

Geometry of Three-Membered Rings in Triangulanes: an X-ray Structural Study and Additivity Scheme for Carbon–Carbon Bond Lengths in Triangulanes

BY KIRILL A. LUKIN, SERGEI I. KOZHUSHKOV AND NIKOLAI S. ZEFIROV*

Department of Chemistry, Moscow State University, Moscow 119899, Russia

AND DMITRY S. YUFIT AND YURI' T. STRUCHKOV*

Nesmeyanov Institute of Organoelement Compounds, Vavilov St. 28, Moscow 117813, Russia

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Abstract

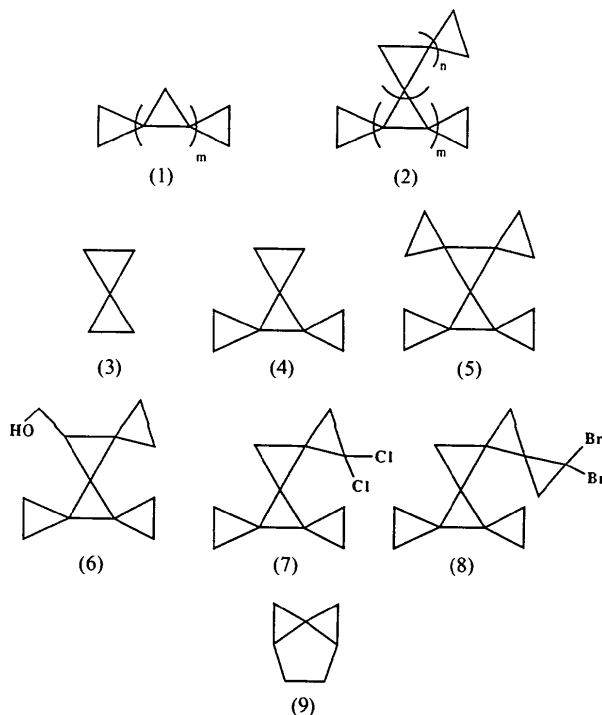
An X-ray structural study of two *gem*-dihalosubstituted triangulanes, possessing linear fragments of spiroannulated cyclopropanes, allowed us to work out an empirical calculation scheme describing the geometry of triangulanes. The crystal data for 1,1-dichlorotetraspiro[2.0.0.2.0.2.0.1]undecane ($C_{11}H_{12}Cl_2$, $M_r = 215.1$) measured at 173 K are: $P\bar{1}$, $Z = 2$, $a = 6.729$ (2), $b = 9.176$ (2), $c = 9.490$ (3) Å, $\alpha = 94.49$ (2), $\beta = 107.42$ (2), $\gamma = 103.12$ (2)°, $V = 537.7$ (6) Å³, $D_x = 1.33$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 5.56$ cm⁻¹, $F(000) = 224$. The final agreement factor was $R = 0.027$ for 2501 unique reflections. The crystal data for 1,1-dibromopentaspino[2.0.0.0.2.0.2.0.1.1]tridecane ($C_{13}H_{14}Br_2$, $M_r = 330.1$) measured at 183 K are: $P\bar{1}$, $Z = 2$, $a = 7.433$ (5), $b = 9.508$ (6), $c = 10.120$ (9) Å, $\alpha = 111.69$ (2), $\beta = 93.81$ (6), $\gamma = 100.23$ (5)°, $V = 647.1$ (8) Å³, $D_x = 1.69$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 61.7$ cm⁻¹, $F(000) = 324$. The final agreement factor was $R = 0.047$ for 2987 unique reflections.

Introduction

Recently, Zefirov, Kozhushkov, Kuznetzova, Kokoreva, Ugrak, Lukin & Tratch (1990) defined triangulanes as a unique class of strained hydrocarbons constructed exclusively from spiroannulated three-membered rings. They have demonstrated that, as a result of stereochemical and topological diversity, the number of isomeric triangulanes increases sharply with the number of three-membered rings. Thus one can speak about the 'land of triangulanes.' For the purpose of classification these compounds were subdivided into linear triangulanes (1) and branched triangulanes (2) (Zefirov *et al.*, 1990). Preliminary syntheses and studies of the chemistry of these compounds have shown the importance of steric effects in the chemistry of triangulanes (Zefirov *et al.*, 1990; Lukin, Andrievski', Kozhushkov, Ugrak

& Zefirov, 1991; Lukin, Masunova, Ugrak & Zefirov, 1991). It is, therefore, highly desirable to obtain a calculation scheme describing the geometry of triangulanes.

Most theoretical studies of simple triangulanes predict substantial asymmetry of the three-membered rings in these compounds (Rasmussen & Tori, 1985; Ioffe, Svyatkin & Nefedov, 1987). Calculated lengthening of C—C bonds distal to the spirocarbon probably results in partial release of strain induced by spiroannulation. Recently these predictions were supported by a structural study of spiro-pentane (3) (Boeze, Baser, Gomann & Blinker, 1989), the revised structure of 3-rotane (4) (Boeze, Miebach & DeMeijere, 1991), as well as by our structural studies of [6]triangulane (5) (Kozhushkov, Yufit, Lukin, Boeze, DeMeijere, Struchkov & Zefirov, 1991), and



* To whom correspondence should be addressed.

hydroxymethyl-[5]triangulane (6) – the first triangulane derivative possessing a linear fragment of spiroannulated cyclopropanes (Yufit, Kozhushkov, Lukin, DeMeijere, Struchkov & Zefirov, 1991). Here we report an X-ray structural study of triangulanes (7) and (8) (also possessing linear fragments) as well as a calculation scheme to predict the geometry of triangulanes.

Experimental

1,1-Dichlorotetraspiro[2.0.0.2.0.2.0.1]undecane (7)

Sodium hydroxide (4.5 g of a 40% aqueous solution) was added to a stirred solution of 1-methylenetrispiro[2.0.2.0.2.0]nonane (396 mg, 3 mmol) [prepared as described by Lukin, Andrievski', Kozhushkov, Ugrak & Zefirov (1991)] and benzyltriethylammonium chloride (50 mg) in chloroform (10 ml). The reaction mixture was stirred for 10 h at room temperature. Water (30 ml) was added and the organic layer was separated, washed with water, and dried with $MgSO_4$. The solvent was evaporated, and column chromatography gave dichloride (7) (561 mg, 87%): m.p. 299 K.

X-ray data were collected at 173 K, using a transparent prism-shaped crystal (size $0.2 \times 0.3 \times 0.5$ mm) with a Siemens P3/PC four-circle diffractometer, using graphite-monochromatized $Mo K\alpha$ radiation. Unit-cell parameters were determined from 24 reflections with $23 < 2\theta < 24^\circ$. The low temperature was achieved with a continuous N_2 -gas flow cryostat.

3017 reflections were measured ($-7 < h < 7$, $-12 < k < 12$, $-12 < l < 13$). 2774 unique reflections were obtained ($R_{int} = 0.013$). 2516 reflections had $F > 4\sigma(F)$ and were considered as observed. The intensities of two standard reflections were measured after every 98 reflections and their deviations during data collection were less than 2%. No absorption correction was applied. The structure was solved by direct methods and refined anisotropically by full-matrix least squares. All H atoms were obtained from the difference Fourier map and refined isotropically. Final $R = 0.027$; $wR = 0.027$ with $w = 1/[\sigma^2(F) + 0.0001F^2]$.*

The atomic scattering factors were taken from *SHELX* (Sheldrick, 1976). Final difference map excursions were 0.00 to $0.28 e \text{ \AA}^{-3}$. The maximum shift in the final refinement cycle was $\Delta/\sigma = 0.34$.

The programs in *SHELX-Plus* (PC version) (Sheldrick, 1990) were used in all calculations. Bond

* Lists of structure factors, anisotropic thermal parameters, 1H and ^{13}C NMR spectra of (7) and (8), and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55887 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0431]

distances are given in Fig. 1. Atomic coordinates and isotropic temperature factors are given in Table 1 and bond angles are given in Table 2.

1,1-Dibromopentaspiro[2.0.0.2.0.2.0.1.1]tridecane (8)

Sodium hydroxide (1.5 g of a 40% aqueous solution) was added to a stirred solution of 1-methylenetetraspiro[2.0.0.2.0.2.0.1]undecane (158 mg, 1 mmol) [prepared as described by Lukin, Andrievski', Kozhushkov, Ugrak & Zefirov (1991)], tributylamine (0.05 ml) and bromoform (6 mmol, 0.52 ml) in dichloromethane (2 ml). The reaction mixture was stirred for 10 h at room temperature. Water (30 ml) was added, and the organic layer was separated, washed with water, and dried with $MgSO_4$. The solvent was evaporated, and column chromatography gave dibromide (8) (210 mg, 65%): m.p. 328 K.

X-ray data collection was performed at 183 K as above, using a transparent prism-shaped crystal (size $0.7 \times 0.35 \times 0.2$ mm). Unit-cell parameters were determined from 20 reflections with $22 < 2\theta < 23^\circ$.

3217 reflections were measured ($0 < h < 9$, $-12 < k < 12$, $-13 < l < 13$). 3217 unique reflections were obtained ($R_{int} = 0.029$). 2010 reflections had $F > 4\sigma(F)$ and were considered observed. The intensities of two standard reflections were measured after every 98 reflections and their deviations during data collection were less than 2%. The absorption correction was applied using the *XEMP* (Sheldrick, unpublished) procedure from φ -scan data of 11 reflections (minimum transmission 0.051, maximum transmission 0.021). The structure was solved by direct methods and refined anisotropically by full-matrix least squares. All H atoms were obtained from the difference Fourier map and refined isotropically. Final $R = 0.047$; $wR = 0.049$ with $w = 1/[\sigma^2(F) + 0.0001F^2]$.

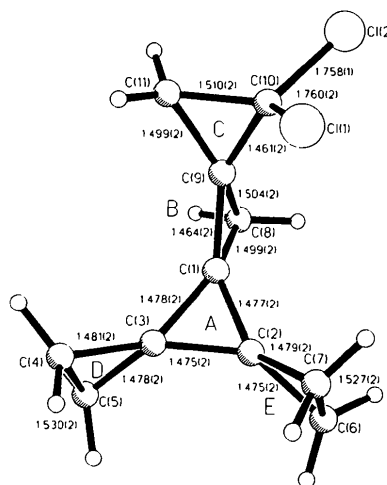


Fig. 1. X-ray structure of dichloride (7). Distances are given in Å.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) in structure (7)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_i tensor.

	x	y	z	U_{eq}
Ci(1)	1504 (1)	3384 (1)	5781 (1)	32 (1)
Ci(2)	2731 (1)	570 (1)	6297 (1)	40 (1)
C(1)	1574 (2)	2035 (1)	2280 (1)	22 (1)
C(2)	-432 (2)	2474 (1)	1572 (1)	21 (1)
C(3)	1545 (2)	3138 (1)	1225 (1)	23 (1)
C(4)	2829 (3)	4661 (2)	1169 (2)	32 (1)
C(5)	2185 (3)	3354 (2)	-121 (2)	33 (1)
C(6)	-2689 (2)	1657 (2)	718 (1)	28 (1)
C(7)	-2160 (2)	2959 (2)	1989 (1)	26 (1)
C(8)	2229 (3)	591 (2)	2501 (1)	29 (1)
C(9)	2911 (2)	1885 (1)	3767 (1)	23 (1)
C(10)	2877 (2)	2105 (1)	5299 (1)	24 (1)
C(11)	4949 (2)	2733 (2)	4983 (2)	29 (1)

Table 2. Bond angles ($^\circ$) in structure (7)

C(2)—C(1)—C(3)	59.9 (1)	C(3)—C(4)—C(5)	58.8 (1)
C(2)—C(1)—C(8)	137.0 (1)	C(3)—C(4)—C(5)	58.9 (1)
C(3)—C(1)—C(8)	138.3 (1)	C(2)—C(6)—C(7)	59.0 (1)
C(2)—C(1)—C(9)	139.4 (1)	C(2)—C(7)—C(6)	58.8 (1)
C(3)—C(1)—C(9)	138.5 (1)	C(1)—C(8)—C(9)	58.4 (1)
C(8)—C(1)—C(9)	61.0 (1)	C(1)—C(9)—C(8)	60.6 (1)
C(1)—C(2)—C(3)	60.1 (1)	C(1)—C(9)—C(10)	137.4 (1)
C(1)—C(2)—C(6)	135.5 (1)	C(8)—C(9)—C(10)	137.3 (1)
C(3)—C(2)—C(6)	136.6 (1)	C(1)—C(9)—C(11)	139.8 (1)
C(1)—C(2)—C(7)	139.5 (1)	C(8)—C(9)—C(11)	137.3 (1)
C(3)—C(2)—C(7)	139.5 (1)	C(10)—C(9)—C(11)	61.4 (1)
C(6)—C(2)—C(7)	62.3 (1)	Ci(1)—C(10)—Ci(2)	112.0 (1)
C(2)—C(3)—C(4)	137.9 (1)	Ci(1)—C(10)—C(11)	118.5 (1)
C(1)—C(3)—C(5)	137.5 (1)	Ci(2)—C(10)—C(11)	118.2 (1)
C(2)—C(3)—C(5)	137.7 (1)	C(9)—C(10)—C(11)	60.6 (1)
C(4)—C(3)—C(5)	62.3 (1)	C(9)—C(11)—C(10)	58.1 (1)
C(1)—C(3)—C(2)	60.0 (1)	Ci(1)—C(10)—C(9)	118.7 (1)

The atomic scattering factors were taken from *SHELX*. Final difference map excursions were -0.85 to 0.77 e \AA^{-3} . The maximum shift in the final refinement cycle was $\Delta/\sigma = 0.86$.

The programs in *SHELX-Plus* (PC version) were used in all calculations. Bond distances are given in Fig. 2. Atomic coordinates and isotropic temperature factors are given in Table 3, and bond angles are collected in Table 4.

Results and discussion

Recently, we suggested a general synthetic approach to both types of triangulanes, linear (1) and branched (2), and reported the preparation of a number of triangulanes containing four, five and six three-membered rings (Zefirov *et al.*, 1990; Lukin, Andrievski, Kozhushkov, Ugrak & Zefirov, 1991). Unfortunately, all attempts to obtain triangulanes possessing linear fragments in crystalline form were unsuccessful. However, it was possible to obtain crystals of some derivatives of such triangulanes, namely, the alcohol (6) (Yufit *et al.*, 1991) and the dihalides (7) and (8). These dihalides were prepared by cycloaddition of dihalocarbenes to the corresponding olefins.

An X-ray structural study of compounds (7) and (8) (Figs. 1 and 2) revealed substantial differences in C—C bond lengths in the three-membered rings. Particular changes in C—C bond lengths include: (a) lengthening of distal bonds and shortening of vicinal bonds adjacent to spirocarbons in terminal cyclopropane rings; (b) significant shortening of bonds connecting two spiro atoms in dispiro-substituted cyclopropane moieties and (c) shortening of C—C bonds in trispiro-substituted cyclopropane fragments. Such changes in the geometry of the three-membered rings in compounds (7) and (8) are in agreement with previous structural studies (Boeze, Baser, Gomann & Blinker, 1989; Boeze, Miebach & DeMeijere, 1991; Kozhushkov *et al.*, 1991; Yufit *et al.*, 1991). Moreover, comparison of structures (4), (7) and (8) shows that introduction of a new spiroannulated cyclopropyl fragment (even possessing halogen substituents) in the β -position to the three-membered ring under consideration does not influence the geometry of the latter.

The structural data now available on triangulanes (3)–(8) enabled us to try to obtain a quantitative estimation of the asymmetry of three-membered rings induced by spiroannulation in triangulanes. Initially we examined the possibility of using the well known Allen approach for describing the geometry of substituted cyclopropanes (Allen, 1980). For this purpose average bond lengths (D) in terminal cyclopropane fragments of triangulanes (3)–(8), as well as in the related compound (9), were calculated. Then a distal-bond lengthening parameter (δ^+) was calculated as the average of $\delta_n^+ = D - D_n$, where D_n is the length of a type D bond in (3)–(8) (for definition see Fig. 3). The vicinal-bond shortening parameter (δ^-) was obtained as $\delta^- = 0.5\delta^+$ (Allen, 1980). Estimated

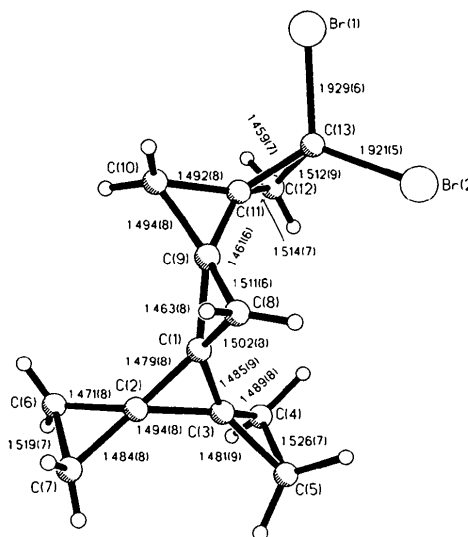


Fig. 2. X-ray structure of dibromide (8). Distances are given in \AA .

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) in structure (8)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	2935 (1)	8509 (1)	8370 (1)	45 (1)
Br(2)	2735 (1)	12043 (1)	9161 (1)	46 (1)
C(1)	8005 (7)	13162 (6)	7656 (5)	28 (2)
C(2)	9286 (7)	13482 (6)	6694 (5)	29 (2)
C(3)	7477 (7)	13962 (6)	6726 (6)	31 (2)
C(4)	5909 (8)	13851 (6)	5673 (6)	36 (2)
C(5)	6823 (9)	15392 (7)	6890 (7)	42 (2)
C(6)	10290 (8)	12592 (7)	5587 (7)	39 (2)
C(7)	11256 (8)	14156 (7)	6734 (7)	40 (2)
C(8)	7975 (8)	13372 (6)	9199 (6)	33 (2)
C(9)	7184 (7)	11829 (6)	7978 (5)	28 (2)
C(10)	7290 (8)	10174 (6)	7600 (6)	32 (2)
C(11)	5484 (7)	10631 (5)	7502 (5)	26 (2)
C(12)	3768 (8)	10135 (7)	6408 (6)	33 (2)
C(13)	3682 (7)	10331 (6)	7953 (6)	31 (2)

Table 4. Bond angles ($^\circ$) in structure (8)

C(2)—C(1)—C(3)	60.5 (4)	C(1)—C(8)—C(9)	58.1 (3)
C(2)—C(1)—C(8)	140.6 (4)	C(1)—C(9)—C(8)	60.6 (4)
C(3)—C(1)—C(8)	136.7 (5)	C(1)—C(9)—C(10)	139.5 (5)
C(2)—C(1)—C(9)	137.3 (5)	C(8)—C(9)—C(10)	137.2 (5)
C(3)—C(1)—C(9)	137.4 (4)	C(1)—C(9)—C(11)	137.3 (5)
C(8)—C(1)—C(9)	61.3 (4)	C(8)—C(9)—C(11)	138.7 (5)
C(1)—C(2)—C(3)	59.9 (4)	C(10)—C(9)—C(11)	60.7 (4)
C(1)—C(2)—C(6)	136.9 (5)	C(9)—C(10)—C(11)	58.6 (3)
C(3)—C(2)—C(6)	136.4 (5)	C(9)—C(11)—C(10)	60.8 (4)
C(1)—C(2)—C(7)	140.1 (5)	C(9)—C(11)—C(12)	137.8 (6)
C(3)—C(2)—C(7)	138.4 (5)	C(10)—C(11)—C(12)	137.3 (4)
C(6)—C(2)—C(7)	61.9 (4)	C(9)—C(11)—C(13)	138.8 (4)
C(1)—C(3)—C(2)	59.5 (4)	C(10)—C(11)—C(13)	138.0 (6)
C(1)—C(3)—C(4)	140.0 (5)	C(12)—C(11)—C(13)	61.1 (4)
C(2)—C(3)—C(4)	137.7 (5)	C(11)—C(12)—C(13)	57.7 (4)
C(1)—C(3)—C(5)	137.8 (5)	Br(1)—C(13)—Br(2)	111.8 (3)
C(2)—C(3)—C(5)	137.0 (5)	Br(1)—C(13)—C(11)	119.4 (4)
C(4)—C(3)—C(5)	61.8 (4)	Br(2)—C(13)—C(11)	119.4 (3)
C(3)—C(4)—C(5)	58.9 (4)	Br(1)—C(13)—C(12)	118.8 (3)
C(3)—C(5)—C(4)	59.3 (4)	Br(2)—C(13)—C(12)	117.8 (4)
C(2)—C(6)—C(7)	59.5 (4)	C(11)—C(13)—C(12)	61.2 (4)
C(2)—C(7)—C(6)	58.6 (4)		

values of $\delta^+ = 0.032$, $\delta^- = 0.016$ \AA were found to be quite satisfactory for describing the geometry of terminal cyclopropane fragments in triangulanes (3)–(8).

Application of the additivity principle to bispiro- and trispiro-substituted cyclopropyl moieties in triangulanes (3)–(8) gave the following results:

(a) For disubstituted three-membered rings the additivity scheme gave a good prediction for the

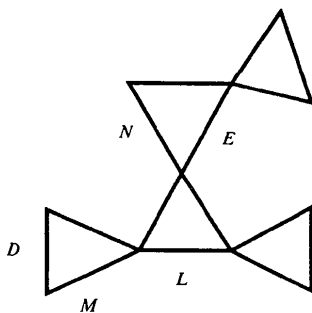


Fig. 3. Definition of C—C bond types in triangulanes.

Table 5. Experimental and calculated bond lengths in compound (7)

Bond	Bond type	Experimental	Calculated	Bond	Bond type	Experimental	Calculated
C(1)—C(2)	<i>L</i>	1.477	1.481	C(1)—C(3)	<i>L</i>	1.478	1.481
C(1)—C(8)	<i>N</i>	1.499	1.500	C(1)—C(9)	<i>E</i>	1.464	1.463
C(2)—C(3)	<i>L</i>	1.475	1.481	C(2)—C(7)	<i>M</i>	1.479	1.480
C(2)—C(6)	<i>M</i>	1.475	1.480	C(3)—C(5)	<i>M</i>	1.478	1.480
C(3)—C(4)	<i>M</i>	1.481	1.480	C(4)—C(5)	<i>D</i>	1.530	1.528
C(6)—C(7)	<i>D</i>	1.527	1.528	C(8)—C(9)	<i>N</i>	1.504	1.500
C(9)—C(10)	<i>M</i>	1.461	—	C(9)—C(11)	<i>M</i>	1.499	—
C(10)—C(11)	<i>D</i>	1.510	—				

Table 6. Experimental and calculated bond lengths in compound (8)

Bond	Bond type	Experimental	Calculated	Bond	Bond type	Experimental	Calculated
C(1)—C(2)	<i>L</i>	1.479	1.481	C(1)—C(3)	<i>L</i>	1.485	1.481
C(1)—C(8)	<i>N</i>	1.502	1.500	C(1)—C(9)	<i>E</i>	1.463	1.463
C(2)—C(3)	<i>L</i>	1.494	1.481	C(2)—C(7)	<i>M</i>	1.484	1.480
C(2)—C(6)	<i>M</i>	1.471	1.480	C(3)—C(5)	<i>M</i>	1.481	1.480
C(3)—C(4)	<i>M</i>	1.489	1.480	C(4)—C(5)	<i>D</i>	1.526	1.528
C(6)—C(7)	<i>D</i>	1.519	1.528	C(8)—C(9)	<i>N</i>	1.511	1.500
C(9)—C(10)	<i>N</i>	1.494	1.500	C(9)—C(11)	<i>E</i>	1.461	1.463
C(10)—C(11)	<i>N</i>	1.492	1.500	C(11)—C(12)	<i>M</i>	1.514	—
C(11)—C(13)	<i>M</i>	1.459	—	C(12)—C(13)	<i>D</i>	1.512	—

bond length between two spiro atoms (bond type *E*) $E = 1.464$ \AA [compare with the values $E = 1.464$ and 1.463 , 1.461 \AA in compounds (7) and (8) respectively]. For type *N* bonds the predicted value $N = 1.512$ \AA is also satisfactory.

(b) For trisubstituted three-membered rings the Allen scheme predicts no change in type *L* bond lengths in comparison with unsubstituted cyclopropanes ($C = 1.509$ \AA); this is in contradiction with the experimental data obtained for compounds (4)–(8), which displayed substantial shortening of type *L* bonds [average $L = 1.481$ \AA for compounds (4)–(11)].

(c) For dihalosubstituted three-membered rings application of the Allen δ^+ value for the chlorine atoms ($\delta^+ = 0.025$ \AA ; Allen, 1980) gave good agreement with experimental values, predicting $C(9)—C(10) = 1.467$, $C(10)—C(11) = 1.515$ and $C(9)—C(11) = 1.505$ \AA in (7) (compare with the data in Fig. 1).

However, for dibromide (8) the Allen value ($\delta^+ = 0$; Allen, 1980) does not describe the actual geometry of the bromine-substituted cyclopropyl fragment in (8). Corresponding bond lengths could be described using $\delta^+ = 0.036$ \AA for the bromine substituents.

In summary, application of the Allen approach for the prediction of the geometry of three-membered rings in triangulanes gave good results for mono- and disubstituted cyclopropane fragments. However, it overestimates the bond lengths in trispiro-substituted three-membered rings.

Fortunately, we have found that an even simpler empirical scheme could be used for correctly describing the geometry of cyclopropane and spiro-pentane shows

that spiroannulation results in lengthening of distal bonds ($\alpha = 0.018 \text{ \AA}$), and shortening of bonds vicinal to spiro atoms ($\beta = 0.032 \text{ \AA}$). The corresponding average values for terminal three-membered rings in compounds (3)–(8) are $\alpha = 0.020$ and $\beta = 0.028 \text{ \AA}$. Disubstituted cyclopropanes in (5)–(8) exhibit further shortening of the bonds connecting two spiro atoms. However, the corresponding β' value differs slightly from the additive one ($\beta' = 2\beta - 0.012 = 0.046 \text{ \AA}$). We have found that these three parameters, namely α , β and β' , and the standard value of C—C bond length in cyclopropane ($C = 1.508 \text{ \AA}$; Allen, 1980) can be used for correctly predicting bond lengths for all types of C—C bonds in triangulanes (3)–(8). Estimated values (Tables 5 and 6) for different types of C—C bonds in the triangulanes (for definitions see Fig. 3) are: $D = C + \alpha = 1.528$, $E = C - \beta' = 1.463$, $L = C + \alpha - 2\beta = 1.481$, $M = C - \beta = 1.480$, $N = C + \alpha - \beta = 1.500 \text{ \AA}$.

In conclusion, the X-ray structural study of triangulanes (7) and (8) allowed us to calculate an empirical scheme, providing an accurate description of the geometries of triangulanes (3)–(8), and hopefully, of other possible triangulanes.

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'Jumping Crystals': X-ray Structures of the Three Crystalline Phases of (\pm)-3,4-Di-*O*-acetyl-1,2,5,6-tetra-*O*-benzyl-*myo*-inositol

BY THOMAS STEINER, WINFRIED HINRICHS AND WOLFRAM SAENGER*

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, W-1000 Berlin 33, Germany

AND ROY GIGG

Laboratory for Lipid and General Chemistry, National Institute for Medical Research, Mill Hill, London NW7 1AA, England

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Abstract

(\pm)-3,4-Di-*O*-acetyl-1,2,5,6-tetra-*O*-benzyl-*myo*-inositol, $C_{38}H_{40}O_8$, $M_r = 624.7$ ('jumping crystal'). Three monoclinic crystal forms. Form I, $T = 18^\circ\text{C}$, $P2_1/n$, $a = 28.883$ (3), $b = 15.189$ (2), $c = 15.566$ (2) \AA , $\beta = 100.37$ (1)°, $V = 6717$ (1) \AA^3 , $Z = 8$, $R = 0.090$ for 5788 reflections [$F > \sigma(F)$]. Form II, $T = 18^\circ\text{C}$ [$T = 60^\circ\text{C}$], $P2_1/c$, $a = 14.269$ (2) [14.464 (6)], $b = 14.862$ (2) [14.923 (5)], $c = 16.506$ (3) \AA [16.385 (6) \AA], $\beta = 103.21$ (1)° [102.73 (3)°], $V = 3407$ (1) \AA^3 [3450 (2) \AA^3], $Z = 4$, $R = 0.086$ [0.093] for 3505 [2338] reflections [$F >$

$\sigma(F)$]. Form III, $T = 80^\circ\text{C}$, $P2_1/c$, $a = 16.261$ (8), $b = 15.230$ (8), $c = 14.385$ (7) \AA , $\beta = 96.73$ (4)°, $V = 3533$ (3) \AA^3 , $Z = 4$, $R = 0.083$ for 1651 reflections [$F > \sigma(F)$]. Cu $K\alpha$, Ni-filtered, $\lambda = 1.542 \text{ \AA}$. Phase transitions I \rightarrow II at 30°C , II \rightarrow III at 70°C , III \rightarrow II at 40°C , II \rightarrow I at 11°C . The transitions II \leftrightarrow III are accompanied by vigorous mechanical movements ('thermosalient behaviour') associated with large changes of the unit-cell constants ($\sim 12\%$ change in a and c , and 2.0% in V). The temperature dependence of the unit-cell constants was determined for forms II and III. The principal features of the packing are similar in all crystal forms, but the conformations of the flexible benzyl groups differ to some

* To whom correspondence should be addressed.