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Substituted Cyclopropanes. 4.* *cis*-1,2,3-Tribromocyclopropane and Hexabromocyclopropane

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Abstract. $C_3H_3Br_3$, $M_r = 278{\cdot}78$, orthorhombic, *Pnma*, $a = 5{\cdot}376$ (2), $b = 9{\cdot}921$ (3), $c = 11{\cdot}662$ (5) Å, $V = 621{\cdot}9$ Å^3, $Z = 4$, $D_x = 2{\cdot}98$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 19·1 mm^{-1}, $F(000) = 504$, $T = 293$ K, $R = 0{\cdot}053$ for 356 unique observed reflections. $C_3H_3Br_3$ is not isostructural with its trichloro analogue despite the fact that both crystallize in the same space group with imposed mirror symmetry. C_3Br_6, $M_r = 515{\cdot}49$, monoclinic, $P2_1/c$, $a = 11{\cdot}501$ (5), $b = 6{\cdot}448$ (3), $c = 13{\cdot}261$ (7) Å, $\beta = 112{\cdot}39$ (3)°, $V = 909{\cdot}4$ Å^3, $Z = 4$, $D_x = 3{\cdot}76$ Mg m^{-3}, μ(Mo $K\alpha$) = 26·2 mm^{-1}, $F(000) = 912$, $T = 293$ K, $R = 0{\cdot}063$ for 1034 unique observed reflections. C_3Br_6 is isostructural with C_3Cl_6. The mean C—C bond lengths of 1·465 Å ($C_3H_3Br_3$) and 1·544 Å (C_3Br_6) are interpreted in terms of a molecular mechanical model that relates the relaxation of non-bonded strain to the ease of deformation of the C—C–halogen angle.

Introduction. We have determined the crystal structures of *cis*-1,2,3-trichlorocyclopropane (1) and hexachlorocyclopropane (2) (Schrumpf & Jones, 1987*a,b*) to study the effect of chlorine substituents on the geometry of the cyclopropane ring. This appeared necessary because there had been conflicting results from studies on monochlorocyclopropane (Schwendeman, Jacobs & Krigas, 1964) and 1,1-dichlorocyclopropane (Hedberg, Hedberg & Boggs, 1982). In the trisubstituted molecule, we observed a marginally smaller (1·505 Å) and in the hexasubstituted derivative a substantially larger average CC bond (1·537 Å) than in either cyclopropane (1·510 Å; Bastiansen, Fritsch & Hedberg, 1964) or monochlorocyclopropane (1·514 Å; Schwendeman *et al.*, 1964). In (1), we interpreted this as a result of a balance between (*a*) an electronic interaction between the three chlorine substituents and the ring and (*b*) steric interaction among the chlorines. We suggested that the long ring bonds in (2) originate from non-bonded repulsive Cl···Cl interactions. Apparently, geminal disubstitution causes interactions basically different from vicinal disubstitution. All of this conflicts with occasional earlier statements that substitution by chlorine is not accompanied by significant bond-length changes in the cyclopropane ring (*e.g.* Jason & Ibers, 1977; Allen, 1980). Replacement of hydrogen by bromine in cyclopropane is also considered to cause no detectable changes of the cyclopropane geometry; this was concluded from the structures of a number of mixed multiply-substituted cyclopropanes with different substituents (Jason & Ibers, 1977).

The bonding situation in bromocyclopropane strongly resembles that in the chloro analogues; for instance, the substitution structure of bromocyclopropane observed in the gas phase shows a scarcely distorted cyclopropane triangle with an average ring bond length of 1·515 Å (Lam & Dailey, 1968), identical to that of chlorocyclopropane. Unfortunately, there is no published structure of 1,1-dibromocyclopropane to allow a comparison with 1,1-dichlorocyclopropane with its unusual bonding (Hedberg *et al.*, 1982; Skancke, 1977). To our knowledge, there are no other published structure determinations of other cyclopropanes substituted by bromine only. To observe the effect of bromine on the geometry of cyclopropane using simple model molecules containing bromine substituents only, we carried out X-ray analyses on *cis*-1,2,3-tribromocyclopropane and hexabromocyclopropane. These might indicate whether the concept of σ-inductive and π-conjugative electron transfer (and their consequences for bond lengths) is also applicable to bromine substituents.

Experimental. The sample of hexabromocyclopropane used in the present investigation was synthesized in four steps *via* pentachlorocyclopropane (Tobey & West, 1966). After two successive sublimations, the compound was further purified by repeated crystallization

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* Part 3: Schrumpf & Jones (1987*b*).

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from ethanol to constant melting point. *cis*-1,2,3-Tribromocyclopropane was obtained by controlled reduction of the hexabromo derivative by tributylstannane in refluxing diethyl ether; it was sublimed out of the mixture of the reduction products. Recrystallization from ethanol furnished a spectroscopically pure sample. Details of the synthesis and the characterization of this substance will be given elsewhere (Schrumpf, 1987). Single crystals of both compounds were obtained by diffusion of water into concentrated solutions in glacial acetic acid.

$C_3H_3Br_3$: crystal 0·3 × 0·2 × 0·1 mm, 928 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer. Monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 50°; octant $+h+k+l$ and some $-h-k-l$ equivalents. Three check reflections, no significant intensity change. Empirical absorption correction based on ψ scans; transmissions 0·39–0·99. R_{int} 0·034 for 583 unique reflections (index ranges after merging $0 \leq h \leq 6$, $0 \leq k \leq 11$, $0 \leq l \leq 13$), 356 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Cell constants refined from 2θ values of 36 reflections in the range 20–24°.

Structure solution by heavy-atom method; refinement on F to R 0·053, wR 0·055 [Br anisotropic, C isotropic, H subject to restraint C—H = 0·96 (2) Å; 29 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0005F^2$, $S = 1{\cdot}37$, slope of normal probability plot 1·26]. Max. Δ/σ 0·01; max. and min. heights in final $\Delta\rho$ map ± 1 e Å^{-3}. Atomic scattering factors as incorporated in *SHELXTL*.

C_3Br_6: crystal 0·2 × 0·2 × 0·1 mm. Data collection as for $C_3H_3Br_3$ except: quadrant $+h-k\pm l$ and some $+k$ equivalents, transmission factors 0·27–0·97, 1830 reflections, 1602 unique (R_{int} 0·020, index ranges $|h| \leq 13$, $k \leq 7$, $l \leq 15$), 1034 with $F > 4\sigma(F)$. Structure solution by direct methods, refinement to R 0·063, wR 0·066 [67 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0007F^2$, $S = 1{\cdot}46$, slope of normal probability plot 1·28]. Max. Δ/σ 0·002; max. and min. heights in final $\Delta\rho$ map +1·7, −1·2 e Å^{-3}.

Discussion. Final atomic coordinates and derived bond lengths and angles are presented in Tables 1–4.* The molecules are illustrated in Figs. 1 and 3, and the crystal packing in Figs. 2 and 4.

C_3Br_6 is isostructural to C_3Cl_6 (Schrumpf & Jones, 1987*b*); $C_3H_3Br_3$ is, however, not isostructural to $C_3H_3Cl_3$ (Schrumpf & Jones, 1987*a*) despite the fact that both compounds crystallize in *Pnma* with imposed mirror symmetry.

Table 1. *Atom coordinates* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3) *for cis*-1,2,3-*tribromocyclopropane*

	x	y	z	U/U_{eq}
Br(1)	2424 (3)	2500	3632 (1)	66 (1)*
Br(2)	2121 (2)	746 (1)	6247 (1)	64 (1)*
C(1)	5097 (33)	2500	4716 (15)	54 (5)
C(2)	4976 (19)	1766 (8)	5810 (10)	45 (3)
H(1)	6229 (195)	2500	4082 (75)	56
H(2)	6107 (132)	1144 (65)	6145 (73)	47

* Equivalent isotropic U calculated from anisotropic U: $U_{\text{eq}} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Atom coordinates* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3) *for hexabromocyclopropane*

	x	y	z	U_{eq}
Br(11)	610 (2)	2861 (3)	3374 (2)	45 (1)*
Br(12)	1149 (2)	2233 (3)	5832 (2)	43 (1)*
Br(21)	2275 (2)	7430 (3)	4000 (2)	48 (1)*
Br(22)	2804 (2)	6690 (3)	6448 (2)	46 (1)*
Br(31)	3747 (2)	2870 (3)	3923 (2)	47 (1)*
Br(32)	4303 (2)	2194 (3)	6390 (2)	43 (1)*
C(1)	1767 (14)	3348 (20)	4825 (13)	26 (3)
C(2)	2503 (15)	5421 (21)	5080 (14)	30 (4)
C(3)	3188 (15)	3368 (21)	5070 (14)	29 (4)

* Equivalent isotropic U calculated from anisotropic U: $U_{\text{eq}} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 3. *Bond lengths* (Å) *and angles* (°) *for cis*-1,2,3-*tribromocyclopropane*

Br(1)—C(1)	1·914 (19)	Br(2)—C(2)	1·908 (11)
C(1)—C(2)	1·470 (20)	C(2)—C(2$^{\text{i}}$)	1·455 (18)
C(2)—C(1)—C(2$^{\text{i}}$)	59·3 (11)	Br(2)—C(2)—C(1)	122·0 (10)
Br(2)—C(2)—C(2$^{\text{i}}$)	122·0 (4)	C(1)—C(2)—C(2$^{\text{i}}$)	60·3 (6)
Br(1)—C(1)—C(2)	122·7 (11)		

Symmetry operator (i): x, 0·5—y, z.

Table 4. *Bond lengths* (Å) *and angles* (°) *for hexabromocyclopropane*

Br(11)—C(1)	1·903 (15)	Br(12)—C(1)	1·879 (20)
Br(21)—C(2)	1·875 (18)	Br(22)—C(2)	1·899 (19)
Br(31)—C(3)	1·892 (22)	Br(32)—C(3)	1·891 (16)
C(1)—C(2)	1·549 (21)	C(1)—C(3)	1·539 (25)
C(2)—C(3)	1·543 (22)		
Br(11)—C(1)—Br(12)	110·4 (9)	Br(11)—C(1)—C(2)	118·5 (12)
Br(12)—C(1)—C(2)	119·9 (14)	Br(11)—C(1)—C(3)	119·4 (14)
Br(12)—C(1)—C(3)	120·7 (12)	C(2)—C(1)—C(3)	59·9 (11)
Br(21)—C(2)—Br(22)	110·8 (8)	Br(21)—C(2)—C(1)	121·6 (12)
Br(22)—C(2)—C(1)	117·8 (15)	Br(21)—C(2)—C(3)	120·6 (16)
Br(22)—C(2)—C(3)	118·0 (12)	C(1)—C(2)—C(3)	59·7 (11)
Br(31)—C(3)—Br(32)	111·0 (9)	Br(31)—C(3)—C(1)	119·1 (12)
Br(32)—C(3)—C(1)	118·9 (14)	Br(31)—C(3)—C(2)	118·9 (13)
Br(32)—C(3)—C(2)	120·3 (13)	C(1)—C(3)—C(2)	60·3 (11)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43716 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

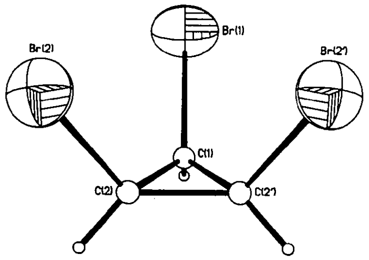

Fig. 1. The molecule of *cis*-1,2,3-tribromocyclopropane in the crystal. Br atoms are shown as 50% probability ellipsoids, C and H as circles of arbitrary radius.

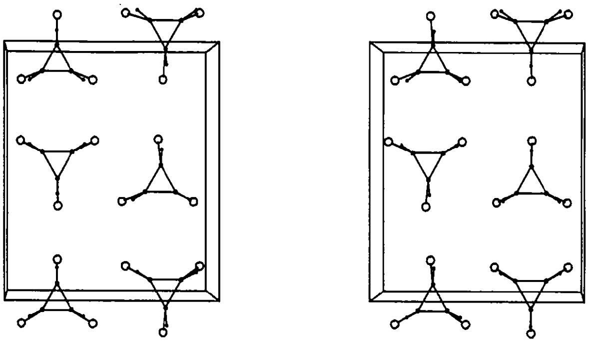

Fig. 2. Stereo packing diagram of *cis*-1,2,3-tribromocyclopropane viewed approximately parallel to the *x* axis. Open circles represent Br.

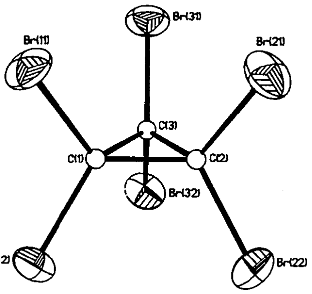

Fig. 3. The molecule of hexabromocyclopropane in the crystal. Br atoms are shown as 50% probability ellipsoids, C atoms as circles of arbitrary radius.

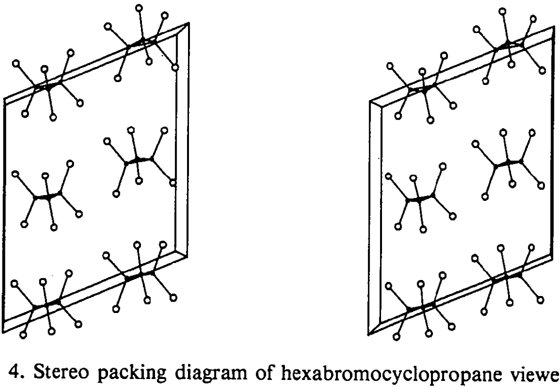

Fig. 4. Stereo packing diagram of hexabromocyclopropane viewed approximately parallel to the *y* axis.

As in our previous communications, we wish to compare solid-state bond lengths and angles with those determined in the gas phase by microwave spectroscopy and electron diffraction. Even for the vapour-phase structures, there are at least two types of differently defined distances, r_s from microwave spectra and r_a or r_g from electron diffraction data. Although the differences between these are seldom larger than a few thousandths of an ångström, the differences between solid- and gas-phase data tend to be somewhat larger (solid-state bond lengths usually being a little smaller, although there is no systematic trend). We have in our other studies obtained precise solid-state bond lengths (typical least-squares e.s.d.'s 0·005 Å for C—C bonds) and subjected these to appropriate libration corrections. For the bromine derivatives, the C—C bond lengths are inherently less precise (e.s.d.'s *ca* 0·02 Å) and, because no reliable anisotropic thermal parameters for the carbon atoms are available, we are unable to estimate a libration correction. Furthermore, the crystals do not diffract strongly, yet we were forced to use small crystals to avoid extreme absorption effects. In the following qualitative discussion, however, it is assumed that the observed differences in C—C bond lengths are large enough to be regarded as significant despite all these problems.

There is little indication of any difference between the average CBr bond lengths in the two title molecules and that in monobromocyclopropane.

The mean uncorrected ring CC bond length in *cis*-1,2,3-tribromocyclopropane is 1·465 Å, *i.e.* smaller than in cyclopropane (1·510 Å; Bastiansen *et al.*, 1964), in the trichloro analogue (1·505 Å, libration-corrected) and in bromocyclopropane [1·515 Å (Lam & Dailey, 1968); in the vapour phase, the ring bond asymmetry of bromocyclopropane of about 0·010 Å is within the error limits given]. This shortening is unexpected in view of the literature data, which suggest a negligible effect of bromine substitution on the ring geometry.

We suggest the following interpretation. First, it will be assumed that vicinal triple substitution by halogen will generally shorten the CC ring bonds. The concomitant decrease of the non-bonded Hal···Hal distances, which are probably on the repulsive side of the non-bonded Hal···Hal potential-energy curve, would counteract the CC bond contraction if not relaxed in other ways, *e.g.* by opening the CCHal bond angles. This is easier in the tribromo molecule with a lower bending force constant, *i.e.* a softer angle-deformation mode than in the trichloro derivative. This is deduced from the frequency of the A_1 CCHal bending mode in the trihalogenocyclopropanes, which is 187 and 126 cm^{-1} for Cl and Br derivatives, respectively (Schrumpf & Bergholz, 1982; Schrumpf, 1987). Thus, the anticipated ring bond contraction in the trichlorocyclopropanes relative to cyclopropane, which is presumably caused by the σ-electron withdrawal from the ring by the chlorine substituents, is not observed because of insufficient non-bonded strain relaxation, whereas in the tribomo compound, the shortening is realized, because repulsive non-bonded interaction is better relaxed.

This interpretation is supported by the observed CCHal bond angles. In tribromocyclopropane, the average CCBr bond angle of 122·2° is about 3° larger than in monobromocyclopropane (119·3°; Lam & Dailey, 1968). For comparison, the corresponding angle in the trichloro derivative is 120·8°, and in monochlorocyclopropane 118·7°, a difference of 2°. The non-bonded Hal···Hal distances in the tribromo compound are thus relaxed by 0·17 Å from 3·33 to 3·50 Å, in the trichloro analogue by 0·09 Å from 3·21 to 3·30 Å. Both structures show non-bonded distances well below the van der Waals contacts of 3·60 (ClCl) and 3·90 Å (BrBr) (Pauling, 1960). In crystals, these values might actually be smaller. In the trihalogenocyclopropanes, the shortest intermolecular non-bonded Hal···Hal contacts are 3·66 Å (ClCl) and 3·76 Å (BrBr); in the hexahalogenocyclopropanes they are even shorter, at 3·43 Å (BrBr). It thus appears that the actual intramolecular non-bonded distances in the tribromo compound are close to the minimum of the corresponding potential-energy curve, whereas in the trichloro derivative, they are somewhat shorter.

The mean uncorrected CC bond length in hexabromocyclopropane (1·544 Å) is larger than in either cyclopropane, monobromocyclopropane or trichlorocyclopropane. A libration correction would probably raise this value to above 1·550 Å, thus exceeding the bond distance in hexachlorocyclopropane of 1·537 Å. As in the latter molecule, we suggest that this CC bond lengthening is due to the repulsive non-bonded Br···Br interaction. Unlike the situation in tribromocyclopropane, the non-bonded strain cannot be relaxed by opening of the CCBr bond angles. This is documented by the experimental CCBr bond angles, which – although with appreciable scatter – are all within the error limits of the average of 119·5°, very similar to the value in monobromocyclopropane (119·2°; Lam & Dailey, 1968). The buttressing effect of the geminal bromine substituents is responsible for the failure of the bond angles to relax the non-bonded Br···Br repulsion, which results in the observed lengthening of the ring bonds.

That this is not the complete story is borne out by the gas-phase data on *cis*-1,2,3-trifluorocyclopropane (Gillies, 1976) and hexafluorocyclopropane (Chiang & Bernett, 1971). The CC bond lengths in both molecules (1·507 and 1·505 Å) are practically identical and slightly smaller than in cyclopropane. The CCF bond angle in trifluorocyclopropane (116·5°) is *smaller* than in the hexafluoro analogue (118·9°), and the non-bonded F···F distances in both cases are larger than the expected F···F van der Waals contacts (2·70 Å; Pauling, 1960). All of this is contrary to the findings in the chloro- and bromo-substituted molecules. The data on the fluorocyclopropanes imply that, although there is apparently no non-bonded strain, the CC bonds are *not* shortened at all, contrary to our assumption for chlorine and bromine substitution.*

Other interpretations for the variation of substituent effects on the cyclopropane ring have been advanced in the literature, such as a rehybridization of the cyclopropane carbon atoms on halogen substitution of the hydrocarbon (Chiang & Bernett, 1971; Bernett, 1969; Bent, 1960). More *p* character in the C—F bonds to aid the transfer of electron density from C to the more electronegative F atom means more *s* character in the orbitals constituting the ring bonds, which are thus weakened, *i.e.* lengthened relative to those in chloro- and bromo-substituted cyclopropanes and cyclopropane itself. However, we feel that this concept is insufficient as a sole interpretation of all the geometrical data available for halogenocyclopropanes.

If one decides to interpret the observed geometry changes in this class of compounds on the basis of the Hoffmann concept, additional problems arise. The Hoffmann concept was developed using perturbation theory for the interaction between a cyclopropane moiety and a substituent (Hoffmann, 1970). The perturbation in monosubstituted cyclopropanes reduces the D_{3h} symmetry of cyclopropane to C_s and allows orbital interactions that are symmetry-forbidden in the hydrocarbon. As long as only monosubstituted molecules are compared, this is tolerable for qualitative reasoning. However, if molecules of C_{3v} or D_{3h} symmetry are studied, as in the present work, there is no or greatly reduced mixing of cyclopropane orbitals compared with C_s-type molecules. Since, the orbital coefficients and energies of the cyclopropane moieties are different, as for example in chloro-substituted cyclopropanes of C_s, C_{3v} and C_{3h} symmetry, the extent of electron-density transfer between the cyclopropane part and the substituents may vary with total symmetry. Thus, additivity of substituent effects on the bond lengths of the cyclopropane ring and on their asymmetry cannot be expected, and trends observed in monosubstituted molecules cannot be transferred to cyclopropanes substituted by the same class of substituent, but of different total molecular symmetry.

In summary, we propose a molecular mechanical explanation of the observed decrease of the CC bond lengths in tribromocyclopropane and increase in hexa-

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* *Note added in proof:* Microwave studies of *cis-* and *trans-*1,2-difluorocyclopropane have recently been reported (Sengupta, Justnes, Gillies & Craig, 1986; Justnes, Zozom, Gillies, Sengupta & Craig, 1986). The complete substitution structures obtained in these studies showed that all C—C bonds are shortened relative to cyclopropane. This is additional support for our above assumptions.

bromocyclopropane; the availability of relaxation of nonbonded strain is related to the stiffness of the deformation mode of the CCHal angle. A molecular-orbital interpretation of the geometrical data on the basis of the Hoffmann scheme alone is inconsistent at the moment, but it is suggested that this should be performed with due consideration of the symmetry differences of the molecules under investigation. For our part, we hope to improve the statistical significance of the bond-length effects in the bromo derivatives by neutron diffraction. Attempts to grow suitable crystals are in progress.

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References

ALLEN, F. H. (1980). *Acta Cryst.* B**36**, 81–96.

BASTIANSEN, O., FRITSCH, J. E. & HEDBERG, K. (1964). *Acta Cryst.* **17**, 538–543.

BENT, H. A. (1960). *J. Chem. Phys.* **33**, 1260–1261.

BERNETT, W. A. (1969). *J. Org. Chem.* **34**, 1772–1776.

CHIANG, J. F. & BERNETT, W. A. (1971). *Tetrahedron*, **27**, 975–980.

CLEGG, W. (1981). *Acta Cryst.* A**37**, 22–28.

GILLIES, C. W. (1976). *J. Mol. Spectrosc.* **59**, 482–492.

HEDBERG, L., HEDBERG, K. & BOGGS, J. E. (1982). *J. Chem. Phys.* **77**, 2996–3002.

HOFFMANN, R. (1970). *Tetrahedron Lett.* pp. 2907–2909.

JASON, M. E. & IBERS, J. A. (1977). *J. Am. Chem. Soc.* **99**, 6012–6021.

JUSTNES, H., ZOZOM, J., GILLIES, C. W., SENGUPTA, S. K. & CRAIG, N. C. (1986). *J. Am. Chem. Soc.* **108**, 881–887.

LAM, F. M. K. & DAILEY, B. P. (1968). *J. Chem. Phys.* **49**, 1588–1593.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca, NY: Cornell Univ. Press.

SCHRUMPF, G. (1987). In preparation.

SCHRUMPF, G. & BERGHOLZ, R. (1982). *J. Mol. Struct.* **102**, 209–214.

SCHRUMPF, G. & JONES, P. G. (1987*a*). *Acta Cryst.* C**43**, 1182–1185.

SCHRUMPF, G. & JONES, P. G. (1987*b*). *Acta Cryst.* C**43**, 1185–1187.

SCHWENDEMAN, R. H., JACOBS, G. D. & KRIGAS, T. M. (1964). *J. Chem. Phys.* **40**, 1022–1028.

SENGUPTA, S. K., JUSTNES, H., GILLIES, C. W. & CRAIG, N. C. (1986). *J. Am. Chem. Soc.* **108**, 876–880.

SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.

SKANCKE, A. (1977). *J. Mol. Struct.* **42**, 234–241.

TOBEY, S. W. & WEST, R. (1966). *J. Am. Chem. Soc.* **88**, 2481–2488.

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Diketones from the Oxidation of Two *syn*-Sesquinorbornene Derivatives

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Abstract. Dimethyl 3,5,6,7,8,10-hexahydro-3,10:5,8-dimethanocyclodecene-4,9-dione-1,2-dioate (5), $C_{16}H_{18}O_6$, $M_r = 306\cdot31$, triclinic, $P\bar{1}$, $a = 12\cdot535\ (3)$, $b = 15\cdot947\ (3)$, $c = 7\cdot896\ (1)$ Å, $\alpha = 111\cdot00\ (1)$, $\beta = 92\cdot86\ (1)$, $\gamma = 96\cdot09\ (1)^\circ$, $V = 1458\cdot6\ (5)$ Å^3, $Z = 4$, $D_x = 1\cdot395$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 8\cdot55$ cm^{-1}, $F(000) = 648$, $T = 300$ K, $R = 0\cdot052$ for 3807 independent reflections. 5,7,8,9,10,12-Hexahydro-5,12:7,10-dimethanobenzocyclodecene-6,11-dione (6), $C_{16}H_{16}O_2$, $M_r = 240\cdot30$, monoclinic, $P2_1/c$, $a = 8\cdot078\ (2)$, $b = 11\cdot814\ (2)$, $c = 13\cdot106\ (2)$ Å, $\beta = 96\cdot58\ (1)^\circ$, $V = 1242\cdot5\ (4)$ Å^3, $Z = 4$, $D_x = 1\cdot284$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 6\cdot30$ cm^{-1}, $F(000) = 512$, $T = 300$ K, $R = 0\cdot049$ for 1436 reflections. The strained central double bonds of *syn*-sesquinorbornenes are easily oxidized to diketone derivatives resulting in eight-membered rings which exhibit flattened crown conformations. The ketone systems are not planar but are folded along an axis passing through the carbonyl C atoms forming interplanar angles of 161·4 (5), 163·0 (5)° for the two independent molecules of (5) and 173·5 (5)° for (6). The C(1)—C(10) double-bond systems deviate slightly from planarity.

Introduction. The reactivity of the double bond in *syn*-sesquinorbornene and its derivatives has been of considerable interest because its stereospecificity reflects the rigid relationship of the various parts of the molecule. The *syn*-sesquinorbornenes (1) and (2) are very reactive toward oxygen. Bubbling oxygen through a dichloromethane solution of (1) at room temperature for 2 d in the dark leads to a mixture of epoxide (3) (60%) and diketone (5) (40%). Similarly autoxidation of (2) has been reported to give a mixture of (4) and (6) (Paquette & Carr, 1980). We have established earlier the structure of (3) from X-ray studies of the epoxide obtained by peracid epoxidation of (1) (Subramanyam, Bartlett, Moltrasio Iglesias, Watson & Galloy, 1982). Since the conformation of the cyclooctanedione might be responsive to the special properties of the ethylene

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