

220. Crystal Structure and Electron-Density Distribution of Two [1.1.1]Propellane Derivatives at 81 K

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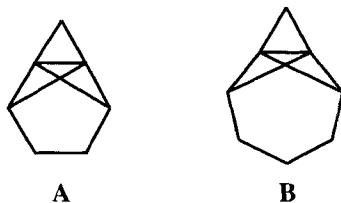
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The molecular structure and electron-density distribution of two [1.1.1]propellane derivatives have been determined from accurate single-crystal X-ray diffraction measurements at 81 K. The crystals of these highly reactive compounds (both are liquid at room temperature) were grown directly on the X-ray diffractometer at *ca.* 208 and 228 K, respectively. Both compounds crystallize in the space group $P2_1/c$ with one molecule in the asymmetric unit. The symmetry of the propellane C-atom skeleton is close to D_{3h} for both molecules. The distances between the two bridgehead C-atoms are 1.587 and 1.585 Å, and the mean lengths of the propellane side bonds are 1.525 and 1.528 Å, respectively. The deformation density peaks of the propellane side bonds (*ca.* 0.25 e/Å³) lie somewhat outside the internuclear connection lines and so correspond to 'bent bonds' as expected. On the other hand, the difference electron density between the bridgehead nuclei is slightly negative in both molecules. An interesting feature, observed in these difference maps, is the presence of a diffuse, positive difference density at each inverted C-atom, outside the bridgehead bond, a probable site of electrophilic attack.

Introduction. – The small-ring propellanes such as [1.1.1]propellane have been the subject of a series of experimental [1-5] and theoretical [6][7] studies. With regard to chemical-bonding theories, the nature of the central C–C bond in such strained molecules is of particular interest. For example, it has been stated by *Newton* and *Schulman* [6] that 'no evidence for a central bond is found in [1.1.1]propellane in terms of the charge distribution, although the bond length of 1.60 Å is significantly shorter than the corresponding nonbonded distance of 1.89 Å in bicyclo[1.1.1]pentane'. More recently *Wiberg et al.* [7] have analyzed the total (calculated) density of [1.1.1]propellane by examining its *Laplacian*, *i.e.* its second derivative. These authors came to a different conclusion, namely that the propellane molecule is accumulating charge at the midpoint of the central bond, and that the bridgehead nuclei are bonded to one another, in contrast to the related bicyclic compound.



In the present article, we report the molecular geometry, the crystal packing, and the electron-density distribution in the [1.1.1]propellane derivatives, tetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptane (**A**) and tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane (**B**) [2][8], as found by low-temperature (81 K) crystal structure analysis.

Preliminary results of the structure analysis of [1.1.1]propellane itself are also described.

Experimental. – The X-ray measurements were made on an *Enraf-Nonius CAD4* diffractometer equipped with graphite monochromator (MoK α radiation, $\lambda = 0.7107 \text{ \AA}$) and a locally modified *Enraf-Nonius* gas-stream low-temperature device. Temperature fluctuations, as monitored by a Pt 100- Ω resistor, were less than 0.3 K during the experiments.

The preparation of single crystals of **A** and **B** of good quality for an accurate X-ray diffraction study is not trivial. Both compounds are liquid at r.t. and highly unstable above *ca.* 233 K as well as in presence of traces of humidity. Thus, all manipulations with **A** and **B** were carried out in a pure N₂ atmosphere below 223 K. Crystals of **A** and of **B** were obtained by very slow cooling ($\sim 1 \text{ K}/24 \text{ h}$) of one drop of liquid enclosed in a glass capillary mounted on the diffractometer. The crystallization process could be observed through a telescope, and diffraction measurements carried out without disturbing the crystals, once they had formed. After several crystallization attempts, almost spherical crystals of good optical quality could be obtained at *ca.* 208 K for **A** ($\phi \approx 0.6 \text{ mm}$) and *ca.* 228 K for **B** ($\phi \approx 0.4 \text{ mm}$). Unit cell dimensions (81 K) listed in *Table 1* were obtained by least-squares refinement of setting angles for 24 reflections with 2θ values in the range of 40 to 60°. For each data set, six standard reflections, distributed between $\mathbf{H} = (2 \sin \theta/\lambda) 0.3$ and 1.8 \AA^{-1} , were monitored at intervals of 2.8 h radiation time. The intensity loss of the standard reflections, especially for **A**, depends not only on the radiation time but also on the scattering angle, as observed in a previous electron-density study [9].

Table 1. *Experimental Details of the X-Ray Diffraction Measurements for the Two [1.1.1]Propellane Derivatives C₇H₈ (molecule A) and C₈H₁₀ (molecule B)*

Data set	A	B
Temperature of data collection [K]	81	81
Melting point [K]	206-209	226-230
Crystal diameter [mm]	~ 0.6	~ 0.4
Space group	$P2_1/c$	$P2_1/c$
Cell dimensions		
a [\AA]	8.299(2)	9.171(2)
b [\AA]	5.956(1)	5.940(1)
c [\AA]	11.026(2)	11.483(2)
β [°]	102.92(2)	105.42(2)
Unit cell contents	$4 \times \text{C}_7\text{H}_8$	$4 \times \text{C}_8\text{H}_{10}$
D_c [g/cm ³]	1.05	1.17
$2 \sin \theta/\lambda$ range [\AA^{-1}]	1.808	1.99
Scan mode	ω/θ	ω/θ
No. of symmetry equivalent orientations measured	4	2
No. of measured reflections	~ 14900	~ 10300
$R_{\text{int}} = (\sum_H \sum_N I_{H,N} - \langle I_H \rangle) / \sum_H N \langle I_H \rangle$	0.025	0.014
No. of unique reflections	3278	4957
No. of observed reflections ($I > 3 \sigma(I)$)	2312	3172
No. of variables in final least-squares analysis	96	114
Type of refinement	F	F
Exponentially modified weight factor r [\AA^2]	3.0	2.5
Extinction correction	isotropic	isotropic
$y = P/P_k$ for the strongest reflection	0.82	0.94
$R(F)$	0.035	0.032
$R_w(F)$	0.043	0.033

Table 2. Positional and Displacement Parameters [\AA^2] with Standard Deviations in Parenthesis (molecule A above, molecule B below)

Atom	x	y	z	U_{11} (OR U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.84545(8)	-0.1370(1)	0.29304(6)	0.0176(2)	0.0203(2)	0.0190(2)	0.0042(2)	0.0038(2)	-0.0043(2)
C(2)	0.81288(7)	0.10866(9)	0.31627(5)	0.0158(2)	0.0157(2)	0.0192(2)	-0.0023(2)	0.0032(2)	-0.0005(2)
C(3)	0.71322(9)	0.1659(1)	0.18772(6)	0.0213(3)	0.0264(3)	0.0202(2)	0.0011(2)	0.0057(2)	0.0069(2)
C(4)	0.67036(7)	-0.0497(1)	0.24520(5)	0.0146(2)	0.0199(2)	0.0160(2)	-0.0015(2)	0.0015(2)	-0.0013(2)
C(5)	0.66974(8)	0.0421(1)	0.37384(5)	0.0176(2)	0.0192(2)	0.0173(2)	0.0044(2)	0.0064(2)	0.0011(2)
C(6)	0.72721(9)	-0.1393(1)	0.46989(6)	0.0257(3)	0.0241(2)	0.0187(2)	0.0032(2)	0.0064(2)	0.0053(2)
C(7)	0.85312(9)	-0.2686(1)	0.41158(6)	0.0259(3)	0.0154(2)	0.0240(3)	0.0051(2)	0.0003(2)	-0.0004(2)
H(1)	0.915(1)	-0.176(2)	0.234(1)	0.033(3)					
H(31)	0.766(1)	0.152(2)	0.115(1)	0.032(3)					
H(32)	0.634(1)	0.291(2)	0.179(1)	0.025(2)					
H(5)	0.589(1)	0.154(2)	0.3806(9)	0.025(2)					
H(61)	0.780(1)	-0.075(2)	0.552(1)	0.030(3)					
H(62)	0.637(1)	-0.233(2)	0.481(1)	0.030(3)					
H(71)	0.823(2)	-0.425(2)	0.396(1)	0.039(3)					
H(72)	0.966(1)	-0.264(2)	0.467(1)	0.032(3)					
C(1)	0.25790(4)	-0.02028(7)	0.86952(3)	0.0140(1)	0.0143(1)	0.0116(1)	0.0005(1)	0.00438(9)	0.0017(1)
C(2)	0.26135(4)	0.22141(7)	0.82657(3)	0.0132(1)	0.0121(1)	0.0137(1)	0.0013(1)	0.00447(9)	-0.0011(9)
C(3)	0.42306(5)	0.26940(8)	0.89715(4)	0.0153(1)	0.0182(2)	0.0150(1)	-0.0027(1)	0.0033(1)	-0.0041(1)
C(4)	0.39396(4)	0.05247(7)	0.82458(3)	0.0111(1)	0.0145(1)	0.0128(1)	0.0016(1)	0.00310(9)	-0.0005(1)
C(5)	0.29857(4)	0.16343(7)	0.70856(3)	0.0143(1)	0.0127(1)	0.0114(1)	-0.0009(1)	0.00417(9)	0.00064(9)
C(6)	0.18966(5)	0.02049(7)	0.61545(3)	0.0173(1)	0.0163(1)	0.0111(1)	-0.0015(1)	0.0023(1)	0.0003(1)
C(7)	0.16621(5)	-0.20926(7)	0.66782(4)	0.0206(2)	0.0138(1)	0.0159(1)	-0.0030(1)	0.0038(1)	-0.0018(1)
C(8)	0.14467(5)	-0.18482(7)	0.79477(4)	0.0163(1)	0.0140(1)	0.0170(1)	-0.0023(1)	0.0052(1)	0.0023(1)
H(1)	0.280(1)	-0.036(2)	0.9583(9)	0.024(2)					
H(31)	0.475(1)	0.388(2)	0.8654(8)	0.025(2)					
H(32)	0.446(1)	0.251(2)	0.9869(8)	0.023(2)					
H(5)	0.350(1)	0.283(2)	0.6807(9)	0.027(2)					
H(61)	0.093(1)	0.105(2)	0.5876(8)	0.025(2)					
H(62)	0.229(1)	0.003(2)	0.5452(9)	0.024(2)					
H(71)	0.259(1)	-0.306(2)	0.6755(9)	0.026(2)					
H(72)	0.080(1)	-0.291(2)	0.6134(9)	0.029(2)					
H(81)	0.158(1)	-0.329(2)	0.8358(8)	0.024(2)					
H(82)	0.042(1)	-0.133(2)	0.7920(7)	0.021(2)					

For example, after a four-week irradiation period of a crystal of **A**, a low-order reflection at $H = 0.33 \text{ \AA}^{-1}$ decreased by *ca.* 6.5%, whereas a reflection at $H = 1.67 \text{ \AA}^{-1}$ lost about 13%. The nonlinear intensity fall-off, produced by radiation damage in the crystal, was accompanied by a small but significant increase of the unit cell volume of *ca.* 0.13% and a marked increase of the monoclinic β angle of 0.11° . For data set of **B**, the intensity loss of the individual standard reflections was in the range 4 to 7% after a three-week irradiation period. An appropriate scaling correction was made for both data sets to compensate for the nonlinear intensity drift [10].

The structures were solved by direct methods [11] and refined by full-matrix least-squares analysis [12], using modified weights [13] and an isotropic extinction correction. Additional experimental details are summarized in *Table 1*. The atomic coordinates and displacement parameters are listed in *Table 2*.

ADP Analyses. – Preliminary analyses of the atomic displacement parameters (ADP's) listed in *Table 2* show that the rigid-body tests [14] are satisfied well for both molecules. The largest differences between mean-square vibrational amplitudes of pairs of atoms along their respective interatomic vectors are $4 \times 10^{-4} \text{ \AA}^2$ in **A** and $6 \times 10^{-4} \text{ \AA}^2$ in **B**. The **T**, **L**, **S** analyses [15] with the program THMA11 [16] lead to excellent agreement between observed and calculated U_{ij} components, with *R* factors [$R = \sum\{(w\Delta U_{ij})^2/\sum(wU_{ij})^2\}^{1/2}$] of 0.011 and 0.024 for molecule **A** and **B**, respectively. The eigenvalues of **L** are 28.4, 12.3, and 9.9 deg^2 in **A**, and 9.2, 7.2, and 5.2 deg^2 in **B**. The eigenvalues of **T** are 0.016, 0.013, and 0.012 \AA^2 in **A** and 0.012, 0.011, and 0.010 \AA^2 in **B**. The largest libration is nearly about the longest molecular axis in both molecules. The estimated librational corrections of the C–C bond lengths are *ca.* 0.008 \AA for **A** and 0.003 \AA for **B**.

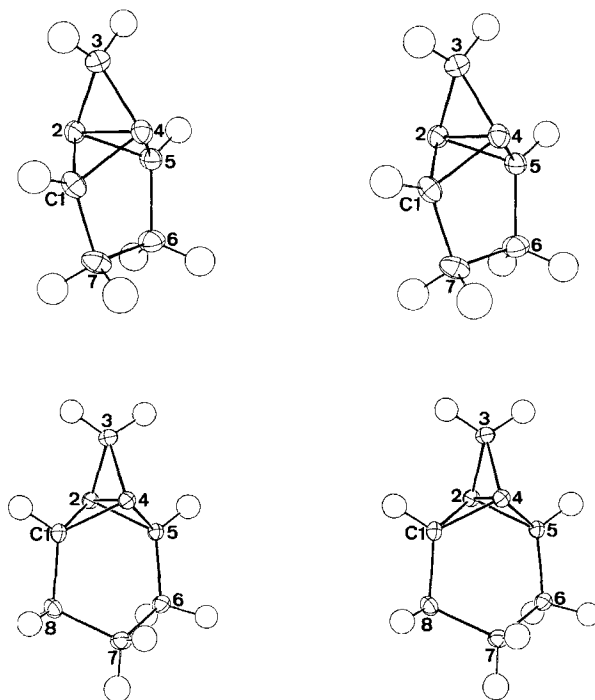


Fig. 1. Stereoscopic view of molecule **A** (above) and **B** (below) at 81 K. Vibrational ellipsoids, isotropic for H-atoms, are shown at the 50% probability level.

Molecular Geometry. – Bond lengths and bond angles for molecules **A** and **B** are listed in Table 3, and a drawing of **A** and **B** is shown in Fig. 1. Although the low-temperature X-ray data (81 K) extend to relatively high resolution for this type of compounds ($H = 1.8 \text{ \AA}^{-1}$ for data set **A**, $H = 2.0 \text{ \AA}^{-1}$ for data set **B**), the systematic errors in the C–C bond lengths are probably several times larger than the estimated standard deviations ($\sim 0.0008 \text{ \AA}$ for **A** and $\sim 0.0006 \text{ \AA}$ for **B**). For example, there is an appreciable systematic shortening of the C–C distances due to librational motion of the molecules even at 81 K (see above). The values given in parentheses should compensate for this error.

Table 3. a) Bond Lengths [\AA] from the Two 81-K X-Ray Analyses. Values in parentheses are corrected for librational motion. E.s.d.'s are less than 0.001 \AA for both structures.

	Molecule A	Molecule B
C(1)–C(2)	1.520 (1.529)	1.521 (1.524)
C(1)–C(4)	1.522 (1.529)	1.534 (1.537)
C(2)–C(3)	1.512 (1.517)	1.516 (1.519)
C(2)–C(4)	1.577 (1.587)	1.582 (1.585)
C(2)–C(5)	1.519 (1.528)	1.522 (1.526)
C(3)–C(4)	1.509 (1.517)	1.519 (1.522)
C(4)–C(5)	1.521 (1.529)	1.535 (1.538)
C(5)–C(6)	1.513 (1.519)	1.515 (1.517)
C(6)–C(7)	1.549 (1.557)	1.529 (1.533)
C(7)–C(1)	1.513 (1.519)	
C(7)–C(8)		1.529 (1.533)
C(8)–C(1)		1.515 (1.518)

b) C–C–C Bond Angles [$^\circ$] from the Two 81-K Analyses. E.s.d.'s are $ca. 0.05^\circ$ for molecule **A** and $ca. 0.03^\circ$ for molecule **B**.

C(1)–C(2)–C(4)	58.84	59.21
C(3)–C(2)–C(4)	58.45	58.69
C(5)–C(2)–C(4)	58.81	59.22
C(1)–C(4)–C(2)	58.70	58.43
C(3)–C(4)–C(2)	58.60	58.50
C(5)–C(4)–C(2)	58.69	58.47
C(2)–C(1)–C(4)	62.46	62.36
C(2)–C(3)–C(4)	62.95	62.81
C(2)–C(5)–C(4)	62.50	62.31
C(1)–C(2)–C(3)	98.03	96.08
C(1)–C(4)–C(3)	98.04	95.42
C(1)–C(2)–C(5)	90.25	95.97
C(1)–C(4)–C(5)	90.09	94.94
C(3)–C(2)–C(5)	97.80	95.71
C(3)–C(4)–C(5)	97.82	95.07
C(4)–C(5)–C(6)	109.25	119.26
C(2)–C(5)–C(6)	108.97	119.56
C(5)–C(6)–C(7)	101.58	110.97
C(6)–C(7)–C(1)	101.48	
C(6)–C(7)–C(8)		110.94
C(7)–C(8)–C(1)		111.01

The crucial distance in these propellane molecules is that between the inverted C-atoms C(2) and C(4), amounting to 1.577 (1.587) Å in **A** and to 1.582 (1.585) Å in **B**. Both values are only slightly (0.013 and 0.011 Å) longer than the bridgehead-bridgehead distance in a [3.1.1]propellane derivative, determined at 95 K [17]. The lengths of the propellane side bonds are in the range of 1.509 (1.517) to 1.522 (1.529) Å (mean 1.525 Å) for **A** and 1.516 (1.519) to 1.535 (1.538) Å (mean 1.528 Å) for **B**. Structurally equivalent C-C bond lengths in each molecule agree within 0.002 Å (see *Table 3*). The six C-C-C bond angles of the three-membered rings, formed by the central and the individual side bonds range from 58.5 to 58.8° in **A** and from 58.4 to 59.2° in **B**; the three C-C-C angles formed by the two side bonds are close to 62.5° in both molecules. There is a slight deviation from D_{3h} in that the bridgehead-methylene C-C bonds are significantly shorter than the other side bonds (*Table 4*).

Table 4. Bond Lengths in [1.1.1]Propellane by Various Methods

		Central C-C [Å]	Side C-C [Å]
Newton and Schulman [6]	4-31G	1.60	1.53
Hedberg and Hedberg [4]	Electron diffraction	1.596(5)	1.525(2)
Wiberg et al. [3]	IR/Raman	1.60(2)	1.522(2)
	6-31G*-MP2	1.594	1.515
	6-31G*-MP3	1.572	1.514
Present work	C ₇ H ₈ (molecule A , 81 K)	1.587(1)	1.525(3) ^{a)} 1.517(1) ^{b)}
	C ₈ H ₁₀ (molecule B , 81 K)	1.585(1)	1.528(3) ^{a)} 1.520(2) ^{b)}

^{a)} Averaged over all six side bonds.

^{b)} Averaged over the two bridgehead-methylene side bonds C(2)-C(3) and C(3)-C(4) only.

Long before its actual preparation [1], the molecular structure of [1.1.1]propellane was established by *ab initio* MO calculations (4-31G basis set) [6]. These gave the bridgehead-bridgehead distance as 1.60 Å and the length of a side bond as 1.53 Å. More recently, the geometry of this molecule was redetermined by higher-level calculations (6-31G* basis set, including increasing degree of electron correlation) [3], by analysis of its vibrational spectrum [3], and by a gas-phase electron-diffraction study [4]. The C-C distances obtained by the various methods, summarized in *Table 4*, are in good agreement with our experimental results. In fact, the side-bond lengths agree within 0.016 Å. The mean value of our bridgehead-bridgehead distances (1.586 Å) is 0.014 and 0.01 Å shorter than the experimental values reported in [3][4] and lies between the latest theoretical values [3].

Results of a recent room-temperature X-ray crystal structure analysis of a coupled [1.1.1]propellane derivative [18] show only minor deviations from the molecular geometry observed in **A** and **B**. The C-C distances are *ca.* 0.01 Å shorter on average than our corrected values.

Crystal Packing. - As C-H distances obtained by least-squares refinement are characteristically *ca.* 0.1 Å too short, the H-positions, listed in *Table 2*, were moved along the corresponding bond direction to give C-H distances of 1.09 Å.

For crystal **A**, the packing is looser than in **B** (*cf.* the densities listed in *Table 1*). In **A**, there are no intermolecular H···H distances less than 2.4 Å and only eight such contacts in the range of 2.45 to 2.65 Å to eight neighbouring molecules. We also find five short intermolecular C···H contacts less than 2.8 Å; four of these occur between the bridgehead C-atoms and four neighbouring molecules. *Fig. 2* shows that C(2) is in contact with H(1'), H(71') and H(72'); the corresponding distances being 2.67, 2.79, and 2.74 Å, and the C(2)···H-C' angles 149, 163, and 150°, respectively. On the opposite side of the molecule, C(4) makes only one such contact with H(5'); the distance is 2.78 Å, and the C(4)···H(5')-C(5') angle is 146°. There is also a short distance of 2.78 Å between C(5) and H(32'), of 2.80 Å between the centre of the C(2)-C(3) side bond and H(1'), and of 2.74 Å between the centre of the C(4)-C(5) side bond and H(32').

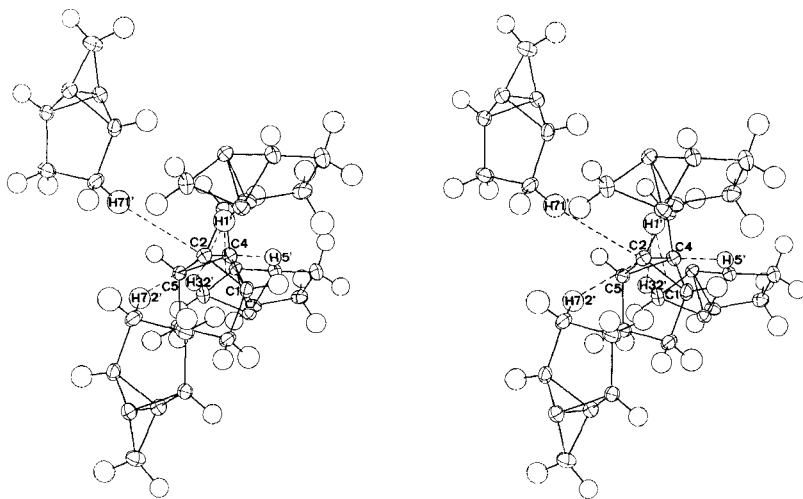


Fig. 2. Stereoscopic view of the reference molecule A and four of its nearest neighbours

The packing of crystal **B** is more compact with one intermolecular H···H distance of 2.35 Å and 13 H···H distances in the range of 2.44 to 2.65 Å between **B** and nine neighbouring molecules. In contrast to **A**, there are only two intermolecular C···H contacts less than 2.8 Å, one (2.75 Å, 143°) between the bridgehead atom C(2) and H(81'), the other (2.73 Å, 154°) between the bridgehead atom C(4) and H(5'). In addition, there is one short distance between the centre of the C(4)-C(5) side bond and H(31') of 2.72 Å.

Difference Densities. – The X-X difference maps shown in *Figs. 3* and *4* are based on all ($F_o - F_c$) coefficients with $F_o > 3 \sigma(I)$ and $H < 1.5 \text{ \AA}^{-1}$, a total of 1562 reflections for molecule **A** and 1717 reflections for molecule **B**. The noise level is low, partly because the weakest, inaccurately measured reflections were eliminated from this analysis. The average standard deviation of the difference density, estimated as $[2\sum\sigma^2(F_o)]^{1/2}/V$ is 0.01 e/Å³ in **A** and 0.013 e/Å³ in **B**. Close to the atomic centers, however, the effective error may be much larger because the difference density is there the difference between large values of the electron density. The difference maps calculated in the mean planes of the molecules **A** and

B (Fig. 3), defined by C(1), C(3), and C(5), show characteristic accumulation of electron density along the C–C and C–H bonds. For molecule **A**, the highest difference-density peaks occur in the five-membered ring, along C(5)–C(6), C(6)–C(7), and C(1)–C(7), and range from 0.35 to 0.40 $e/\text{\AA}^3$. In molecule **B**, the difference-density peaks along C(5)–C(6) and C(1)–C(8), the only C–C bonds in the mean molecular plane, amount to 0.4 and 0.45 $e/\text{\AA}^3$. The slightly lower peak heights in **A** are partly due to the larger atomic vibration amplitudes in this crystal.

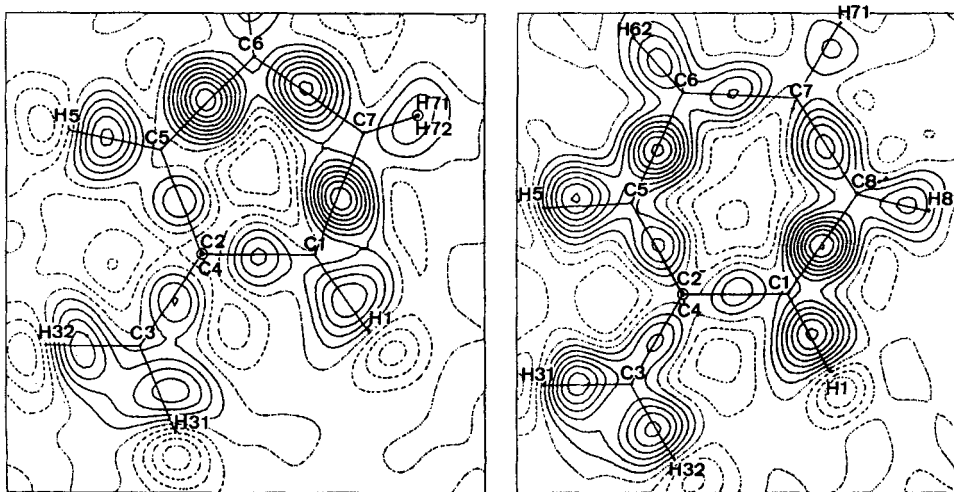


Fig. 3. Electron-density difference maps through the mean plane of **A** (left) and **B** (right). Contours are drawn at intervals of $0.05 e/\text{\AA}^3$, full for positive, dotted for zero, dashed for negative.

The difference-density maps in the planes of the three-membered rings of the propellane skeletons are shown in Fig. 4, a-f. In all six maps, only the side bonds exhibit a positive difference density, and the individual density maxima (0.2 to $0.3 e/\text{\AA}^3$) lie somewhat outside the internuclear connection lines, a typical feature of 'bent bonds' [17][19]. These peaks overlap to give an accumulation of electron density ($\sim 0.15 e/\text{\AA}^3$) at the ring centers. The three peaks, in the mirror plane of the propellane skeleton, arranged around each C(2)–C(4) line (Fig. 3), represent sections through these overlap densities. The difference density along the C(2)–C(4) line in **A** (Fig. 4, a-c) and **B** (Fig. 4, d-f) is slightly negative, similar to the difference density observed earlier between inverted C-atoms in a [3.1.1]propellane derivative [17]. The most interesting feature in these difference maps, however, is the rather diffuse, positive density close to each inverted C-atom along the extensions of the internuclear connection lines C(2)–C(4) and mostly linked to the 'bent-bond' maxima. In molecule **B**, the diffuse densities at C(2) and C(4) are quite symmetric (Fig. 4, d-f), i.e. both reaching ca. $0.1 e/\text{\AA}^3$, in contrast to molecule **A**, where the diffuse density at C(2) ($\sim 0.15 e/\text{\AA}^3$) is about double of that at C(4) (Fig. 4, a-c). While this asymmetry is hardly significant in view of the large error in $\Delta\rho$ near the atomic centers, it is tempting to connect it to the asymmetry in the packing of the bridgehead atoms in **A**. Recall (Fig. 2) that C(2) makes three short intermolecular C··H contacts but C(4) only one, in contrast to molecule **B** where each bridgehead atom exhibits one short C··H contact. With the present data, we can not decide,

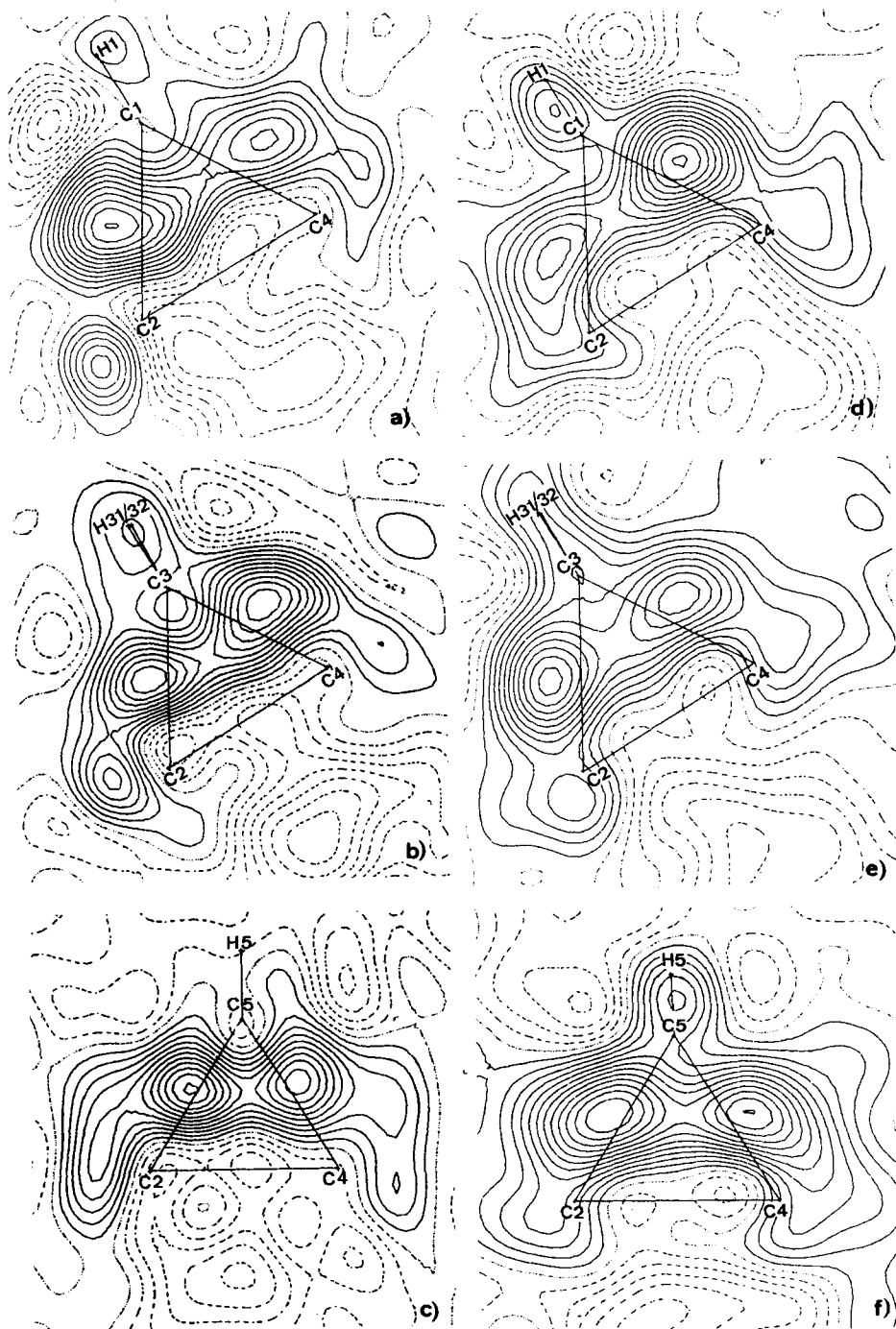


Fig. 4. Electron-density difference maps through the planes of the three-membered rings in molecules **A** (a-c) and **B** (d-f). Contours are drawn at intervals of $0.025 \text{ e}/\text{\AA}^3$.

whether this asymmetry of the difference density in molecule **A** is caused by experimental error or by packing effects.

In a recent theoretical study of hydrocarbon molecules, *Wiberg et al.* [7] have analyzed the total electron density of [1.1.1]propellane by examining the *Laplacian*, i.e. the second derivative of the electron density. According to this analysis, 'the valence shell of an inverted carbon atom exhibits five local charge concentrations, four bonded and one nonbonded'. The nonbonded charge concentration, exposed outside the bridgehead bond is designated as a site of electrophilic attack. *Wiberg et al.* also state that there is an appreciable accumulation of charge between the bridgehead nuclei ($\sim 4/5$ of a normal C-C bond at the bond critical point) and conclude that the bridgehead atoms are bonded to one another in contrast to bicyclo[1.1.1]pentane, where the bridgehead atoms are separated by 1.89 Å. The nonbonded charge concentrations found in the *Laplacian* analysis can be identified with the diffuse, nonbonded difference-density peaks close to C(2) and C(4) shown in *Fig. 4*. In contrast to the theoretical analysis of [1.1.1]propellane, we do not observe an accumulation of charge between the bridgehead nuclei. The slightly negative difference density along the C(2)-C(4) connection lines in **A** and **B** requires comments.

First, it is clear that the accurate determination of very weak density features in an X-X map depends critically on the experimental details such as the accuracy of the X-ray data, the resolution of the diffraction experiment, the refinement procedure, and others [10b]. For example, a small change in scale factor could raise or lower the deformation density by one or two contours. Second, the observed difference density along the central C-C bonds is weak or negative, because the reference density for [1.1.1]propellane, built from spherical, neutral atoms, removes too much charge from this region. In fact, as pointed out by several authors, weak or even negative difference density may occur in certain covalent bonds [9] because of the choice of a spherical-atom reference state [7][20]. Third, because of the finite resolution of the X-ray diffraction experiment, and because F_o and F_c are not exactly equal, series-termination errors may still produce appreciable ripples close to the atomic centers and strong difference-density peaks and troughs. Thus, weak deformation-density peaks close to much stronger ones may be lost, because they overlap with negative ripples produced by the stronger ones.

Preliminary Results for [1.1.1]Propellane. - The structure analysis of [1.1.1]propellane is not trivial. After much effort, a single crystal could be obtained from the melt at about 263 K, using the same procedure as described (see *Experimental*).

Although this compound is not as reactive as the two propellane derivatives **A** and **B**, we observed a slow decomposition of our sample during the crystallization process and also during data collection. The diffraction pattern can be indexed in terms of a centered monoclinic cell with $a = 18.228(5)$ Å, $b = 10.833(3)$ Å, $c = 11.109(3)$ Å, $\beta = 128.44(2)^\circ$ (at 138 K), $Z = 16$. The systematic absences are compatible with the space groups $C2$, Cm , and $C2/m$. If the centrosymmetric space group $C2/m$ is assumed, the asymmetric unit consists of two propellane molecules, otherwise four. At lower temperature, the crystal undergoes a phase transition. The transition temperature, in the range of 118 to 128 K, varied from one crystal sample to another. All crystals obtained of the low-temperature phase were twinned, and its space group has not yet been established. A data set of the high-temperature phase

has been recorded at 138 K. It shows a pronounced intensity fall-off with increasing scattering angle, an indication of a highly disordered structure. To obtain an accurate crystal structure of [1.1.1]propellane, it may be necessary to grow a single crystal well below the transition temperature and then measure a data set at 80 K. Although X-ray diffraction studies of this kind have already been carried out [21], crystallization at very low temperatures is often problematic and time-consuming.

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