis.

In the final stage of the study we tried to refine the conformational ratio. The molar fractions determined in this way were approximately 0.5 for both forms, but with a large standard deviation. Refinement of the conformational composition will therefore not give any new information about the relative stability of the two forms, and the final results are therefore based on the assumption of an equimolar mixture of the *cis* and *trans* forms.

The final parameters are presented in Table 3. The theoretical curves in Figs. 1 and 2 correspond to this model.

Discussion

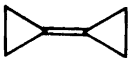
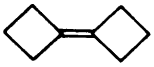
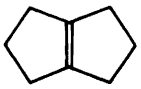
A comparison between the results of the GED study (Table 3) and those of the MM2 calculations (Table 1) show that the MM2 force field reliably predicts the geometry of BCO. All the discrepancies are within the limits of the experimental errors and the possibilities of the theoretical estimates.[18]

Geometrical parameters for a number of structurally related molecules are collected in Table 4. Inspection of the data indicates that there is nothing extraordinary about the stereochemistry of the BCO molecule. The flap angle in BCO might appear to be too low by comparison with the value found in cyclopentene.[17] There are, however, many structural results that indicate that the flap angle reported by Davis and Muecke[17] is too high. Some of this evidence is summarized in the following:

(a) Theoretical estimates of the flap angle in cyclopentene made with three different force fields[18] (19.0°; 19.1°; 21.4°) are systematically lower than the experimental value of 28.8±2.5°.[17] The MM2 results for φ in BCO (19°) are, as expected, indistinguishable from the above theoretical estimates.

(b) On the basis of far-infrared data a value of 23.3° is proposed for the flap angle in cyclopentene.[28] A similar result (21.9±0.5°) was obtained in an ED study of perfluorocyclopentene by Chang and Bauer.[29]

Table 4. A comparison between structural results for some sterically strained alkenes. Distances in Å, angles in degrees.

Molecule	r(C=C)	r(C–C)[a]	r(C–C)	∠C=C–C	φ	Ref.
	1.353(4)	1.511(2)		123.9(5)		6
	1.314(1)	1.468(1)	1.554(2)	148.1(1)		18
	1.336(5)	1.518(4)	1.566(5)	133.3	16.8(45)	19
	1.304(3)	1.519(2)		64.6		20
	1.323(3), ring 1.332(6)	1.441(6)				29
	1.342(5)	1.517(5)	1.566(5)	94.2(5)		21
	1.342(10)	1.519(30)	1.546(35)	111.0(12)	28.8(25)	15
	1.345(5)	1.498(6)	1.564(6)	112.9(2)	17(3)	This work

[a]Adjacent to C=C bond.

(c) For systems structurally related to cyclopentene, such as dihydrofuran ($\varphi = 11.8\pm4.6°$)[23] and bicyclo[3.1.0]hexane ($\varphi = 25.2\pm2.8°$),[24] the flap angles are also smaller.

(d) A molecular statistical calculation of the retention volume of BCO at zero surface coverage on graphitized carbon black, using the atom-atom approximation for the potential energy of intermolecular interaction between adsorbate and adsorbent, has been carried out by one of us (E.Y.A.). By comparing the results of the calculation with the measured retention volume, an estimated value for the flap angle of $\varphi = 14\pm2°$ has been proposed. The results from this study will be published elsewhere (for more information about this metod, called chromatoscopy, see Refs. 24 and 25).

From what has been said above, it might be concluded that the value for the flap angle in cyclopentene reported by Davis and Muecke ($28.8\pm2.5°$) probably is too high.

The average value for the HCH bond angle calculated by MM2 (109.2°) is slightly larger than the experimental result (107.4°). The result based on an empirical relationship ($108.0\pm1.9°$) falls between the above values.[27]

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References

1. Kozina, M. P., Mastryukov, V. S. and Milvitskaya, E. M. *Usp. Khim. 50* (1982) 1337.
2. Vilkov, L. V., Mastryukov, V. S. and Sadova, N. I. *Determination of the Geometrical Structure of Free Molecules,* Mir Publishers, Moscow 1983 (Translated and revised version of the 1978 Russian edition).
3. Glen, R., Gundersen, G., Murray-Rust, P. and Rankin, D. W. H. *Acta Chem. Scand., Ser. A 37* (1983) 853.
4. Zefirov, N. S. and Solokov, V. I. *Usp. Khim. 36* (1967) 243.
5. Kuchitsu, K. *J. Chem. Phys. 44* (1966) 906.
6. Tokue, I., Fukuyama, T. and Kuchitsu, K. *J. Mol. Struct. 23* (1974) 33.
7. Finkelstein, E. Sh., Strelchik, B. S., Vdovin, V. M. and Nametkin, N. S. *Dokl. Akad. Nauk SSSR, Ser. Khim. 220* (1975) 131.
8. Bastiansen, O., Hassel, O. and Risberg, R. *Acta Chem. Scand. 9* (1955) 232.
9. Andersen, B., Seip, H. M., Strand, T. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
10. Schäfer, L., Yates, A. C. and Bonham, R. A. *J. Chem. Phys. 55* (1971) 3055.
11. Tavard, C., Nicolas, D. and Raoult, M. *J. Chim. Phys. 64* (1976) 540.
12. Allinger, N. L. *J. Am. Chem. Soc. 99* (1977) 8127.
13. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett. 15* (1972) 263.
14. Ermer, O. and Lifson, S. *J. Am. Chem. Soc. 95* (1973) 4121.
15. Gwinn, W. D. *J. Chem. Phys. 55* (1971) 477.
16. Kuchitsu, K. and Cyvin, S. J. In: Cyvin, S. J., Ed., *Molecular Structures and Vibrations,* Elsevier, Amsterdam 1972, pp. 183–211.
17. Davis, M. I. and Muecke, T. W. *J. Phys. Chem. 74* (1970) 1104.
18. Burkert, U. and Allinger, N. L. *Molecular Mechanics,* Am. Chem. Soc. Monograph 177, Washington D.C. 1982.
19. Trætteberg, M., Simon, A., Peters, E.-M. and de Meijere, A. *J. Mol. Struct. 118* (1984) 333.
20. Mastryukov, V. S., Tarasenko, N. A., Vilkov, L. V., Finkelstein, E. Sh., Jonvik, T., Andersen, B. and Aanensen, E. *Zh. Strukt. Khim. 22* (1981) 57.
21. Kassai, P. H., Myers, R. J., Eggers, D. F., Jr. and Wiberg, K. B. *J. Chem. Phys. 30* (1959) 512.
22. Bak, B., Led, J. J., Nygård, L., Rastrup-Andersen, J. and Sørensen, G. O. *J. Mol. Struct. 3* (1969) 369.
23. Tamagawa, K. and Hilderbrandt, R. L. *J. Am. Chem. Soc. 106* (1984) 20.
24. Mastryukov, V. S., Osina, E. L., Vilkov, L. V. and Hilderbrandt, R. L. *J. Am. Chem. Soc. 99* (1977) 6855.
25. Kiselev, A. V. *Chromatographia 11* (1978) 691.
26. Dimitrov, L. D., Kiselev, A. V. and Petrova, R. S. *Chromatographia 15* (1982) 245.
27. Mastryukov, V. S. and Osina, E. L. *J. Mol. Struct. 36* (1977) 127.
28. Laane, L. and Lord, R. C. *J. Chem. Phys. 47* (1967) 4941.
29. Chiang, C. H. and Bauer, S. H. *J. Phys. Chem. 74* (1971) 1685.
30. Norden, T. D., Staley, S. W., Taylor, W. H. and Harmony, M. D. *J. Am. Chem. Soc. 108* (1986) 7912.

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