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STRUCTURES OF STRAINED POLYCYCLICS

BOND DISTANCES AND ANGLES IN TRICYCLO[3.3.0.0.^{2,6}]OCT-3-ENE AND IN BICYCLO[2.1.1]HEXENE-2

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Abstract—The structure of tricyclo[3.3.0.0^{2,6}]oct-3-ene in the gas phase has been determined by electron diffraction. From least squares fitting of theoretical to the experimental intensity function (range: $6 \leqslant q \leqslant 106$), the C–C bond lengths in the cyclobutane ring were found to be 1·580 ± 0·015 Å. In the 5-member ring which contains the double bond, the C—C distances are 1·503 ± 0·012 Å, and in the other 5-membered ring, they are 1·505 ± 0·018 Å on the sides and 1·579 ± 0·038 Å at the base. The C=C bond is 1·345 ± 0·010 Å, and the average C—H separation is 1·128 ± 0·010 Å.

The recorded patterns for the bicyclo[2.1.1]hexene-2 covered the angular range of q = 12–125 Å^{-1}. The interatomic distances and bond angles were obtained by applying a least squares analysis to the experimental molecular intensities. The C=C double bond length was found to be 1·332 ± 0·005 Å; C—C single bond, adjacent to the double bond, is 1·537 ± 0·008 Å, while the sp^3-hybrid C—C single bond is 1·549 ± 0·006 Å. The dihedral angle of the 4-membered ring is 123·5 ± 1·3°. Comparison of the structures reported for this family of polycyclic hydrocarbons concludes this paper.

INTRODUCTION

TRICYCLO[3.3.0.0^{2,6}]OCT-3-ENE is one of several highly strained, rigidly fused ring systems investigated in this laboratory by electron diffraction. In the concluding section we have compared the dimensions of its rings with the corresponding ones in bicyclohexane,[1] bicyclohexene, and tricyclo[3.3.0.0^{2,6}]octane.[2] It is interesting to note the geometrical consequences of constraining the cyclobutane ring with a —CH_2—CH_2— on one side and a —CH=CH— on the other. The bicyclohexene

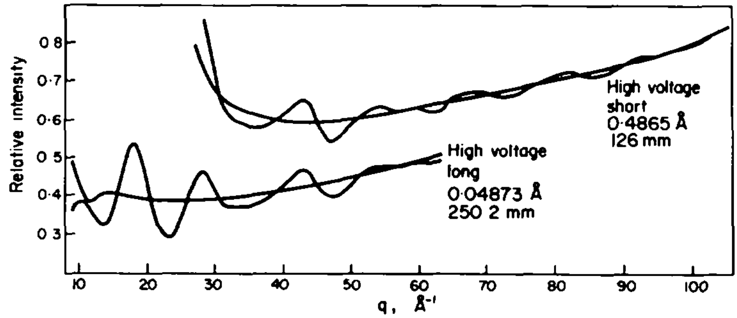


FIG 1. Relative scattered intensity *vs* q for tricyclo[3.3.0.0^{2,6}]oct-3-ene

Table A. Reduced electron diffraction intensities for tricyclo[3.3.0.0^{2,6}]oct-3-ene

q	HVL Intensity	q	Intensity	q	Intensity	q	Intensity
9	0·3622	53	0·4757	55	0·6376	99	0·7910
10	0·3879	54	0·4802	56	0·6307	100	0·7989
11	0·3856	55	0·4801	57	0·6276	101	0·8055
12	0·3613	56	0·4804	58	0·6300	102	0·8160
13	0·3386	57	0·4795	59	0·6348	103	0·8248
14	0·3287	58	0·4817	60	0·6342	104	0·8333
15	0·3495	59	0·4869	61	0·6320	105	0·8410
16	0·4167	60	0·4925	62	0·6254	106	0·8496
17	0·4979	61	0·4932	63	0·6274		
18	0·5449	62	0·4924	64	0·6425		
19	0·5190	63	0·4958	65	0·6588		
20	0·4436	64	0·5093	66	0·6685		
21	0·3667			67	0·6717		
22	0·3168			68	0·6722		
23	0·2970	q	HVS Intensity	69	0·6721		
24	0·3006			70	0·6709		
25	0·3326	27	0·8890	71	0·6669		
26	0·3862	28	0·8808	72	0·6643		
27	0·4358	29	0·8185	73	0·6646		
28	0·4662	30	0·7233	74	0·6684		
29	0·4567	31	0·6563	75	0·6765		
30	0·4203	32	0·6148	76	0·6851		
31	0·3904	33	0·5989	77	0·6948		
32	0·3753	34	0·5922	78	0·7025		
33	0·3728	35	0·5888	79	0·7085		
34	0·3755	36	0·5810	80	0·7150		
35	0·3774	37	0·5834	81	0·7233		
36	0·3794	38	0·5903	82	0·7263		
37	0·3863	39	0·6009	83	0·7244		
38	0·3979	40	0·6154	84	0·7180		
39	0·4088	41	0·6312	85	0·7153		
40	0·4239	42	0·6479	86	0·7162		
41	0·4446	43	0·6551	87	0·7193		
42	0·4615	44	0·6455	88	0·7265		
43	0·4684	45	0·6067	89	0·7353		
44	0·4146	46	0·5682	90	0·7472		
45	0·4373	47	0·5463	91	0·7560		
46	0·4117	48	0·5510	92	0·7657		
47	0·4025	49	0·5711	93	0·7682		
48	0·4035	50	0·5903	94	0·7696		
49	0·4141	51	0·6038	95	0·7705		
50	0·4345	52	0·6186	96	0·7763		
51	0·4545	53	0·6303	97	0·7833		
52	0·4676	54	0·6381	98	0·7874		

was chosen for study because of its rigidity to contrast with cyclopentene and with substituted 4-member ring hydrocarbons. The dihedral angles in these and related compounds are summarized. In addition to these structural considerations, this study clearly illustrates the effects of lower symmetry and high parameter correlation

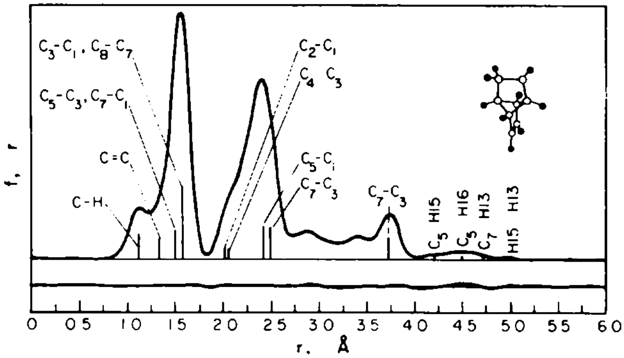


FIG 2. Final radial distribution curve for tricyclo[3.3.0.$0^{2,6}$]oct-3-ene; the lower curve is the difference between the theoretical and experimental values

on the precision attainable in a structure determination. Attention is drawn to the problem of "uniqueness" in establishing molecular models. In the case of the octene the choice between acceptable models had to be made on the basis of geometric data available for similar compounds.

ANALYSIS AND RESULTS

The tricyclooctene. The presence of closely overlapping atom-pair distances lead to an ambiguous interpretation of the radial distribution curves. Examination of that curve (Fig 2) shows overlap of atom pair distances C_3—C_5, C_1—C_7 and C_1—C_3, C_7—C_8 in the region 1·5 to 1·6 Å. In the 2·0 to 2·5 Å region there is overlap of the pairs C_1—C_2 (2·03 Å) and C_3—C_4 (2·06 Å); C_1—C_5 (2·42 Å) and C_3—C_7 (2·49 Å). In addition to these there are two other nonbonded C—C distances in this region, C_2—C_7 (2·34 Å) and C_3—C_6 (2·24 Å). Our initial effort was devoted to finding a single self consistent set of distances and bond angles. Then several acceptable structures were found by least squares fitting of the theoretical intensity to the experimental intensity, assuming the molecule had C_{2v} symmetry. Of course, for the model selected, the final intensity and radial distribution curves which were calculated agreed well with the experimental ones (Fig 3). Table 1 is a listing of the independent geometrical parameters which were used to characterize the model (refer to Fig 4a). These were

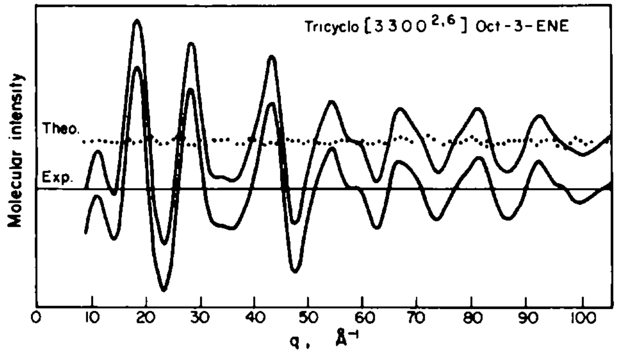
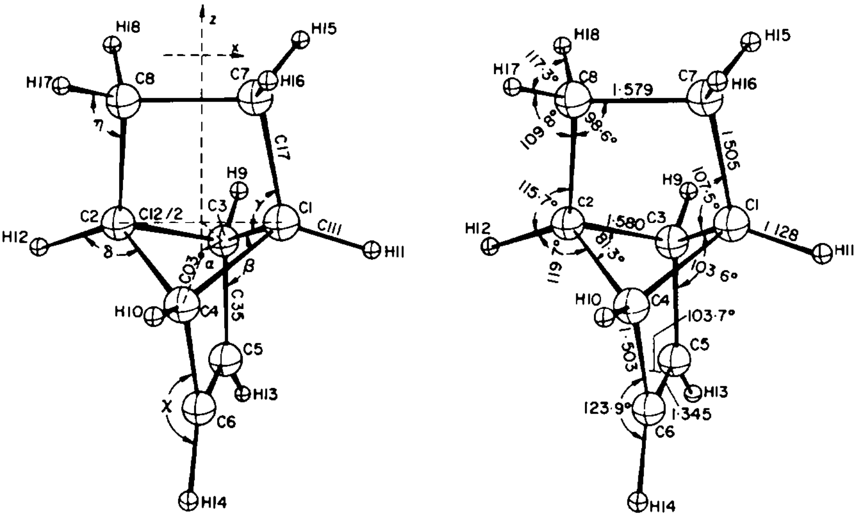


FIG 3. Theoretical and experimental intensity curves *vs* q; the dotted curve is the difference between them.



Parameters
(a)

Bond distances and angles
(b)

FIG 4. Parametrization of tricyclo[3,3,0,$0^{2,6}$]oct-3-ene; one half the flap angle in the cyclobutane ring is defined as α

chosen to make best use of the assumed molecular symmetry based on Hilderbrandt's method[7] for computing the cartesian coordinates. The parameters and the root mean square amplitudes (l_{ij}'s) were then varied sequentially; the starting parameters and l_{ij}'s were those that reproduced the octene's radial distribution pattern. The initial

TABLE 1. PARAMETERS FOR TRICYCLO[3.3.0.$0^{2,6}$]OCT-3-ENE

Symbol	Model I^a σ = 0·0265	Model II^a σ = 0·0268	Definition
C12/2	1·025 (0·0090) Å	1·015 (0·0087) Å	½ distance between C_1 and C_2
C03	1·196 (0·0118)	1·210 (0·0117)	Distance from center to C_3
C35	1·498 (0·0062)	1·503 (0·0062)	Distance between C_3 and C_5
C111	1·118 (0·0024)	1·128 (0·0024)	Distance between C_1 and H_{11} (all assumed equal)
C17	1·507 (0·008)	1·505 (0·008)	Distance between C_1 and C_7
φ	58·1^c (0·11)	58·2^c (0·194)	Flap angle between $C_1C_2C_3$ and XZ planes
β	104·0^c (0·35)	103·6^c (0·32)	$\angle C_1C_3C_5$
γ	107·6^c (0·34)	107·5^c (0·34)	$\angle C_3C_1C_7$
δ	119·7^c (0·60)	119·7^c (0·59)	$\angle C_1C_3H_9$
χ	125·0^c (2·6)	123·9^c (2·6)	$\angle C_3C_5H_{13}$
η	109·8^c (0·63)	109·8^c (0·63)	$\angle C_1C_7H_{16}$

[a] The figures in the parentheses are the calculated standard deviations for the corresponding parameters, as derived from the final least squares analyses, when distances and root mean square amplitudes were varied concurrently.

Table B. Reduced electron diffraction intensities for bicyclo[2.1.1]hexene-2

Set 1		Set 2			
q	Intensity	q	Intensity	q	Intensity
12	1·1980	32	1·0430	79	1·3800
13	1·1810	33	0·7640	80	1·4060
14	1·0230	34	0·5750	81	1·4150
15	0·9430	35	0·4430	82	1·4020
16	1·1380	36	0·5110	83	1·3840
17	1·5780	37	0·6680	84	1·3790
18	2·0710	38	0·7370	85	1·3740
19	2·2800	39	0·7310	86	1·3800
20	2·0240	40	0·7180	87	1·4000
21	1·4480	41	0·7380	88	1·4380
22	0·8560	42	0·7780	89	1·4730
23	0·5570	43	0·8160	90	1·5170
24	0·6300	44	0·8070	91	1·5660
25	0·9660	45	0·7330	92	1·6150
26	1·3600	46	0·6280	93	1·6570
27	1·6770	47	0·5300	94	1·6860
28	1·8720	48	0·4740	95	1·7130
29	1·9010	49	0·4680	96	1·7260
30	1·8000	50	0·5100	97	1·7320
31	1·5790	51	0·5770	98	1·7250
32	1·3330	52	0·6400	99	1·7480
33	1·1130	53	0·7770	100	1·7620
34	1·0750	54	0·8580	101	1·7950
35	1·1480	55	0·9130	102	1·8430
36	1·4060	56	0·9060	103	1·8900
37	1·5640	57	0·8730	104	1·9460
38	1·6500	58	0·8370	105	2·0000
39	1·7290	59	0·8120	106	2·0440
40	1·7040	60	0·8110	107	2·0810
		61	0·8440	108	2·1260
		62	0·8720	109	2·1550
		63	0·9000	110	2·1750
		64	0·9310	111	2·2130
		65	0·9760	112	2·2430
		66	1·0150	113	2·2770
		67	1·0640	114	2·3060
		68	1·0980	115	2·3520
		69	1·1140	116	2·3950
		70	1·1050	117	2·4350
		71	1·0850	118	2·4770
		72	1·0610	119	2·5200
		73	1·0590	120	2·5620
		74	1·0770	121	2·5970
		75	1·1070	122	2·6410
		76	1·1770	123	2·6710
		77	1·2420	124	2·7200
		78	1·3190	125	2·7600

choice of l_{ij}'s had little effect on the final parameters, and the bonded pair l_{ij}'s changed very little during the entire course of analysis. At first, concurrent variations of distances and root mean square amplitudes led to divergence of the least squares computations. Eventually, all of the root mean square amplitudes of vibration were allowed to vary except those of HH16, which were fixed at 0·091 Å, estimated from the first few cycles in the least squares computer sequence. In the final calculations, parameters C17, C35 and β were constrained to the values shown in Table 1. Two distinct models were found for which convergence was obtained. Table 2 is a listing of bond distances and l_{ij}'s, with their uncertainties, which were set at about twice the calculated standard deviations, where the final standard deviations for the parameters and l_{ij}'s were taken from a least squares refinement when all the parameters were allowed to vary simultaneously. Because of the inherent lack of symmetry in this molecule, the r_{ij} matrix for the carbon atoms calculated for the "best" model, and the correlation matrix for the final run, when all the parameters were varied simultaneously, are given as Tables C and D.

The first acceptable model (I) has a total standard deviation of 0·0265. All the bond distances are "reasonable" except C_7—C_8, for which 1·614 Å seems exceptionally large. A second least squares minimum was found in the parameter hypersurface

TABLE 2. INTERATOMIC DISTANCES AND BOND ANGLES IN TRICYCLO[3.3.0.0^{26}]OCT-3-ENE

	Model I	Model II
C_1—C_3	1·576 Å	1·580 (0·015)
C_3—C_5	1·498	1·503 (0·012)
C_5=C_6	1·344	1·345 (0·010)
C_1—C_7	1·507	1·505 (0·018)
C_7—C_8	1·614	1·579 (0·038)
$\langle C\text{—}H\rangle_{av}$		1·128 (0·010)
$\angle H_{17}C_8H_{18}$		117·3° (6·6°)
$\angle C_2C_8C_7$		98·6° (0·9°)
$\angle H_{12}C_2C_4$		119·7° (1·6°)
$\angle C_4C_6C_5$		103·7° (0·7°)
$\angle C_3C_2C_4$		81·3° (0·6°)
$\angle H_{12}C_2C_8$		115·7° (2·5°)
	$\sigma = 0·0265$	$\sigma = 0·0268$

l_{ij}'s for Model II (Å)

C_1C_2, C_3C_4	0·055 (0·015)
C_1C_3, C_3C_5, C_1C_7, C_7C_8	0·051 (0·008)
C_1C_5, C_1C_6	0·070 (0·010)
C_2C_7	0·070 (0·036)
C_5C_7	0·067 (0·012)
C_5C_6	0·033 (0·012)
$\langle CH\rangle_{av}$	0·092 (0·006)
$\langle HH\rangle_{av}$	0·080 (0·070)

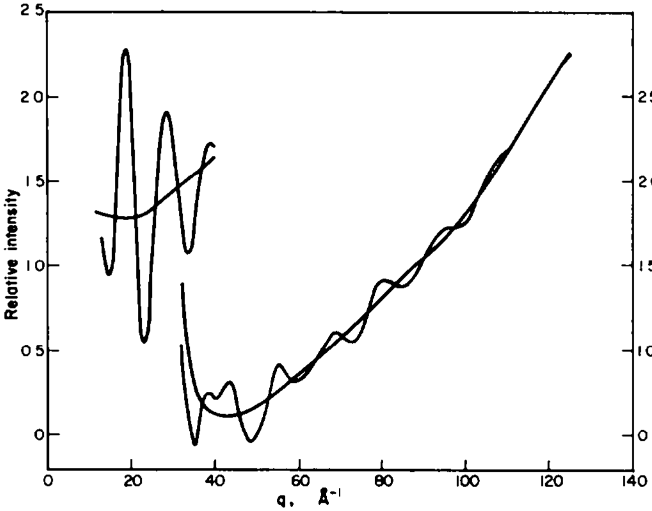


FIG 5. Relative scattered intensity *vs* q for bicyclo[2.1.1]hexene-2

at which the total standard deviation is 0·0268. We consider this model (II) to be preferable.

The bicyclohexene. The relative total scattered intensity and the refined background are shown in Fig 5. The theoretical and reduced experimental molecular intensity curves are plotted in Fig 6 and the final experimental radial distribution curve is illustrated in Fig 7; here the lower oscillating curve is the difference between the experimental function and the radial distribution function calculated for the "best" model. The structure of bicyclo[2.1.1]hexene-2 is shown in Fig 8. C_{2v} symmetry was assumed in calculating the geometrical parameters, with the two fold axis in the plane of C atoms 3.5.6.4. and bisecting $C_5{=}C_6$ and $C_3 \ldots C_4$. A model with C_2

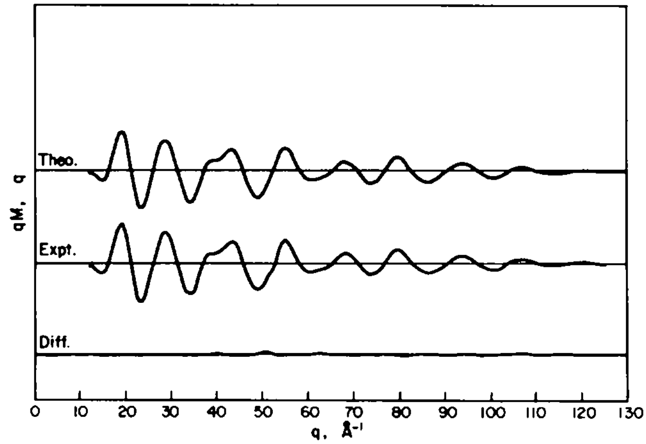


FIG 6. Theoretical and experimental intensity curves *vs* q (bicyclo-hexene); the bottom curve is the difference between the theoretical and experimental values

TABLE C. FINAL r_{ij} MATRIX FOR TRICYCLO[3.3.0.0^{2,6}]OCT-3-ENE

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
C_1								
C_2	2·032							
C_3	1·580	1·580						
C_4	1·580	1·580	2·060					
C_5	2·425	2·425	1·503	2·243				
C_6	2·425	2·425	2·243	1·503	1·345			
C_7	1·505	2·340	2·490	2·490	3·732	3·732		
C_8	2·340	1·505	2·490	2·490	3·732	3·732	1·579	

symmetry, with non-bisecting $\angle$HCH's at C_2 and C_1, has also been tested; it converged to C_{2v} in the least squares analysis. The molecular geometry is specified by $C_3—C_5$, $C_5{=}C_6$, $C_3—C_2$, $C_5—H$, $C_2—H$, $\angle C_3C_5C_6$; α, κ, the angles between C_2---C_1 and $C_1—H_{13}$, $C_1—H_{14}$ respectively; 2φ, the dihedral angle of the cyclobutane ring; ε, the angle between $C_5—H$ and $C_5{=}C_6$, and θ, the angle between $C_3 \ldots C_4$ and $C_3—H$. The values of the geometrical parameters were refined by a least squares analysis of the reduced molecular intensity. All the geometrical parameters were allowed to vary except the C—H bond lengths, which were estimated from the refined radial distribution curve. The following root mean square amplitudes of vibration were also allowed to vary: $l(C_3—C_5)$, $l(C_3—C_6)$, $l(C_3—C_4)$, $l(C_5{=}C_6)$, $l(C_3—C_2)$. The final values of these parameters were listed in Table 3. The error matrix

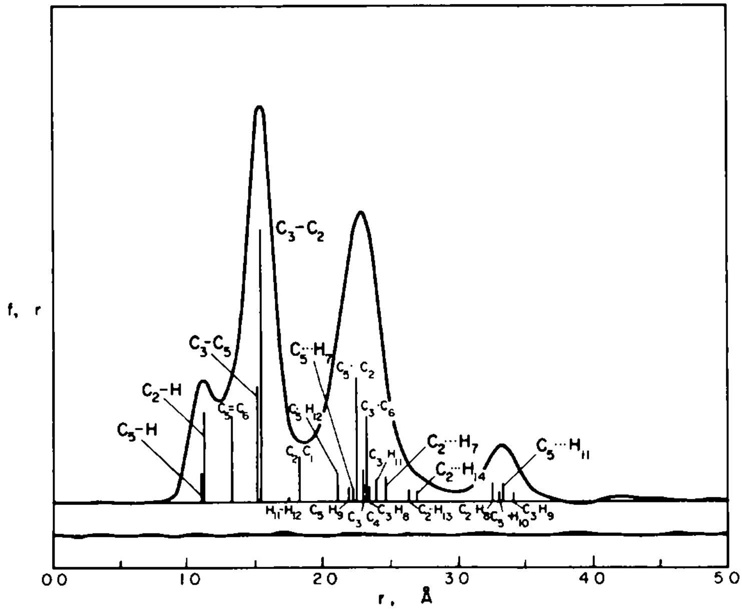


FIG 7. Final radial distribution curve for the bicyclohexene; the lower curve is the difference between the theoretical and experimental values

TABLE 3. STRUCTURAL PARAMETERS FOR BICYCLO [2.1.1] HEXENE-2

	r_{ij}	l_{ij}
$C_5{=}C_6$	1·332 (0·003) Å	0·062 (0·003) Å
$C_3{—}C_5$	1·537 (0·010) Å	0·088 (0·008) Å
$C_3{—}C_2$	1·548 (0·005) Å	0·071 (0·003) Å
$C_5{—}H$	1·110A[a]	0·078A[a]
$C_2{—}H$	1·120A[a]	0·078A[a]
$\angle C_3C_5C_6$	108·4 (0·4°)	
ε	127·2 (3·8°)	
θ	4·8 (3·5°)	
α	54·0 (2·4°)	
κ	48·5 (0·6°)	
2φ	123·5 (1·2°)	

[a] Assumed values.

is attached as Table E. The error limits cited in Table 3 are three times the standard deviations (or slightly more); the latter are the diagonal elements in the error matrix.

In the radial distribution curve (Fig 7), the first peak is contributed by the C—H bonded distances, while the second peak is a superposition of the following bonded and non-bonded distances: $C_5{=}C_6 = 1{\cdot}332$ Å, $C_3{—}C_5 = 1{\cdot}537$ Å, $C_3{—}C_2 = 1{\cdot}548$ Å, $C_2 \ldots C_1 = 1{\cdot}826$ Å and $H_{11}{—}H_{12} = 1{\cdot}747$ Å. The third peak is mainly due to $C_5 \ldots C_2 = 2{\cdot}252$ Å, $C_3 \ldots C_4 = 2{\cdot}304$ Å, $C_3 \ldots C_6 = 2{\cdot}331$ Å, all $\overset{\text{H}}{\text{C—C}}$ distances, such as $C_3 \ldots H_8 = 2{\cdot}350$ Å, $C_3 \ldots H_{11} = 2{\cdot}396$ Å, $C_3 \ldots H_{12} = 2{\cdot}045$ Å, $C_5 \ldots H_7 = 2{\cdot}230$ Å, $C_5{—}H_9 = 2{\cdot}190$ Å, $C_5 \ldots H_{12} = 2{\cdot}100$ Å, $C_2 \ldots H_7 = 2{\cdot}476$ Å,

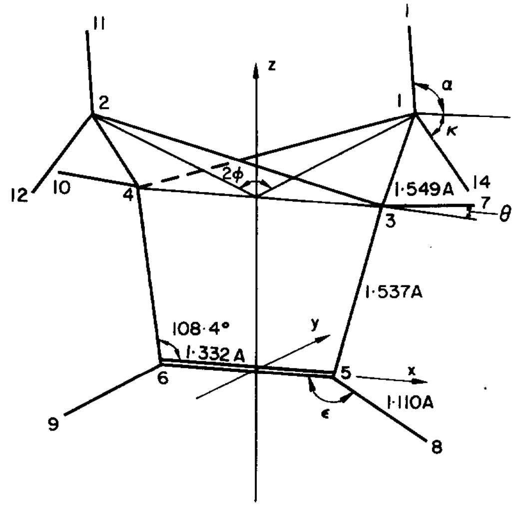
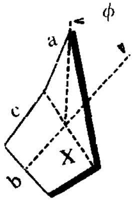
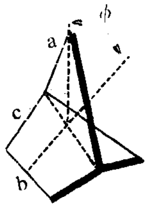
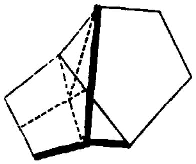
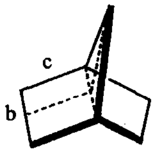
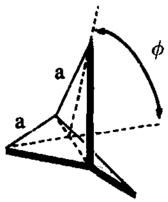
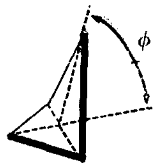
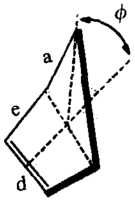
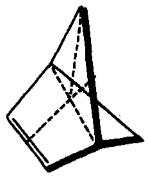
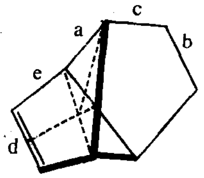
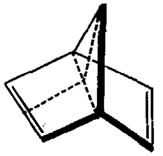


FIG 8. Diagram of the structure of bicyclo[2.1.1]hexene-2

TABLE 4. SUMMARY

						
a	1·546 Å^{a}	1·544 Å^{b}	1·558 Å^{c}	1·559 Å^{d}	1·544 Å^{e}	1·548 Å^{f}
b	1·546	1·513	1·516	1·551	—	—
c	1·546	1·565	1·569	1·556	—	—
X	2·414	2·172	2·077	2·317	1·845	2·180
φ	psuedo-rot (12·5°)	62·5°	63·4°	54·0°	60·0°	37°^{g}

				
a	1·546 Å^{h}	1·549 Å^{i}	1·580 Å^{i}	1·545 Å^{j}
b	—	—	1·579	—
c	—	—	1·505	—
d	1·342	1·332	1·345	1·342
e	1·519	1·537	1·503	1·538
X	2·441	2·302	2·030	2·292
φ	28·8°	61·8°	58·2°	52·0°

[a] W. J. Adams, H. J. Geise and L. S. Bartell, in press

[b] J. F. Chiang, *J. Am. Chem. Soc.* **93**, 5044 (1971)

[c] J. F. Chiang and S. H. Bauer, *Trans. Farad. Soc.* **64**, 2247 (1968)

[d] J. F. Chiang, C. F. Wilcox, Jr. and S. H. Bauer, *J. Am. Chem. Soc.* **90**, 3149 (1968)

[e] J. F. Chiang and S. H. Bauer, *Ibid.* **92**, 1614 (1970)

[f] A. Almenningen and O. Bastiansen, *Acta Chem. Scand.* **15**, 711 (1961)

[g] S. Meiboom and C. C. Snyder, *J. Am. Chem. Soc.* **89**, 1038 (1967)

~~[h] M. I. Davis and T. W. Muecke, *J. Phys. Chem.* **74**, 1104 (1970)~~

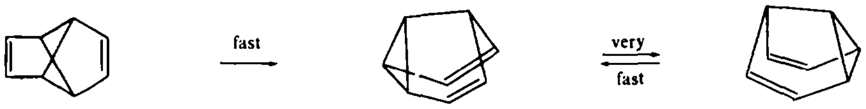
[i] This work

[j] G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.* **87**, 805 (1968)

$C_2 \ldots H_{13} = 2{\cdot}641$ Å, $C_2 \ldots H_4 = 2{\cdot}700$ Å and other H—H bonded distances: H_7—$H_8 = 2{\cdot}607$ Å, H_7--$H_{12} = 2{\cdot}842$ Å, H_8--$H_9 = 2{\cdot}674$ Å and H_8--$H_{12} = 2{\cdot}915$ Å. The last peak is mostly due to non-bonded H...H distances and some C...H distances. The locations of most of these atom pair contributions are indicated by vertical lines in Fig 7, where the height of each is proportional to the quantity: $C_{ij} = n_{ij}Z_iZ_j/r_{ij}$. The atomic coordinates of this hexene are cited in Table F.

DISCUSSION

Comparison of the structures of the complete sequence tricyclo-octane, -octene, and -octadiene would demonstrate the effect of successive constraints on the structure of the central cyclobutane ring. Regrettably, the compound tricyclo$[3.3.0.0^{2,6}]$octa-3,7-diene is too unstable for investigation with current electron diffraction techniques.[8] At about 30° it rapidly converts to "semi-bullvalene",[9] which undergoes rapid conformational inversions:



Tricyclo$[3.3.0.0^{2,6}]$oct-3,7-diene

Semi-bullvalene

The structure of the latter has been determined by Dr. Y. C. Wang in our laboratory.

Several unexpected differences were found between the structures of tricyclo$[3.3.0.0^{2,6}]$oct-3-ene and tricyclo$[3.3.0.0^{2,6}]$octane,[2] Table 4. In the cyclobutane ring the C—C distances (a) are 0·022 Å longer in the former compound, but the sides in its five member ring (c) are shorter by 0·066 Å, while the base of the ring (b) is longer by 0·064 Å. The flap angle (2φ) in the octane is 10° greater than in the octene. However, one should note that the structure of the octene is not as precisely determined as that of the octane. Because of the lower symmetry of the former [C_{2v} *vs* D_{2d}], a larger number of independent parameters must be introduced to specify the structure. Then

TABLE D. CORRELATION MATRIX FOR FINAL RUN, WHERE ALL PARAMETERS WERE VARIED SIMULTANEOUSLY: TRICYCLO$[3.3.0.0^{2,6}]$OCT-3-ENE

	C12/2	C03	C35	C111	φ	β	γ	δ	χ	η	C17
C12/2	1·00	−0·94	−0·54	0·17	−0·28	0·68	−0·80	0·52	0·10	−0·43	0·53
C03		1·00	0·33	−0·08	0·38	−0·81	0·58	−0·57	−0·18	0·47	−0·30
C35			1·00	−0·24	−0·02	−0·05	0·66	−0·16	0·06	0·13	−0·91
C111				1·00	0·18	−0·07	−0·31	0·22	−0·12	−0·43	0·33
φ					1·00	−0·83	−0·25	0·32	0·12	−0·33	0·33
β						1·00	−0·13	0·15	0·05	−0·10	−0·12
γ							1·00	−0·49	−0·03	0·44	−0·80
δ								1·00	0·23	−0·77	0·33
χ									1·00	−0·04	−0·01
η										1·00	−0·31
C17											1·00

TABLE E. ERROR MATRIX FOR BICYCLO[2.1.1]HEXENE-2
(Distances in Å units; angle in degrees)

	$C_5{=}C_6$	$C_3{-}C_5$	$C_3{\cdots}C_2$	$\angle C_3C_5C_6$	ε	θ	α	κ	2φ	$lC_3{\cdots}C_5$	$lC_3{-}C_6$	$lC_3{-}C_4$	$lC_5{=}C_6$	$lC_3{-}C_2$
$C_5{=}C_6$	0·0010													
$C_3{-}C_5$	−0·0006	0·0027												
$C_3{-}C_2$	0·0008	−0·0018	0·0016											
$\angle C_3C_5C_6$	0·0054	−0·0138	0·0121	0·1113										
ε	0·0125	0·0414	−0·0130	−0·1568	1·2807									
θ	0·0196	−0·0316	0·0391	0·3103	0·7581	1·2522								
α	0·0046	0·0281	−0·0158	−0·0661	0·1838	−0·3212	0·8030							
κ	0·0087	0·0101	−0·0122	−0·0932	−0·1905	−0·3667	0·1452	0·2137						
2φ	0·0045	0·0307	−0·0191	−0·1301	0·4098	−0·2986	0·4181	0·1194	0·4356					
$lC_3{-}C_5$	−0·0009	0·0022	−0·0017	−0·0144	0·0423	−0·0227	0·0192	0·0170	0·0244	0·0042				
$lC_3{-}C_6$	0·0001	−0·0005	0·0002	0·0073	−0·0276	−0·0117	0·0174	0·0110	0·0073	−0·0008	0·0017			
$C_3{-}C_4$	0·0010	0·0033	0·0023	−0·0134	0·1445	0·1185	−0·0480	−0·0360	0·0099	0·0053	−0·0045	0·0199		
$lC_5{-}C_6$	−0·0002	0·0007	−0·0005	0·0052	−0·0142	−0·0070	0·0059	0·0068	0·0081	0·0017	−0·0004	0·0019	0·0010	
$lC_3{-}C_2$	0·0002	0·0009	0·0008	0·0068	−0·0170	0·0118	−0·0056	−0·0081	−0·0105	−0·0020	0·0005	−0·0022	−0·0009	0·0011

the near equality of distances results in high correlations between their magnitudes. It has been generally observed that on varying two parameters whose values are very close, the least squares analysis tends to increase the magnitude of the larger one and decrease that of the smaller. For example, the correlation between parameters C35 and C17 is −0·91; i.e. a positive change in C35 has approximately the same effect on the intensity pattern as a negative change of about the same magnitude in C17. In such cases, other data must be introduced to provide guidance for selecting the direction of change. One must also decide whether to constrain one or both of the parameters. On examining these two bond distances we note that within experimental error they are equal. However, many previous structure determinations of similar compounds showed that if these distances did differ, C35 would be the shorter one because it is adjacent to the C_5—C_6 double bond.

When one examines the gas phase structures of compounds with a central cyclobutane ring, it appears that its dimensions are little affected unless it is constrained on opposite sides by two loops, or on one side by a distance-contracting feature, such as a cyclopropane ring. The size of the cyclobutane ring in the octene is significantly different from that of a free cyclobutane ring; the C—C distance is 0·032 Å longer in the former, and the flap angle (2φ) in the cyclobutane is 42^{c} smaller than the corresponding one in the octene. Loops with —CH_2—CH_2— and —CH=CH— groups appear to increase the bond lengths and increase the flap angle; in the octene the flap angle is smaller than in the corresponding octane. The bond distances in the five-member ring of the octene are similar to those in cyclopentene. The C_7—C_8 and C_1—C_3 bonds (1·579 and 1·580 Å, respectively) are examples of "long C—C bonds".

One may consider the structure of bicyclo[2.1.1]hexene-2 as derived from bicyclo[1.1.1]pentane by replacing one of the methylene groups in the latter with a $\overset{\diagdown}{\text{HC}}{=}\overset{\diagup}{\text{CH}}$ unit. Also, one may imagine it is derived from cyclopentene by bridging the

TABLE F. COORDINATES OF BICYCLO[2.1.1]HEXANE-2*

	X	Y	Z
C_3	1·1511	0·0	1·4584
C_5	0·6660	0·0	0·0
C_6	−0·660	0·0	0·0
C_4	−1·1511	0·0	1·4564
C_2	0·0	−0·9117	1·9482
C_1	0·0	0·9117	1·9482
H_7	2·2673	0·0	1·5514
H_8	1·3371	0·0	−0·8841
H_9	−1·3371	0·0	−0·8841
H_{10}	−2·2673	0·0	1·5514
H_{11}	0·0	−1·5694	2·8548
H_{12}	0·0	−1·6541	1·1097
H_{13}	0·0	1·5694	2·8548
H_{14}	0·0	1·6541	1·1097

* For numbering system, see Fig 8.

3,5-positions of cyclopentene with a methylene. The dihedral angle for the four-membered ring in this bicyclohexene is close to those found in tricyclo[3.3.0.0^{2,6}]-octane, bicyclobutane, bicyclo[1.1.1]pentane, and bicyclo[2.1.1]hexane. The double bond length agrees with that in ethylene, propene, and cyclohexene, within experimental error. The reader's attention is called to the summary in Table 4.

EXPERIMENTAL

The synthesis of tricyclo[3.3.0.0^{2,6}]oct-3-ene from *cis*-1,5-cyclooctadiene was carried out by Dr. Douglas Schmidt who followed the method of Meinwald and Kaplan.[3] The sample of bicyclo[2.1.1]hexene-2 was furnished by Dr. F. Uno, Professor Meinwald's coworker. Two independent sets of sectored photographs were taken with the Cornell diffraction apparatus.[4] An MgO sample was rigidly mounted above the nozzle tip, and its diffraction pattern was recorded for each position of the nozzle, concurrent with each gas sample run. In this manner the wavelength and nozzle-plate distance were determined.[5] During the course of the first set of experiments with the octene the MgO sample holder was accidently bumped, knocking it slightly out of alignment. This necessitated taking a second set of photographs for cross-checking and recalibration. The first set yielded data in the range $q = 9$ to 64 Å^{-1} [$q \equiv (40/\lambda)\sin(\theta/2)$; $\lambda = 0{\cdot}04873$ Å; nozzle to plate distance = 250·2 mm] which will be designated HVL, and the range $q = 27$ to 106 Å^{-1} [$\lambda = 0{\cdot}04865$ Å; nozzle to plate distance = 126·0 mm] designated HVS. The second set of photographs gave diffraction data in the range $q = 8$ to 55 Å^{-1} [$\lambda = 0{\cdot}04866$ Å; nozzle to plate distance = 252·0 mm] and $q = 20$ to 91 Å^{-1} [$\lambda = 0{\cdot}04866$ Å; nozzle to plate distance = 124·2 mm]. The sample was kept at 0°C during both runs. For the bicyclohexene several sets of photographs were taken covering the range $q = 12$ to 68 Å^{-1} and $q = 32$ to 125 Å^{-1}.

Plate transmittances were recorded with a modified Jarrell-Ash microdensitometer coupled to a chart recorder or to a digital converter and printer. Points were read at intervals of 100 μm for HVS and 250 μm for HVL. Optical densities were converted to intensities and the data reduced according to the procedure described in previous publications from this laboratory.[6] The second set of data for the octene was of somewhat poorer quality than the first; hence the structure determination was based entirely on the recalibrated first set. The relative intensities for this compound are plotted in Fig 1; the reduced intensities are listed as Table A.

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REFERENCES

[1] G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.* **86**, 171 (1967) and J. F. Chiang, *J. Am. Chem. Soc.* **93**, 5044 (1971)

[2] J. F. Chiang and S. H. Bauer, *Trans. Faraday Soc.* **64**, 2247 (1968)

[3] Jerrold Meinwald and Bruce E. Kaplan, *J. Am. Chem. Soc.* **89**, 2611 (1967)

[4] [a] S. H. Bauer and K. Kimura, *J. Phys. Soc. Japan* **17**, Supplement B-II, 300 (1962);
[b] S. H. Bauer, *Electron Diffraction Studies at High Temperature.* Report: Nor-401(41), Project NR092-504, ARPA, order # 23-53, December (1967)

[5] For details refer to Ph.D. dissertation submitted by R. L. Hilderbrandt, Cornell University, 1969. This procedure was subsequently checked by cross-calibration with CS_2 [C. H. Chang, A. L. Andreassen and S. H. Bauer, manuscript in press]

[6] [a] J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.* **89**, 5527 (1967);
[b] W. Harshbarger, G. Lee, R. F. Porter and S. H. Bauer, *Inorg. Chem.* **8**, 1683 (1969);
[c] R. L. Hilderbrandt and S. H. Bauer, *J. Mol. Structure* **3**, 325 (1969)

[7] R. L. Hilderbrandt, *J. Chem. Phys.* **51**, 1654 (1969)

[8] Jerrold Meinwald, Personal communication

[9] H. E. Zimmerman, *et al.*, *J. Am. Chem. Soc.* **91**, 3316 (1969)