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Gas-phase Molecular Structure of Bicyclo[3.3.3]undecane (Manxane) Studied by Electron Diffraction

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The electron-diffraction data from the vapour of bicyclo[3.3.3]undecane at 373K are consistent with C_{3h} symmetry of the molecule which exhibits flattening of the skeleton at the bridgeheads and wide carbon valence angles in the bridges. The two types of C–C bonds are not significantly different in length. Some independent and dependent geometrical parameters are (r_a, $\angle_a$ and θ_a): r(C–C) average=154.2(2) pm, $\angle$(C2–C1–C8)=113.5(9)°, $\angle$(C1–C2–C3)=120.3(11)°, $\angle$(C2–C3–C4)=117.7(8)°, θ(C1–C2–C3–C4) =67.4(15)°, θ(C1–C2···C4–C3)=124.4(11)°, θ(C3–C2–C1–C8)=36.1(24)° and θ(C3–C2–C1–C9)=95.4(9)°. The distortion from tetrahedral valence angles is such as to give the shortest H···H interaction between the bridges of 220(4) pm rather than 130 pm, which would result from the tetrahedral model.

Bicyclo[3.3.3]undecane (known as manxane because of similarity between the projection of the proposed structure and the coat of arms of the Isle of Man) was first prepared in 1970,[1,2] and it was said to exist in a molecular conformation with C_{3h} symmetry, as reflected in its high melting point (465K) and its simple infrared spectrum; and as suggested by evaluation of steric interactions in various models.[2]

Manxane and some of its derivatives have been studied by dynamic NMR.[1,3] and most of the properties were rationalized on the basis of a proposed flattening of the bridgehead regions. Molecular mechanics calculations[4] also favoured the C_{3h} model and it was shown that even this conformation was highly strained, in contrast to the flexibility observed for most monocyclic eight-membered rings. The strain is reflected in considerable deviations from the tetrahedral value for the C–C–C angles, with flattening of the bridgehead regions and the angles in the chains approaching 120°. Conversion of a bridgehead to a trigonal center was found to relieve strain and this was related to the enhanced cation and radical reactivity at these sites.[5] Crystal-structure determinations have shown that the two derivatives, 1-azabicyclo [3.3.3]undecane hydrochloride[6] and bicyclo[3.3.3]undecane-1,5-diol,[7] have the expected structural features. However, the heat of formation, calculated from a force field,[8] is not in good agreement with the experimental value.[9]

Manxane itself is not a good subject for crystallographic investigations since it is disordered, sublimes readily, and reacts rapidly with atmospheric oxygen. Hence it was decided to study the molecular structure of manxane by gas-phase electron diffraction: the results are reported in the present paper.

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Table 1. Weighing functions, correlation parameters and scale factors.[a]

Camera height	Wave-length	Δs	s_{min}	sw_1	sw_2	s_{max}	Correlation parameter	Scale factor
mm	pm	nm^{-1}						
247.8	5.871	4	40	50	250	292	−0.145	0.700(12)
497.8	5.871	2	20	50	120	148	−0.031	0.732(10)

[a] See Ref. 13 for explanation of the symbols.

EXPERIMENTAL

Manxane was prepared according to literature procedures.[1] The electron-diffraction photographs were taken in Oslo using a Balzers' Eldigraph KDG-2,[10] Kodak Electron Image plates, nozzle-to-plate distances of 497.82 and 247.84 mm, an accelerating voltage of 42 kV, and a nozzle temperature of about 380 K. The electron wavelength was calibrated against diffraction patterns of gaseous benzene and its estimated uncertainty is 0.1 %.

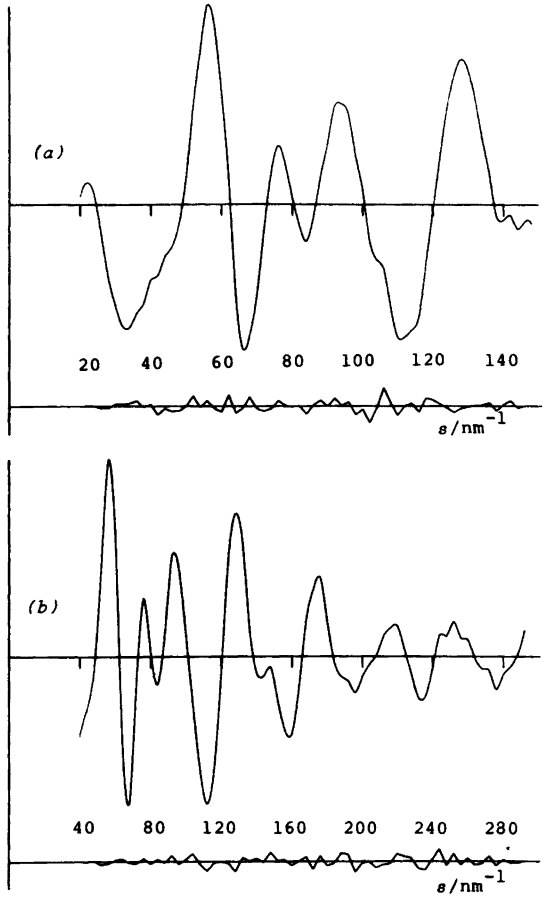

Fig. 1. Experimental molecular scattering intensities for nozzle-to-plate distances of (a) 248 and (b) 498 mm; and the corresponding final weighed difference curves according to the parameter values of Tables 2 and 3.

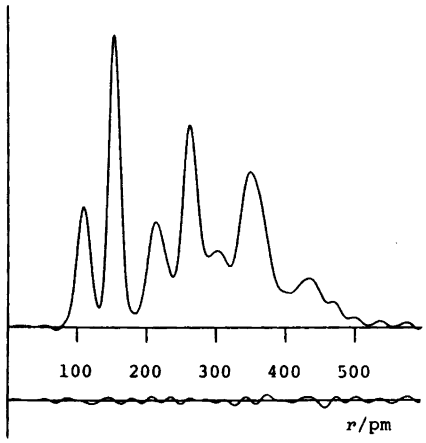

Fig. 2. Experimental radial distribution curve, $P(r)/r$, and difference curve corresponding to the intensities in Fig. 2. Before Fourier inversion the data were multiplied by s. $\exp[-0.000020\ s^2]/(Z_c-f_c)^2$.

The optical densities (D) of three and four plates for the long and short camera distances, respectively, were recorded using the Joyce-Loebl Microdensitometer 6 at the S.E.R.C. Laboratory, Daresbury.[11] The data reduction was carried out by the established programs[12] modified to accomodate sector- and blackness-$[1.+0.03D+0.09D^2+0.03D^3]$ corrections appropriate for data from the Balzers' Eldigraph in Oslo. At the final stage handdrawn background subtractions were replaced by automatic corrections using spline functions. An established least-squares refinement program[13] was used in the structure analysis. The data ranges and the parameters of the off-diagonal weighting functions are given in Table 1 together with the scale factors and the correlations parameters. The complex scattering factors of Schäfer *et al.*[12] were used, and all calculations were carried out on an ICL 2972 computer.

The experimental molecular intensities and the corresponding radial distribution curve are shown in Fig. 1 and 2, respectively.

STRUCTURE ANALYSIS

Preliminary analysis showed that the data could be interpreted in terms of a molecular structure of C_{3h} symmetry with geometrical parameters compatible with those obtained in molecular mechanics calculations,[4] and crystallographic studies of related compounds.[6,7]

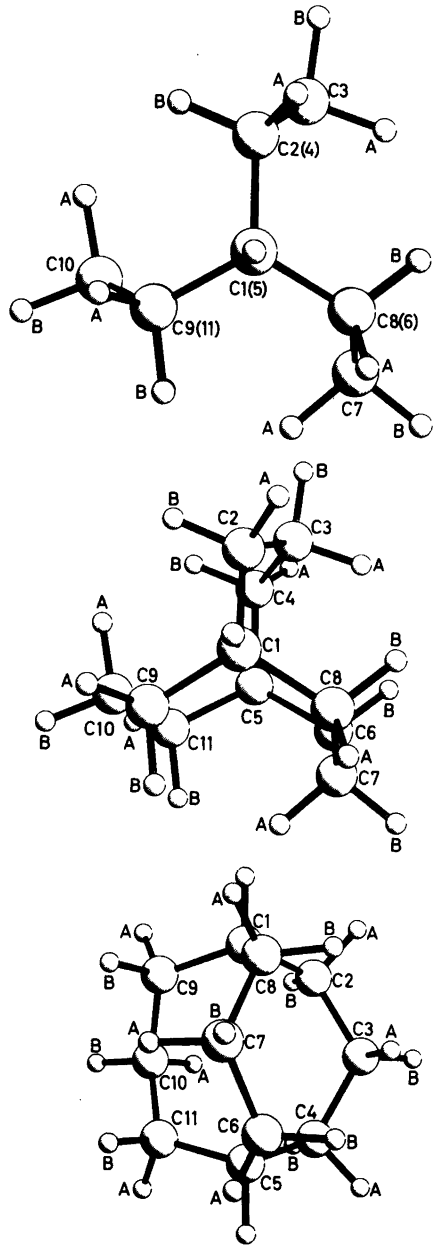

Fig. 3. Three views of the manxane molecule corresponding to the parameter values of Table 2. The numbering of the carbon atoms and the A- and B-labelling of the methylene hydrogen atoms are included. Fig. 3(a) is a projection along the threefold axis through H1, C1, C5 and H5, and Figs. 3(b) and 3(c) are perspective views.

The first two peaks of the radial distribution curve (Fig. 2) represent three types of C–H and two types of C–C bond distances, at 110 and 150 pm, respectively. The next feature, at about 215 pm, contains all one-angle C···H distances. The other types of C···H interactions are found over the whole range of r>260 pm and they are, together with H···H distances, the only contributors to the area beyond 400 pm. However, the main components of the peaks at 260, 300 and 350 pm are C···C distances: three types of one-angle distances at 260 pm; the C3···C8 interactions (see Fig. 3 for numbering of the carbon atoms) at 300 pm and the remaining five types at about 350 pm. The distance distribution is fairly complex and the identification of the C···C distances is obscured by significant contributions from C···H distances in the 260–390 pm region. However, the position of the peak containing the one-angle C···C distances at a large r-value gives direct evidence for the flattening of the bridgehead and widening of ∠(C–C–C) at C2 and C3.

Two perspective views of the manxane molecule and a projection down the C_3 axis are shown in Fig. 3 which also includes the numbering of the atoms. In addition to the C_{3h} molecular symmetry it was assumed that the methylene groups (C–CH_2–C) deviated from local C_{2v} symmetry only by possible differences Δr(C–C) and by a tilt in the CH_2-plane. The tilt parameter (γ) is the angular deviation from co-linearity of the bisectors for ∠(HCH) and ∠(CCC). Inspection of molecular models showed that such tilt could effectively contribute a relief in steric strain: H3A···H8B is lengthened by positive tilt of $C2H_2$ and by negative tilt of $C3H_2$, *i.e.* for γ(C2)>0 and γ(C3)<0°. It was not found worthwhile to distinguish the C–H bond length for the two bridgehead hydrogens from that associated with the eighteen hydrogens of the C–CH_2–C groups. The two *symmetrically* different types of r(C–C) were described by an average, $r(C-C)_{av,}$, and a difference, $\Delta(CC)=r(C2-C3)-r(C1-C2)$. The two types of tilt parameters, γ(C2) and γ(C3), were maintained, but the two types of valence angles, ∠(H–C2–H) and ∠(H–C3–H), were assumed to be of equal magnitude. The molecular geometry was thus described by nine parameters as given in Table 2, which also contains dependent geometrical quantities.

Normal coordinate calculations were carried out to provide a basis for assumptions regarding the magnitudes of the root-mean-square amplitudes of vibration (u-values); and for shrinkage corrections valid for small amplitude molecular vibrations, *i.e.* r_a-refinements. In the r_a-refinements, $r_a=r_\alpha-u^2/r+K$ where K is the calculated perpendicular amplitude correction coefficient; and u is the calculated or refined value in the actual least-squares fitting procedure.

Such calculations of u- and K-values for other cyclic hydrocarbons have been performed using Urey-Bradley force constants taken from force fields for cyclohexane. Two sets of values are currently in use, derived from the force fields

Table 2. Geometrical parameters[a] for manxane, and final least-squares results.[b] See Table 3 for the corresponding interatomic distances and amplitude parameters and Table 4 for elements of the correlation matrix.

Independent parameters (r_a, ∠$_a$, θ_a)		Dependent angles (∠$_a$, θ_a)	
p1, r(C–H)	108.8(2)	∠(C2–C3–C4)	117.7(8)
p2, r (CC_{AV})	153.8(1)	∠(C2–C1–C8)	113.5(9)
p3, Δ(CC)	−0.3(27)	θ(C1–C2···C4–C3)	124.4(11)
p4, ∠(C2–C1–H1)	105.1(11)	θ(C1–C2–C3–C4)	67.4(15)
p5, ∠(C1–C2–C3)	120.3(11)	θ(C3–C2–C1–C8)	36.1(24)
p6, θ(H1–C1–C2–C3)	150.4(8)	θ(C3–C2–C1–C9)	95.4(9)
p7, ∠(H–C–H)	101.6(15)		
p8, γ(C2)	4.8 fixed[c]		
p9, γ(C3)	2.6 fixed[c]		

a See text for model restrictions and explanation of symbols. *b* Ditances (r) in pm and angles in degrees; values in parentheses are least-squares standard deviations, *i.e.* systematic uncertainties are not accounted for. R_G=0.069 [R_D=0.073]. *c* See text.

Table 3. Interatomic distances[a] (r_a) and amplitudes of vibration (u) corresponding to the electron-diffraction structural parameters of Table 2; and u- and K-values calculated from force field A (Table 5) for manxane at 373K.

	Electron diffraction			Force-field calculations[c]	
	r_a/pm	u/pm[b]		u/pm	K/pm
C1–H1	109.7(2)	7.0(3)	*u1*	7.88	1.41
C2–H2A	110.4(2)	7.0		7.94	2.08
C3–H3A	110.3(2)	7.0 } −*u1*		7.93	1.98
C1–C2	154.3(13)	5.2(2)	*u2*	5.37	0.48
C2–C3	154.1(14)	5.2 −*u2*		5.31	0.60
C2···C4	263.3(32)	7.1(7)	*u3*	7.67	0.48
C1···C3	267.0(15)	7.1		7.54	0.31
C2···C8	257.7(15)	7.1 } −*u3*		7.83	0.45
C3···C8	304.9(9)	11.5(6)	*u4*	12.66	0.26
C1···C4	337.5(12)	9.6(12)	*u5*	9.12	0.19
C1···C5	343.0(40)	9.6		9.08	0.11
C3···C7	353.8(11)	12.1 } −u5		11.72	0.22
C2···C7	356.2(5)	9.6		8.72	0.27
C2···C6	367.9(18)	12.1		10.95	0.19
C2···H1	210.7(25)	10.8(4)	*u6*	10.74	0.94
C1···H2A	212.9(12)	10.8		10.70	1.48
C1···H2B	218.0(12)	10.8		10.71	1.47
C3···H2A	212.8(13)	10.8		10.68	1.55
C3···H2B	217.9(14)	10.8 } −*u6*		10.69	1.62
C2···H3A	214.9(9)	10.8		10.68	1.55
C2···H3B	217.7(9)	10.8		10.66	1.45
C3···H1	347.1(17)	12.1 −u5		11.42	0.58
C2···H5	437.7(13)	15.5(12)	*u7*	11.71	0.42
C1···H5	451.7(39)	15.5 −*u7*		11.46	0.34
C1···H3A	287.8(22)	16.5 −*u4*		15.77	0.92
C1···H3B	356.4(12)	11.0 (fixed)		10.95	0.88
C2···H4A	351.3(31)	12.1 −*u5*		10.98	1.16
C2···H4B	292.1(44)	16.5 −*u4*		16.07	1.12
C1···H4A	435.9(13)	15.5 −*u7*		11.53	0.69
C1···H4B	377.3(20)	21.4 −*u5*		18.61	0.59
C3···H8B	285.7(26)	23.1 −*u4*		22.97	0.77
C3···H8A	408.0(11)	19.1(25)	*u8*	15.62	0.75
C3···H9A	421.5(18)	19.1 −*u8*		14.54	0.72
C3···H9B	438.7(11)	20.6 −*u7*		14.28	0.72
C3···H7A	418.5(21)	19.1 −*u8*		15.91	0.62
C3···H7B	441.2(11)	20.6 −*u7*		16.11	0.61
C3···H10A	312.6(25)	23.1 −*u4*		22.38	0.64
C3···H10B	458.0(15)	20.6 −*u7*		14.89	0.60
C2···H8A	340.0(16)	12.1 −*u8*		11.90	1.12
C2···H8B	265.8(19)	16.5 −*u4*		15.93	1.14
C2···H9A	297.7(30)	16.5 −*u4*		14.96	1.09
C2···H9B	350.4(16)	12.1 −*u5*		11.17	1.08
C2···H7A	399.4(14)	19.1 −*u8*		16.08	0.68
C2···H7B	449.5(11)	15.5 −*u7*		12.26	0.69
C2···H10A	269.2(25)	21.4 −*u5*		22.35	0.82
C2···H10B	400.9(13)	19.1 −*u8*		15.96	0.71
C2···H6A	475.7(16)	15.5 −*u7*		12.75	0.60
C2···H6B	378.5(35)	23.1 −*u4*		22.32	0.50
C2···H11A	446.5(10)	20.6 −*u7*		16.67	0.67
C2···H11B	442.0(27)	20.6 −*u7*		16.60	0.62

[a] H···H distances were included in refinements, but are not listed here. [b] Eight groups of independent amplitude variables, *u1* to *u8*; the remainder of the u-values are tied to these as indicated by −*u1* to −*u8*. [c] Based on atomic coordinates corresponding to preliminary geometrical parameters: p_1=110.2, p_2=154.2, p_3=0, p_4=105.6, p_5=120.3, p_6=149.2, p_7=107.5, p_8=p_9=0. (See Table 2 for definitions and results.)

given by, (a): Schachtschneider and Snyder,[15] by (b): Takahasi *et al.*,[16] as for example in electron-diffraction studies of bicyclo[3.1.0]hexane,[17] and bicyclo[3.3.1]nonane,[18] respectively. We carried out calculations for manxane with both sets of force constants using a computer program originally written by R. L. Hilderbrandt.[19] The literature values[16] for set B were scaled, and since several interaction elements of the original force field were omitted, the selected force constants were adjusted to optimize the fit to the observed normal frequencies for cyclohexane before they were transferred to manxane. The two force fields are given in Table 5. Similar values for the calculated amplitude quantities were obtained in both cases. The *u*- and *K*-values corresponding to force field A were chosen for the final structure refinements and they are given for T=373 K in Table 3, omitting the values for the H···H interactions. Complete tables of *u*- and *K*-values for manxane at 0, 273 and 373 K are available upon request.

Optimum values for Δ(CC), $\angle$(H−C−H) and the two tilt parameters were initially determined by refinements in which these parameters were not refined but varied systematically over a range of values. Subsequently they were included with other geometrical parameters in both r_a- and r_α-refinements, although the tilt angles were fixed in the final refinements.

Refinements of *u*-values were included at two levels. Firstly, all amplitudes associated with C···H interactions, except for bond and one-angle distances, were fixed at calculated values, as were those associated with H···H interactions. The remaining amplitudes were refined as independent parameters or in groups in which the amplitudes were tied together by fixed rations as indicated by the magnitudes of the calculated *u*-values. Ultimately, all the amplitudes for the "long" C···H interactions were entered in the refinement scheme, but in this case the refinement diverged unless the two CH_2-tilt parameters were excluded from the refinement.

Table 4. Elements ($\rho_{ij}\times100$) of the least-squares correlation matrix corresponding to parameter values and standard deviations of Tables 2 and 3. Only elements with magnitudes ≥40 are included.

	p1	*p3*	*p4*	*p5*	*p6*	*u1*	*u5*	*u7*	*k1*
p4		−76							
p5		−45	+90						
p6		+82	−87	−64					
p7	+41	+41							+42
u3				−64			−42		
u4		−41	+67	+68	−45		+65		
u5		−56	+91	+86	−74				
u6		−54	+51	+45			+42		
u8								+58	
k1						+70			
k2						+60			

Table 5. Force constants[a] of two approximate Urey-Bradley force fields for manxane, *A* and in parentheses, *B* (see text of article).

K(C−C)	2.23(2.34)	H(CCC)	0.69(0.70)
K(C−H_t)	3.94(4.12)	H(CCH_t)	0.32(0.37)
K(C−H_s)	4.02(4.12)	H(CCH_s)	0.33(0.37)
F(C···C)	0.32(0.20)	H(HCH)	0.52(0.54)
F(C···H)	0.55(0.48)	H_τ	0.078(0.144)
F(H···H)	0.05(0.07)		

[a] In 100 aJ nm^{-2} (K and F) and aJ rad^{-2} (H); 1aJ=1 mdyn Å.

Table 6. Structural parameters for manxane (I) determined by electron diffraction (ED) and molecular mechanics calculations (MM) and for the 1,5-diol (II) and 1-aza (III) derivatives determined by X-ray diffraction (XD).[a].

	I(ED)[b] This work	I(MM) Ref. 4	II(XD)[c] Ref. 7	III(XD)[c] Ref. 6
r(C1–C2)	154.3(26)	154.2	152.9(7)	154.3(6)
r(C2–C3)	154.1(28)	153.5	152.3(8)	151.1(9)[d]
∠(C2–C1–C8)	113.5(18)	115.2	113.8(2)	113.9(6)
∠(C1–C2–C3)	120.3(22)	118.8	118.7(6)	118.1(5)
∠(C2–C3–C4)	117.7(16)	118.3	120.5(5)	119.7(6)
θ(H–C1–C2–C3)	150.1(22)	–	151.5(18)	–
θ(C8–C1–C2–C3)	36.1(48)	–	37.7(8)	39.5(5)
θ(C9–C1–C2–C3)	95.4(18)	–	94.7(8)	96.6(6)
θ(C1–C2–C3–C4)	67.4(30)	–	68.3(8)	67.7(4)
θ(C1–C2···C4–C3)	124.4(22)	–	121.0(–)	–

[a] Distances in pm, angles in degrees. [b] The values in parentheses are 2σ (*cf.* Table 4); the average r(CC) is determined with higher accuracy than the individual bonds, 2σ=0.2 pm; r_a and $\angle_\alpha$ values are given. [c] The values are $\bar{x}=\Sigma x_i/n$, averaged over the C_3- and/or C_h-symmetry equivalent parameters and the uncertainties in parentheses are $[\Sigma(x_i-\bar{x})^2/n\text{-}1]^{\frac{1}{2}}$ as compared to the quoted σ-values for the individual determinations of: II, 0.5–1.0 pm (r), 0.4–0.8° (∠) and 1.0°(θ); III, 0.5 pm (r) and 0.2–0.3° (∠). [d] See text for systematic errors.

In the various refinements the difference in length of the two types of C–C bonds was never significantly different from zero. The angle parameters for the carbon skeletons *p*4, *p*5 and *p*6 (see Table 3) varied in the ranges 104.1(4) to 105.5(13)°, 118.7(4) to 120.6(9)°, and 150.1(9) to 150.7(6)°, respectively. This invariably gave ∠(C1–C2–C3)>∠(C2–C3–C4), although not significantly so in all cases. The r_α-refinements generally gave a smaller ∠(H–C–H) than the corresponding r_a-refinements: 101.0(15) to 102.4(14)° and 102.9(13) to 103.7(13)°, respectively for $\angle_\alpha$ and $\angle_a$. The tilt parameters, γ(C2) and γ(C3), varied in the ranges 2.2(34) to 4.8(18)° and −1.8(24) to 4.8(18)°, respectively.

The possibility that the refined structure could be ambiguous, due to the fairly complex C···C distance overlaps, was considered. Refinements from various starting values for *p*4 to *p*6 (see Table 2) were carried out with special attention to the relative magnitudes on the one-angle C···C distances. However, these refinements ultimately converged to the same minimum, thus indicating that the structural results obtained are unique.

The final results are presented in Tables 2–4. They were obtained in r_α-refinements for which the tilt parameters were fiexed at values γ(C2)=4.8(18) and γ(C3)=2.6(17)°, obtained in a previous r_α-refinements with the amplitude parameters fixed at the calculated values. The *R*-factors for the final results were R_G=0.069 and R_D=0.073, and the corresponding weighted difference molecular intensities and the radial distribution difference curve are shown in Figs. 1 and 2. The fit to the experimental data, as reflected by the difference curves and *R*-factors, is satisfactory considering that the diagrams had low optical density which gave a relatively low signal to noise ratio.

DISCUSSION

The values of the geometrical parameters for the carbon skeleton of manxane are given in Table 6 which also contains corresponding results from the molecular mechanics calculations[4] and from X-ray diffraction studies of two derivatives.[6,7] There is generally a good agreement in the features of the structures.

Compared to tetrahedral arrangements there is flattening of the bridgehead and also a widening of the other chain angles. However, it appears that the MM-results overestimate the flattening somewhat at the expense of the opening of the chain angles, and the ED-results suggest that the central chain angle is smaller than that of C2, contrary to the XD-results. The latter difference could be due to effects from substitution by OH-groups in 1,5-positions and by nitrogen in

the frame at C1. In spite of failed attempts to fit models with reverse relative magnitudes for these angles it should be noted that their determination by electron diffraction is inaccurate: the difference of 2.3° is not significantly different from zero at a 2σ-level, and the analysis is hampered by severe distance overlaps.

It is interesting to note that in the analogous compound with triangularly bridged cyclohexane rings, bicyclo[2.2.2]octane, there are only minor deviations from tetrahedral angles in the carbon skeleton.[20] The flexible cyclooctane has average carbon valence angles of 116.6°,[21] whereas in bicyclo[3.3.1]nonane the bridged cyclooctane ring, which at room temperature exists predominately in the chair, chair conformation with respect to the bridge, has such angles in the range 111.9–113.2°.[18] It has been noted that in molecules with a bridged cyclooctane ring there is an increase in angle strain with the size of the bridge[7] as reflected in the quoted values for bicyclo[3.3.1]nonane, values of 116–117° for a derivative of bicyclo[3.3.2]decane[22] and of 118–120° for bicyclo[3.3.3]undecane derivatives (Table 6). In the bicyclo[3.3.2]decane derivative the eight-membered ring is in a boat, chair conformation with respect to the bridge as is the case of manxane. Steric H···H repulsions between neighbouring bridges are believed to be responsible for the strain in these molecules.[6,7]

Thus in manxane the *endo* hydrogens of C3 are pushed apart from the buttressing intraannular hydrogen atoms of C6 and C8 so as to give the shortest H···H distance between neighbouring bridges of 220(4) pm, rather than about 130 pm which would appear in a model with tetrahedral CCC angles. This repulsion is also seen in the opening of the angles between the C2–C3–C4 and C1–C2–C4–C5 planes to 124.4(22)° from about 96° in the tetrahedral model, as shown in Fig. 3a. The torsional angles about the central C–C bonds are also interesting since staggered conformation is approached with θ(C1–C2–C3–C4)=67.4(30)°, rather than above 90° as in the tetrahedral model. The methylene tilt parameter (Table 3) at C3(C7, C10) is probably not significantly different from zero and it counteracts the lengthening of the H3A···H8B interactions obtained by positive tilt at C2(C4, C8, C6, C9, C11).

The two types of C–C bonds in manxane are not significantly different in length (Table 6). It should be noted that the average value (Table 3) is determined with high accuracy compared with the uncertainty in the determination of the individual bonds, *i.e.* $r_a(C-C)_{average}$ = 154.2(2) pm, including a systematic uncertainty of 0.1 % in the estimated standard deviation.

The length of the C–C bonds in compound III (Table 6) is compatible with the corresponding bonds in manxane (C1–C2/C4–C5) whereas the apparently shorter bonds in compound II may be related to possible substitution effects from the OH-groups in the 1,5 positions. It has been stated that the determined lengths on bonds involving the three central methylene carbon atoms (C3, C7, C10) in III may be systematically too short due to thermal motions.[6]

The average C–C bond length in bicyclo[2.2.2]octane with bridged cyclohexane rings is 154.2(4) pm[20] as compared to a bond length of 153.6(4) pm in cyclohexane.[23] These molecules have similar C–C–C angles. The average C–C bond lengths of cyclooctane,[21] bicyclo[3.3.1]nonane[18] and the present bicyclo[3.3.3]undecane are 154.0, 153.6(1) and 154.2(2) pm, respectively, and it appears that the different steric strain in these molecules is not reflected in significant variations in the C–C bond lengths.

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