266. Structure of [4.4.4]propellane and [4.4.4]propellatriene by *X*-ray Analysis

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Summary. The crystal structures of [4.4.4]propellane (monoclinic, $a = 12.053$, $b = 7.832$, $c = 13.001$ Å, $\beta = 104.89°$, space group $C2/c$, $Z = 4$) and [4.4.4]propellatriene (monoclinic, $a = 7.876$, $b = 12.651$, $c = 13.164$ Å, $\beta = 122.81°$, space group $P2_1/c$, $Z = 4$) have been determined by *X*-ray analysis. In propellane the six-membered rings are in the chair conformation, in propellatriene they adopt the 'half-chair' conformation with a twofold axis passing through the centre of each double bond. In both cases the observed parameters correspond to virtual $D_3(32)$ molecular symmetry. Corrections have been applied for the effect of molecular libration. Strain-minimization calculations based on semi-empirical potential functions have been carried out and the molecular parameters so derived are compared with the experimental values.

Recent interest in the chemistry of propellanes [1] has led us to undertake crystal structure analyses of [4.4.4]propellane (tricyclo[4.4.4.0^{1,6}]tetradecane) and the corresponding symmetrical triene (tricyclo[4.4.4.0^{1,6}]tetradeca-3, 8, 12-triene). Examination of molecular models suggests that the preferred conformations of both molecules have $D_3(32)$ symmetry. For [4.4.4]propellane this would be the case if the three six-membered rings are in chair conformation (Fig. 1A) (or in the less favourable 'symmetrical twist-boat' conformation), for the triene if the six-membered rings have the energetically favourable 'half-chair' conformation (Fig. 1B). 'Boat' conformations of the three unsaturated rings give structures with $C_{3h}(3/m)$ symmetry, provided the ring-folds are in the same sense (Fig. 1C), $C_s(m)$ otherwise (Fig. 1D). However, such structures should be less favourable, not only because of the intrinsic strain of the 'boat' conformations but also because of the concomitant eclipsed arrangement around the central bond. For [4.4.4]propellane the only molecular symmetry required

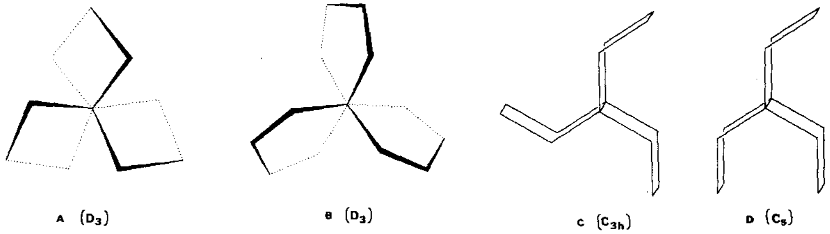

Fig. 1. *Idealized views of [4.4.4]propellane and [4.4.4]propellatriene looking down the central C—C bond in each case*

The conformations of the three six-membered rings are in (A) all 'chair'; in (B) all 'twist-boat' or 'half-chair'; in (C) and (D) all 'boat'

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by the space group is a C_2 axis; for the triene no molecular symmetry is required. However, detailed crystal structure analysis has confirmed that both molecules come very close to the D_3 symmetry expected from model considerations.

Crystallographic Data. [4.4.4]propellane, $C_{14}H_{24}$; m.p. 120° [2]; monoclinic, $a = 12.053$, $b = 7.832$, $c = 13.001$ Å, $\beta = 104.89°$, $U = 1186$ Å^3, $D_m = 1.079$, $D_x = 1.085$, $Z = 4$, space group $C2/c$ (C^6_{2h}) or Cc (C^4_s). The space group of higher symmetry, which requires the molecular symmetry C_2, was assumed and can be regarded as confirmed by the subsequent analysis.

[4.4.4]propellatriene, $C_{14}H_{18}$; m.p. 50° [2]; monoclinic, $a = 7.876$, $b = 12.651$, $c = 13.164$ Å, $\beta = 122.81°$, $U = 1102$ Å^3, $D_m = 1.08$, $D_x = 1.12$, $Z = 4$, space group $P2_1/c$ (C^5_{2h}), no molecular symmetry required.

Crystalline samples of both substances were generously provided by Dr. *J. Altman* (Chemistry Department, Technion, Haifa). For *X*-ray analysis it was necessary to seal the crystals in thin-walled capillaries to prevent sublimation. The cell dimensions listed were obtained from measurements on a 4-circle diffractometer (see below, Mo$K\alpha$-radiation, $\lambda = 0.7107$ Å) and have errors of the order of 0.1%.

Intensity Measurements. Intensity measurements for both crystals were carried out with the *Hilger & Watts* 4-circle diffractometer Y 290 under control of a PDP-8 computer. Typical experimental conditions were as follows:

Mo$K\alpha$ radiation (Sr/Zr balanced filters except for high-order reflexions ($\theta > 18°$) when no filter used), ω-scan (range 1°) scan-step 0.01°, measurement time per step, 0.8–1.0 s. In both cases, but especially for the triene, the quality of the data was adversely affected by the marked fall-off of diffracted intensity with increase in the scattering angle.

For [4.4.4]propellane (crystal dimensions 0.32 × 0.26 × 0.35 mm) 1134 symmetry-independent reflexions were recorded above background in the range out to $\sin\theta/\lambda = 0.59$; for the propellatriene (0.30 × 0.30 × 0.38 mm) the corresponding number was 1352 in the range out to $\sin\theta/\lambda = 0.53$. However, a large proportion of the reflexions recorded were so weak that they could not be included with confidence in the subsequent refinements. Moreover, for the triene measurements, the use of the profile-scan method to estimate integrated intensity and background may be associated with slight systematic underestimation of the background for marginally observable reflexions.

Structure analysis and refinement. Both structures were solved without any special difficulties by direct methods and refined by full-matrix least-squares analysis. Hydrogen atoms were included in the structure model during the latter stages but their positions were not refined. For [4.4.4]propellane, the final *R* value, based on the 582 reflexions included in the final refinement (condition for inclusion: $F_0 \geqslant 4\sigma(F_0)$, $2\sigma(F_0) < F_0 < 4\sigma(F_0)$ only if $F_c > F_0$), was 0.062. For the propellatriene, the final *R* factor, based on the 886 reflexions included according to a similar inclusion criterion, was 0.114. The higher *R* factor is attributable partly to the larger proportion of very weak reflexions included, partly to the systematic error mentioned in the previous section. The estimated standard deviations in the atomic positions, derived by inversion of the least-squares normal-equations matrix are typically 0.004–0.007 Å for propellane and 0.009–0.017 Å for the triene, the larger values being associated with the peripheral atoms which have the largest amplitudes of thermal vibration.

Results. For [4.4.4]propellane, atomic positions (and estimated standard deviations) for C-atoms are listed in Table 1A, atomic vibration tensor components U_{ij} [3] in Table 1B. Hydrogen positions, calculated from stereochemical considerations are listed in Table 1C. The corresponding results for [4.4.4]propellatriene are given in Tables 2A, 2B and 2C. The appropriate atom-numbering systems are shown in Fig. 2.

Table 1A. *[4.4.4]Propellane*

Coordinates of carbon atoms (standard deviations × 10^4)

	x	y	z
C(1)	.4052 (4)	.2848 (7)	.0643 (4)
C(2)	.3756 (4)	.2729 (6)	.1722 (4)
C(3)	.4339 (3)	.1231 (5)	.2429 (3)
C(4)	.3795 (4)	– .0443 (6)	.1912 (4)
C(5)	.4359 (4)	– .2069 (6)	.2455 (5)
C(6)	.4062 (4)	.1414 (6)	.3530 (4)
C(7)	.4647 (4)	.2933 (7)	.4187 (4)

Table 1B. *[4.4.4]Propellane*

Vibration tensor components (in Å^2) in crystal coordinate system. Corresponding standard deviations lie in the range 0.0018–0.0040 Å^2 (mean value, 0.0026 Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0.0681	0.0671	0.0576	– 0.0042	0.0107	0.0052
C(2)	0.0481	0.0510	0.0560	0.0095	0.0060	0.0059
C(3)	0.0378	0.0438	0.0440	0.0002	0.0002	0.0141
C(4)	0.0419	0.0469	0.0688	– 0.0028	0.0007	0.0122
C(5)	0.0605	0.0407	0.0984	– 0.0106	– 0.0065	0.0196
C(6)	0.0467	0.0606	0.0656	0.0072	0.0082	0.0196
C(7)	0.0756	0.0730	0.0528	0.0159	– 0.0105	0.0185

Table 1C. *[4.4.4]Propellane*

Calculated coordinates of hydrogen atoms, assuming C—H distance 1.1 Å, HCH angle 106°, local C_{2v}-symmetry of methylene groups

	x	y	z
H1A	.3700	.1742	.0145
H1B	.3644	.3980	.0204
H2A	.2820	.2615	.1585
H2B	.3995	.3933	.2158
H4A	.3823	– .0459	.1073
H4B	.2880	– .0454	.1903
H5A	.3958	– .3196	.2005
H5B	.4205	– .2185	.3250
H6A	.4314	.0234	.3990
H6B	.3128	.1526	.3407
H7A	.4433	.2957	.4960
H7B	.4314	.4134	.3786

Table 1D. *[4.4.4]Propellane*

Molecular parameters derived from coordinates of Table 1A. See Fig. 2 for numbering system

Bond distances	
C(3)–C(32)	1.556 Å
C(3)–C(4)	1.541 Å
C(3)–C(6)	1.558 Å
C(32)–C(22)	1.554 Å
C(4)–C(5)	1.528 Å
C(6)–C(7)	1.527 Å
C(22)–C(12)	1.537 Å
C(5)–C(52)	1.519 Å
C(7)–C(12)	1.528 Å

Bond angles	
C(32)–C(3)–C(4)	111.1°
C(32)–C(3)–C(6)	110.2°
C(32)–C(3)–C(2)	111.5°
C(2)–C(3)–C(6)	107.8°
C(6)–C(3)–C(4)	108.2°
C(4)–C(3)–C(2)	108.0°
C(3)–C(4)–C(5)	114.7°
C(3)–C(6)–C(7)	114.1°
C(3)–C(2)–C(1)	114.4°
C(6)–C(7)–C(12)	110.8°
C(2)–C(1)–C(72)	110.0°
C(4)–C(5)–C(52)	111.0°

Torsion angles	
C(6)–C(3)–C(32)–C(22)	+49.1°
C(4)–C(3)–C(32)–C(42)	+48.5°
C(3)–C(32)–C(42)–C(52)	−51.7°
C(3)–C(32)–C(22)–C(12)	−52.7°
C(3)–C(32)–C(62)–C(72)	−52.7°

Torsion angles	
C(3)–C(6)–C(7)–C(12)	+56.5°
C(3)–C(4)–C(5)–C(52)	+54.3°
C(3)–C(2)–C(1)–C(72)	+55.3°
C(4)–C(5)–C(52)–C(42)	−53.6°
C(6)–C(7)–C(12)–C(22)	−55.5°

Table 2A. *[4.4.4]Propellatriene*

Coordinates of carbon atoms (standard deviations × 10^4)

	x	*y*	*z*
C(1)	.2661 (11)	.3221 (6)	.1212 (7)
C(2)	.1919 (14)	.2373 (9)	.0238 (8)
C(3)	.1263 (17)	.1383 (10)	.0544 (11)
C(4)	.1679 (18)	.1173 (8)	.1613 (12)
C(5)	.2903 (15)	.1853 (8)	.2676 (9)
C(6)	.4079 (13)	.2721 (7)	.2478 (8)
C(7)	.4761 (17)	.3574 (11)	.3447 (9)
C(8)	.3068 (23)	.4317 (10)	.3220 (12)
C(9)	.1352 (22)	.4363 (9)	.2194 (14)
C(10)	.0847 (16)	.3740 (9)	.1147 (11)
C(11)	.3793 (14)	.4062 (7)	.0972 (9)
C(12)	.5856 (15)	.3717 (10)	.1310 (9)
C(13)	.6770 (15)	.2895 (11)	.1986 (10)
C(14)	.5904 (14)	.2205 (9)	.2527 (9)

Table 2B. *[4.4.4]Propellatriene*

Vibration tensor components (in Å^2) in crystal coordinate system. Corresponding standard deviations lie in the range 0.0050–0.0110 Å^2 (mean value, 0.0062 Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0.0299	0.0383	0.0356	0.0074	0.0009	0.0138
C(2)	0.0523	0.0730	0.0388	−0.0108	0.0047	0.0199
C(3)	0.0910	0.0893	0.0672	−0.0410	−0.0240	0.0476
C(4)	0.0976	0.0515	0.0947	−0.0266	−0.0058	0.0635
C(5)	0.0742	0.0621	0.0575	0.0142	0.0069	0.0391
C(6)	0.0513	0.0491	0.0437	−0.0007	0.0075	0.0247
C(7)	0.0706	0.1115	0.0441	−0.0371	−0.0150	0.0201
C(8)	0.1067	0.0850	0.0811	−0.0244	−0.0295	0.0696
C(9)	0.0972	0.0549	0.1294	−0.0021	−0.0085	0.0788
C(10)	0.0739	0.0492	0.0968	0.0133	0.0126	0.0532
C(11)	0.0608	0.0465	0.0642	−0.0115	0.0051	0.0402
C(12)	0.0558	0.0873	0.0584	−0.0217	−0.0059	0.0359
C(13)	0.0403	0.1070	0.0779	−0.0018	0.0151	0.0337
C(14)	0.0423	0.0914	0.0623	0.0163	0.0165	0.0189

Table 2C. *[4.4.4]Propellatriene*

Calculated coordinates of hydrogen atoms, assuming C—H distance 1.1 Å, HCH angle 106°, local C_{2v}-symmetry of methylene groups

	x	y	z
H2A	.3200	.2151	.0190
H2B	.0697	.2700	−.0608
H3	.0178	.0839	−.0241
H4	.0966	.0453	.1717
H5A	.4052	.1348	.3432
H5B	.1998	.2255	.2955
H7A	.5564	.3150	.4363
H7B	.6023	.4022	.3460
H8	.3217	.4733	.4039
H9	.0388	.5032	.2111
H10A	−.0169	.3146	.1070
H10B	.0149	.4273	.0359
H11A	.4125	.4769	.1558
H11B	.2997	.4295	.0038
H12	.6496	.4057	.0839
H13	.8457	.2793	.2389
H14A	.7073	.2019	.3512
H14B	.5439	.1472	.2027

Bond lengths, bond angles and torsion angles derived from these parameters are given in Table 1D for propellane and in Table 2D for propellatriene.

Thermal motion analysis. Because of the possibility that the observed bond lengths, etc., might be affected by systematic errors arising from the rather large thermal motion, it was of interest to analyse the experimental vibration tensors (Tables 1B, 2B) in terms of the librational and translational motion of the molecules, regarded for this purpose as rigid bodies. The procedure used was that of *Schomaker & True-*

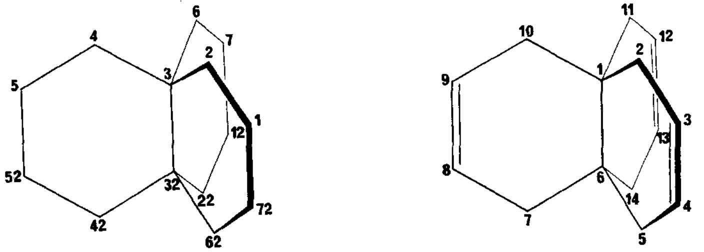

Fig. 2. *Atom-numbering system for [4.4.4]propellane* (twofold rotation axis through mid points of 5–52, 3–32) *and [4.4.4]propellatriene in the crystals studied*

Table 2D. *[4.4.4]Propellatriene*
Molecular parameters derived from coordinates of Table 2A. See Fig. 2 for numbering system

Bond distances		*Bond angles*			
C(1)–C(6)	1.552 Å	C(6)–C(1)–C(2)	110.0°	C(1)–C(2)–C(3)	113.3°
		C(6)–C(1)–C(10)	110.0°	C(1)–C(10)–C(9)	114.5°
C(1)–C(2)	1.524 Å	C(6)–C(1)–C(11)	110.2°	C(1)–C(11)–C(12)	113.4°
C(1)–C(10)	1.532 Å	C(1)–C(6)–C(5)	108.8°	C(6)–C(7)–C(8)	113.5°
C(1)–C(11)	1.527 Å	C(1)–C(6)–C(7)	109.3°	C(6)–C(5)–C(4)	113.5°
C(6)–C(5)	1.547 Å	C(1)–C(6)–C(14)	109.2°	C(6)–C(14)–C(13)	112.6°
C(6)–C(7)	1.529 Å				
C(6)–C(14)	1.548 Å	C(2)–C(1)–C(10)	109.5°	C(2)–C(3)–C(4)	123.2°
		C(10)–C(1)–C(11)	108.7°	C(10)–C(9)–C(8)	124.3°
C(2)–C(3)	1.491 Å	C(11)–C(1)–C(2)	108.5°	C(11)–C(12)–C(13)	123.0°
C(10)–C(9)	1.445 Å	C(5)–C(6)–C(7)	109.5°	C(5)–C(4)–C(3)	124.5°
C(11)–C(12)	1.499 Å	C(7)–C(6)–C(14)	111.4°	C(7)–C(8)–C(9)	122.7°
C(5)–C(4)	1.471 Å	C(14)–C(6)–C(5)	108.7°	C(14)–C(13)–C(12)	124.2°
C(7)–C(8)	1.523 Å				
C(14)–C(13)	1.505 Å				
C(8)–C(9)	1.295 Å				
C(3)–C(4)	1.289 Å				
C(12)–C(13)	1.302 Å				

Torsion angles		*Torsion angles*	
C(7)–C(6)–C(1)–C(10)	−57.7°	C(1)–C(2)–C(3)–C(4)	−14.2°
C(5)–C(6)–C(1)–C(2)	−58.9°	C(1)–C(10)–C(9)–C(8)	−15.1°
C(14)–C(6)–C(1)–C(11)	−60.0°	C(1)–C(11)–C(12)–C(13)	−14.8°
		C(6)–C(5)–C(4)–C(3)	−13.6°
C(6)–C(1)–C(2)–C(3)	44.7°	C(6)–C(7)–C(8)–C(9)	−13.8°
C(6)–C(1)–C(10)–C(9)	44.5°	C(6)–C(14)–C(13)–C(12)	−14.7°
C(6)–C(1)–C(11)–C(12)	45.2°		
C(1)–C(6)–C(5)–C(4)	43.4°	C(2)–C(3)–C(4)–C(5)	−2.2°
C(1)–C(6)–C(7)–C(8)	42.6°	C(10)–C(9)–C(8)–C(7)	−1.1°
C(1)–C(6)–C(14)–C(13)	44.3°	C(11)–C(12)–C(13)–C(14)	−1.1°

blood [4], which requires the least-squares fitting of librational and translational tensors **L** and **T** and of an additional tensor **S** (introduced to account for the average quadratic correlation of translation and libration) to the vibration tensors **U** of the individual atoms. The results are summarized in Tables 3 and 4.

Table 3. *[4.4.4]Propellane*

Analysis of atomic vibration tensors in terms of rigid-body motion. Tensor components (standard deviations × 10^4 in brackets) and eigenvectors are referred to an orthogonal, molecular coordinate system (X, Y, Z) related to the crystal system (x, y, z) by the transformation shown

				(Å)^2	l	m	n	
T		0.0387 (17)	0.0000 (14)	0.0000 (14)	.0483	0.0000	0.9997	-0.0231	
(Å^2)	=		0.0483 (17)	-0.0003 (14)	.0387	1.0000	0	0	
				0.0364 (19)	.0364	0.0000	-0.0231	-0.9997	
					(rad)^2				(deg)^2
L		0.0046 (6)	0.0000 (4)	0.0000 (3)	.0062	0.0000	0.5948	0.8039	20.3
(rad)^2	=		0.0050 (6)	0.0009 (4)	.0046	-1.0000	0	0	15.0
				0.0057 (4)	.0044	0.0000	-0.8039	0.5948	14.5
S		0.0017 (6)	0.0000 (6)	0.0000 (6)					
(rad. Å)	=	0.0000 (6)	0.0000 (6)	-0.0020 (6)					
		0.0000 (5)	-0.0020 (5)	-0.0017 (7)					

$\langle(\varDelta U_{ij})^2\rangle^{1/2} = 0.0029$ Å^2 $\quad$ $\langle\sigma^2(U_{ij})\rangle^{1/2} = 0.0026$ Å^2

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 0 & 7.8320 & 0 \\ 1.1745 & 0.0000 & -12.8302 \\ -11.9956 & 0.0000 & 2.1006 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Origin of X, Y, Z system at $(x, y, z) = (0.50000, 0.12347, 0.25000)$

Table 4. *[4.4.4]Propellatriene*

Analysis of atomic vibration tensors in terms of rigid-body motion. Tensor components (standard deviations × 10^4 in brackets) and eigenvectors are referred to an orthogonal, molecular coordinate system (X, Y, Z) related to the crystal system (x, y, z) by the transformation shown

				(Å)^2	l	m	n	
T		0.0506 (29)	0.0057 (25)	0.0012 (26)	0.0540	-0.8629	-0.4688	-0.1888	
(Å)^2	=		0.0416 (29)	0.0046 (26)	0.0414	-0.4816	0.6495	0.5884	
				0.0374 (36)	0.0341	-0.1532	0.5987	-0.7862	
					(rad)^2				(deg)^2
L		0.0103 (11)	-0.0020 (9)	0.0032 (7)	0.0136	0.7305	-0.5141	-0.4495	44.8
(rad)^2	=		0.0086 (11)	0.0025 (7)	0.0073	0.6016	0.7960	0.0671	23.9
				0.0056 (7)	0.0036	0.3233	-0.3195	0.8907	11.7
S		0.0010 (10)	0.0038 (10)	0.0015 (11)					
(rad Å)	=	-0.0016 (10)	-0.0002 (10)	-0.0037 (11)					
		-0.0013 (8)	-0.0011 (8)	-0.0008 (14)					

$\langle(\varDelta U_{ij})^2\rangle^{1/2} = 0.0079$ Å^2 $\quad$ $\langle\sigma^2(U_{ij})\rangle^{1/2} = 0.0062$ Å^2

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -6.8438 & 4.9730 & 9.5249 \\ 3.7441 & 10.5249 & -0.2247 \\ -1.0842 & 4.9542 & -0.0838 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Origin of X, Y, Z system at $(x, y, z) = (0.33467, 0.29711, 0.18261)$

For propellane the rigid-body approximation seems to hold reasonably well since it yields tensor components U_{ij} that agree tolerably with the observed values. The translational and librational tensors are both reasonably isotropic (in keeping with the roughly isotropic shape of the molecule, with its three moments of inertia in the approximate ratio 4:4:5). The C–C bond lengths, corrected for the effect of libration, are 0.007–0.008 Å longer than the values given in Table 1D; the corresponding corrections to CCC angles and CCCC torsion angles are negligible (less than 0.1°).

For propellatriene the tensor components U_{ij} are much larger than for propellane (compare Tables 1B and 2B) and they are not reproduced nearly so well by the rigid-body analysis. To some extent, the poorer quality of the agreement is due simply to indefiniteness in the structural parameters, associated with the low m.p. of the crystal. In addition, however, the rigid-body approximation may not hold so well. Inspection of space-filling models suggests that, whereas in propellane any internal motion of the molecule is effectively blocked by steric hindrance between peripheral hydrogen atoms, this is not the case in propellatriene (with 6 less hydrogen atoms), for which low-frequency, high-amplitude internal vibrations cannot be excluded³). The correction for the bond-length shortening effect of libration amounts to 0.011–0.013 Å (to be added to the values given in Table 2D), the bond angle and torsion angle corrections being again negligible. The corrected lengths of the double bonds are still shorter than normal by about 0.03 Å. The librational tensor is markedly more anisotropic than in propellane, the smallest 'eigenvalue' being approximately the same, the largest one much larger.

Experimentally observed molecular conformations. The observed conformations of both molecules are close to the expected D_3 symmetry. For propellane, the largest deviations between chemically equivalent parameters are less than 0.02 Å for bond lengths, 1.5° for angles and 2.5° for torsion angles, and have at most a marginal significance. For propellatriene, the observed deviations are somewhat larger – but so are the standard deviations (there is one difference of 0.08 Å, between the observed distances C(7)–C(8) and C(9)–C(10), that we choose to regard as an unexplainable statistical fluctuation!). Discussion of the molecular conformations is greatly simplified if the observed parameters are averaged over D_3 symmetry, as has been done in Fig. 3 and 4, where bond lengths are given both uncorrected and corrected (in brackets) for the effect of libration (see preceeding section). We note that in both molecules the central bond appears to be 0.02–0.03 Å longer than the standard $C(sp^3)$–$C(sp^3)$ distance of 1.53–1.54 Å. This lengthening is certainly significant for the saturated compound ($l_1 = 1.556$ (uncorr.), 1.564 (corr.), $\sigma \sim 0.007$ Å), where the 6-membered rings are also distinctly flatter than cyclohexane ($\theta = 115.5°$, $\phi = 54.7°$ [5] in the region of the central bond ($\phi = 48.9°$). A similar effect in *cis*-decalin has been discussed by *Bucourt & Hainaut* [6] ([4.4.4]propellane contains three overlapping *cis*-decalin systems, *cf.* Fig. 2). A propellane molecule built by fusing the three six-membered rings with geometrical parameters as in cyclohexane itself would contain 6 H...H distances of 1.99 Å and 3 of 2.23 Å. In the observed conformation both kinds of distance are increased by about 0.1 Å, largely as a result of the reduction

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³) The internal vibrations in question leave the torsion angles about the central C(1)–C(6) bond essentially unchanged and hence cannot convert a molecule of given chirality into its enantiomer.

in the torsion angles about the central bond. A decrease in the mean torsion angle of the six-membered ring must be accompanied by an increase in the mean bond angle, because of the ring constraints. This increase is seen to occur mainly in θ_2 – it would certainly not be expected to occur in θ_1, for obvious reasons.

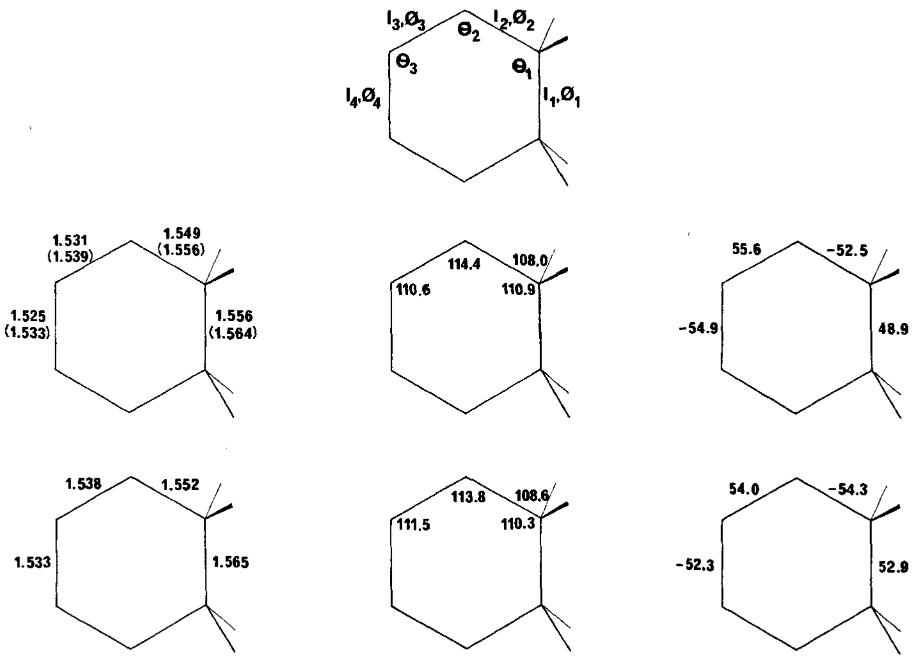

Fig. 3. *[4.4.4]Propellane*

Top: Observed internal parameters averaged over D_3 symmetry (bond lengths in brackets are corrected for the effect of libration). Bottom: Calculated internal parameters

In propellatriene the energetically unfavourable short H...H contacts are not present, and the averaged conformation of the six-membered rings is not significantly different from that of cyclohexene [7] (see Fig. 5).

Strain Minimization Calculations. Minimum-energy conformations of both molecules were calculated using a standard set of potential functions, details of which are given in Table 5. The energy minimization was carried out by the method of steepest descent, using computer programmes made available by Prof. *S. Lifson.* More efficient minimization techniques were not practicable in these cases because of the large number of variables. The main results are summarized and compared with the experimental results in Fig. 3 and 4.

[4.4.4]Propellane. The calculated C–C distances agree very well with the observed values after correction of the latter for the effect of libration. For the bond angles the agreement is less good. Although the trend of the observed values is correctly reproduced, the calculated angles are all somewhat too close to their equilibrium values, suggesting that the angle-bending force constants employed are too large. The agreement in the torsion angles is likewise not completely satisfactory.

One can hardly expect a set of force constants derived from vibrational spectroscopy of unstrained molecules to reproduce exactly the equilibrium parameters of molecules in which geometric constraints are operative. Apart from the notorious difficulties in the choice of appropriate non-bonded interaction potentials, our model is also grossly oversimplified in that important cross-terms in the force field have been neglected. Moreover, the valence-force-field from which the stretching and bonding force constants are taken does not contain non-bonded interaction terms. Although there are several ways in which the potential constants can be adjusted to improve the agreement, it seems clear that such corrections would not be very meaningful in view of the above shortcomings of the model.

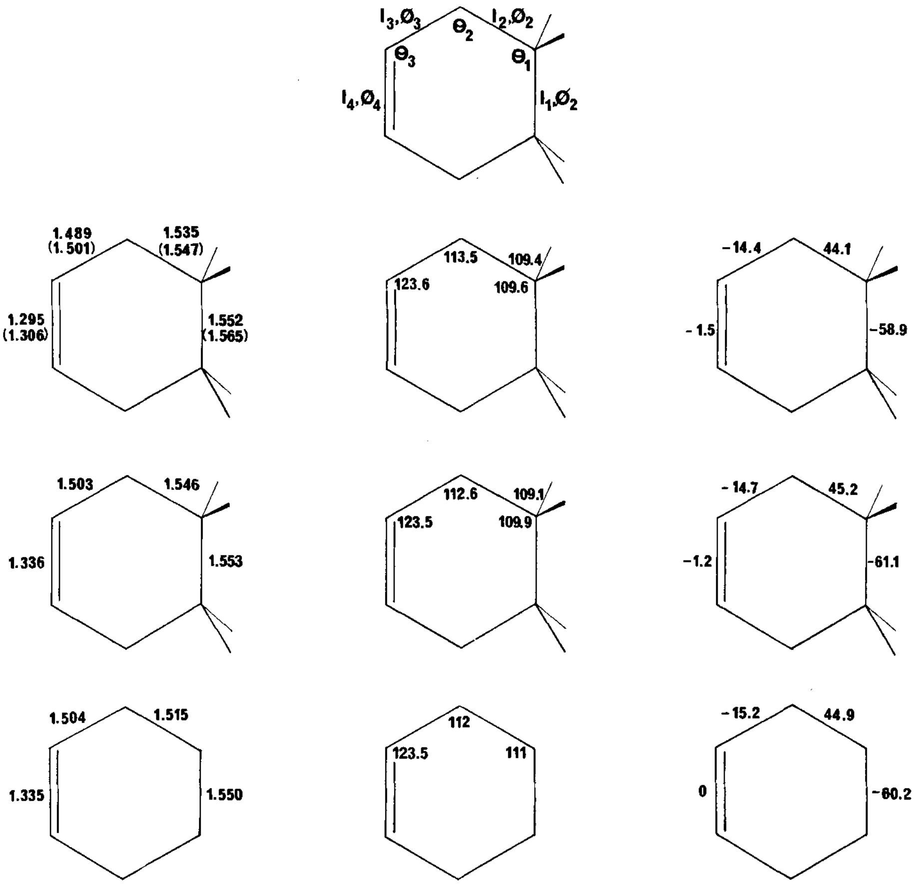

Fig. 4. *[4.4.4]Propellatriene*

Top: Observed internal parameters average over D_3 symmetry (bond lengths in brackets are corrected for the effect of libration). Middle: Calculated internal parameters. Bottom: Observed parameters for cyclohexene [7]

It is worth noting that an energy-minimization calculation (steepest descents) based on the more elaborate consistent force field of *Warshel* & *Lifson* [16] led to

Table 5. *Potential energy terms and constants used in energy-minimization calculations*

a) Bond stretching $V(l) = k_l (l - l_0)^2$;

Bond type	k_l (kcal mole^{-1}A^{-2})	l_0 (Å)
$C(sp^3)$—$C(sp^3)$	313.8 [a]	1.533 [c]
$C(sp^3)$—H	327.7 [a]	1.109 [c]
$C(sp^3)$—$C(sp^2)$	322 [b]	1.501 [d]
$C(sp^2)=C(sp^2)$	698 [b]	1.336 [d]
$C(sp^2)$—H	364 [b]	1.090 [d]

b) Bond angle bending $V(\theta) = (\pi/180)^2 k_\theta (\theta - \theta_0)^2$

Angle type	k_θ (kcal mole^{-1}rad^{-2})	θ_0 (deg)
C—CH_2—C	81.3 [a]	112.4 [e]
C—CCC—C	78.1 [a]	109.5
C—C—H	47.2 [a]	109.5 [f]
H—C—H	39.6 [a]	106.1 [e]
$C(sp^3)$—$C(sp^2)$—H	38.5 [b]	116.7 [d]
$C(sp^2)=C(sp^2)$—$C(sp^3)$	68.1 [b]	124.3 [d]
$C(sp^2)=C(sp^2)$—H	39.8 [b]	119.0 [d]

c) Torsional potentials

Type	K_ϕ (kcal mole^{-1})	Function assumed
$C(sp^3)$—$C(sp^3)$—$C(sp^3)$—$C(sp^3)$	1.7 [g]	$K_\phi (1 + \cos 3\phi)$
$C(sp^3)$—$C(sp^3)$—$C(sp^2)=C(sp^2)$	0.989 [h]	$K_\phi (1 - \cos 3\phi)$
$C(sp^3)$—$C(sp^2)=C(sp^2)$—$C(sp^3)$	19.35 [i]	$K_\phi (1 - \cos 2\phi)$

d) Non-bonded interactions [j]: $V(r) = A \exp(-\mu r) - Br^{-6}$

Type	A	B	μ
H...H	2300	49.2	3.6
H...C	4012	125	3.4
C...C	7000	325	3.2

V, A [kcal mole^{-1}]; B [kcal mole^{-1} Å^6]; r [Å]; μ [Å^{-1}].

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[a] Taken from the force field for saturated hydrocarbons derived by *Snyder & Schachtschneider* [8].

[b] Analogous values for unsaturated hydrocarbons, cited in *Zerbi & Gussoni* [9].

[c] See *Hendrickson* [10].

[d] From microwave analysis of propene by *Lide & Christensen* [11].

[e] From electron-diffraction analysis of *n*-paraffins by *Bartell & Kohl* [12].

[f] Assumes C_{2v}-symmetry of methylene group in polymethylene chain or ring.

[g] Corresponds to barrier of 3.4 kcal mole^{-1} in propane (*Pitzer* [13]). The same torsional potential was used for all $C(sp^3)$—$C(sp^3)$ bonds, with inclusion of 1,4-non-bonded interactions to take account of the different substituents.

[h] Corresponds to barrier of 1.978 kcal mole^{-1} for rotation about $C(sp^3)$—$C(sp^2)$ bond in propene (*vide supra*).

[i] Value derived from twisting force constant of ethylene (*Arnott & Crawford* [14]). We are aware that this simple treatment is very inadequate to deal with the out-of-plane deformations of a double bond, but the function described fulfils our main purpose here of preserving the essential coplanarity of the double-bond system.

[j] Revised parameters due to *Hendrickson* [15].

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good agreement for bond angles and torsion angles but to unreasonable bond lengths ($l_2 = 1.60$ Å!). This may be attributable to the inappropriateness of the *Urey-Bradley* C...C interaction constants for interactions between the central, quaternary substituted, carbon atoms and their neighbours.

[4.4.4]Propellatriene. For this molecule the agreement between observed and calculated internal parameters is less satisfactory, and one may suspect that the

inaccuracy of the experimental results is here more serious than the deficiencies of the calculation. In particular, the calculation does not reproduce the apparent shortening in the observed C=C double-bond length, which is, even after correction for libration, only 1.306 Å, compared with the calculated 1.336 Å (Fig. 4). We have considered the possibility that the assumption of pure rigid-body motion for propellatriene may not be as good as for propellane, since internal motions of the cyclohexene rings in the former may be considerably larger than those of the cyclohexane rings in the latter. Such internal motions, superimposed on the rigid-body motions, could conceivably lead to an additional shortening effect that we have not allowed for. However, the thermal motion analysis does not provide any indication of large internal motions of the peripheral atoms. The agreement between observed and calculated U_{ij} values is not particularly good but it is no worse for the peripheral atoms than for the inner ones. Any additional effect of this kind must be small enough to be obliterated by the general indefiniteness of the structural and vibrational parameters. We tend to think that the experimental value is in error in this case, especially since the double-bonded atoms are among those with the largest standard deviations (Table 2A) and vibrational tensor components (Table 2B).

Crystal packing. Although the molecules of [4.4.4]propellane and propellatriene are very similar in overall shape and size, the cell dimensions and space groups of the crystals are quite different. There is no recognizable similarity between the two crystal packings. It is of interest that the packing in propellatriene appears to be much looser than in propellane. The shortest intermolecular C...C distances in the triene are 3.88 Å, whereas there are four shorter ones (2 · 3.72 Å, 2 · 3.84 Å) in the propellane crystal. Thus the lower melting point and larger vibrational amplitudes of the olefin are parallelled by a less close molecular packing.

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