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Substituted Cyclopropanes. 10. Hexaethyl Cyclopropanehexacarboxylate*

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Abstract. $C_{21}H_{30}O_{12}$, $M_r = 474{\cdot}48$, orthorhombic, *Pccn*, $a = 15{\cdot}397$ (4), $b = 9{\cdot}983$ (2), $c = 16{\cdot}640$ (5) Å, $V = 2558$ Å^3, $Z = 4$, $D_x = 1{\cdot}23$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·1 mm^{-1}, $F(000) = 1008$, $T = 293$ K. The structure was refined to $R = 0{\cdot}061$, $wR = 0{\cdot}063$ for 1623 reflections. The molecule possesses crystallographic twofold symmetry, but its non-crystallographic symmetry is close to S_6. It is a strained molecule with steric repulsion between the three carbonyl O atoms on either side of the cyclopropane ring. Several unusual bond lengths, bond angles and dihedral angles indicate that strain is partially relaxed over different coordinates. The ester groups adopt a *gauche* (*cg*) conformation. The positions of the six methyl carbon atoms are not reliably determined because of libration effects.

Introduction. In a series of recent papers, we have demonstrated that the geometry of substituted cyclopropane rings is determined not only by electronic effects of the kind first suggested by Hoffmann (1970), but in the case of *cis*-trisubstitution also by steric strain, which affects bond lengths and bond angles in these systems in a qualitatively predictable manner (Schrumpf & Jones, 1987*a–d*; Jones & Schrumpf, 1987*a–e*). In the hexasubstituted triethyl *trans*-1,2,3-tricyano-1,2,3-cyclopropanetricarboxylate, the bond distances and the conformation of the ester groups indicate convincingly the repulsion between the substituents at each of the heavily crowded faces of the cyclopropane ring (Jones & Schrumpf, 1987*c*). The main aim of the present investigation was to study the conformation of hexaethyl cyclopropanehexacarboxylate and the effect of steric interactions between substituents on the bond lengths.

Experimental. The title compound was described for the first time by Kötz & Stalmann (1903) as a highly viscous oil, which could not be crystallized. Thereafter, the compound has been prepared only once with similar results (Lablache-Combier & Surpateanu, 1976). Recently, however, a crystalline product has been obtained in this laboratory (Heinrich, 1986). Repeating the old experiments under carefully controlled conditions, we prepared the pure compound in a non-optimized yield of about 40% as colourless crystals (m.p. 388 K). The identity and purity of the product were demonstrated spectroscopically and, since the compound has never been characterized spectroscopically, we present the data here: IR (KBr; cm^{-1}): 2990 *w*, 1750 *s*, 1262 *s*, 1219 *s*, 1100 *m*, 1038 *m*; Raman (solid, cm^{-1}): 2936 *m*, 1766 *m*, 1444 *m*, 1100 *m*, 900 *m*, 958 *s*. ^{1}H (CDCl$_3$, TMS, 200 MHz, p.p.m.): 1·31 (*t*, 3H), 4·34 (*q*, 2H); ^{13}C (CDCl$_3$, TMS, 200 MHz, p.p.m.): 13·85 (CH$_3$), 45·38 (C-ring), 62·58 (CH$_2$), 163·41 (CO). MS (70 eV), *m/e* (rel. int.): 474 (28, M^+), 429 (100), 401 (88), 355 (88), 283 (72), 271 (90), 226 (66).

Single crystals were obtained in two modifications: (i) from acetonitrile–water as colourless, soft, weakly diffracting prisms and tablets and (ii) from acetic acid as colourless parallelepipeds. Modification (i) is monoclinic primitive with approximate cell constants $a = 8{\cdot}90$, $b = 9{\cdot}54$, $c = 14{\cdot}70$ Å, $\beta = 92{\cdot}45°$, $V = 1247$ Å^3, $Z = 2$, but no crystals were of adequate quality for intensity measurements. All further investigations were performed on modification (ii) only.

Crystal 0·7 × 0·35 × 0·3 mm. Intensities measured on Stoe two-circle diffractometer with monochromated Mo $K\alpha$ radiation to $2\theta_{\max}$ 50°; layers $hk0 \rightarrow 16$ (5211 reflections) and (with same crystal remounted) $h0 \rightarrow 9l$ (3910 reflections). Interlayer scale factors by least-squares analysis of common reflections. 2364 unique reflections ($R_{\rm int}$ 0·021), 1623 with $F > 4\sigma(F)$ used for all calculations [program system *SHELXTL* (Sheldrick, 1978)]. Index ranges after merging: $h\,0 \rightarrow 18$, $k\,0 \rightarrow 10$, $l\,0 \rightarrow 19$. Cell constants refined from 2θ values of 40 reflections in the range 20–23°, measured on Stoe–Siemens four-circle diffractometer.

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* Part 9: Jones & Schrumpf (1987*e*).

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Structure solution by routine direct methods. Refinement on F to R 0·062, wR 0·063 [non-H atoms anisotropic, H atoms included using riding model with C—H 0·96 Å, H—C—H 109·5°, $U(\mathrm{H}) = 1{\cdot}2U_{\mathrm{eq}}(\mathrm{C})$; 150 parameters; weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0002F^2$; $S = 2{\cdot}36$]. Max. Δ/σ 0·02, max. features in final $\Delta\rho$ map $\pm 0{\cdot}25\,\mathrm{e\,Å^{-3}}$. Atomic scattering factors those of *SHELXTL*.

Discussion. Final atomic coordinates and derived structural parameters are given in Tables 1 and 2.* A rigid-body libration correction was not feasible because of the flexible ethoxycarbonyl groups; bond lengths quoted here are thus uncorrected (unless otherwise stated). A view of the molecule is given in Fig. 1.

The crystallographic symmetry of the title molecule is imposed by the twofold axis 0·25, 0·75, z passing through C(1). The actual symmetry is somewhat distorted from S_6. The deviations arise from small differences in the dihedral angles about the C—O ester single bonds and the ethoxy O—C single bonds. The conformations about the bonds between the ring and the ester groups are similar, *viz.* about C(1)—C(11) 53, C(2)—C(21) 48 and C(2)—C(31) 53° away from the *cis*-bisected (*cb*) position. These *cis–gauche* (*cg*; Allen, 1980) conformations avoid serious steric interference between the *cis* carbonyl O atoms on either side of the cyclopropane ring, but also prevent conjugative interaction between the ester groups and the cyclopropane ring. According to Hoffmann (1970), such conjugative interactions would lead to ring-bond asymmetry. However, as all ester groups are rotated into the *cg* position, the cyclopropane ring is (within 1σ) an equilateral triangle with an average CC bond distance (1·516 Å) resembling that of cyclopropane itself with $r_g(\mathrm{CC}) = 1{\cdot}514$ Å (Yamamoto, Nakata, Fukuyama & Kuchitsu, 1985).

Other heavily substituted ethoxycarbonylcyclopropanes have been studied. The average ring bond distance in ethyl 1,2,2-tricyano-3,3-dimethylcyclopropanecarboxylate (ETDC) (1·531 Å; Ramasubbu, Rajaram & Venkatesan, 1982), ethyl 2′,3′,3′-tricyanocyclohexanespirocyclopropane-2′-carboxylate (ETSC) (1·536 Å; Ramasubbu *et al.*, 1982), ethyl 1,2,2-tricyano-3-(4-nitrophenyl)cyclopropanecarboxylate (ETNC) (1·529 Å; Ramasubbu & Venkatesan, 1982) and triethyl *trans*-1,2,3-tricyanocyclopropanetricarboxylate (ETTC) (1·529 Å; Jones & Schrumpf, 1987*c*) are lengthened by about 0·01–0·02 Å relative to cyclopropane.

Table 1. *Atom coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²×10³)

	x	y	z	U_{eq}
C(1)	2500	7500	3749 (2)	41 (1)
C(2)	2508 (1)	6740 (2)	4538 (1)	41 (1)
C(11)	3313 (1)	7488 (3)	3235 (1)	53 (1)
O(11)	3900 (1)	8257 (2)	3277 (1)	72 (1)
O(12)	3241 (1)	6475 (2)	2721 (1)	67 (1)
C(12)	3980 (2)	6219 (4)	2196 (2)	94 (2)
C(13)	4040 (3)	4792 (4)	2061 (2)	123 (2)
C(21)	3328 (1)	6033 (2)	4800 (1)	48 (1)
O(21)	3939 (1)	5795 (2)	4384 (1)	68 (1)
O(22)	3239 (1)	5679 (2)	5564 (1)	65 (1)
C(22)	3958 (2)	4963 (3)	5933 (2)	88 (1)
C(23)	3643 (3)	4103 (4)	6545 (3)	142 (2)
C(31)	1696 (1)	5972 (2)	4771 (1)	46 (1)
O(31)	1097 (1)	6412 (2)	5143 (1)	60 (1)
O(32)	1770 (1)	4733 (2)	4497 (1)	60 (1)
C(32)	1009 (2)	3882 (3)	4587 (2)	79 (1)
C(33)	1117 (2)	2744 (3)	4038 (2)	111 (2)

Equivalent isotropic U calculated from anisotropic U:

$$U_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·515 (4)	C(1)—C(11)	1·516 (4)
C(2)—C(21)	1·512 (4)	C(2)—C(31)	1·516 (4)
C(2)—C(2ⁱ)	1·518 (5)	C(11)—O(11)	1·188 (4)
C(11)—O(12)	1·329 (4)	C(12)—O(12)	1·457 (5)
C(12)—C(13)	1·445 (7)	C(21)—O(21)	1·191 (4)
C(21)—O(22)	1·326 (4)	C(22)—O(22)	1·454 (4)
C(22)—C(23)	1·417 (7)	C(31)—O(31)	1·195 (4)
C(31)—O(32)	1·323 (4)	C(32)—O(32)	1·455 (4)
C(32)—C(33)	1·468 (6)		
C(2)—C(1)—C(11)	118·6 (2)	C(2)—C(1)—C(2ⁱ)	60·1 (3)
C(11)—C(1)—C(11ⁱ)	111·3 (3)	C(2)—C(1)—C(11ⁱ)	119·9 (2)
C(1)—C(2)—C(21)	119·4 (3)	C(1)—C(2)—C(31)	117·9 (3)
C(21)—C(2)—C(31)	112·3 (3)	C(1)—C(2)—C(2ⁱ)	59·9 (2)
C(21)—C(2)—C(2ⁱ)	118·7 (3)	C(31)—C(2)—C(2ⁱ)	119·5 (3)
C(1)—C(11)—O(11)	126·1 (3)	C(1)—C(11)—O(12)	107·4 (3)
O(11)—C(11)—O(12)	126·4 (3)	C(11)—O(12)—C(12)	117·0 (3)
O(12)—C(12)—C(13)	108·5 (4)	C(2)—C(21)—O(21)	125·8 (3)
C(2)—C(21)—O(22)	108·4 (3)	O(21)—C(21)—O(22)	125·8 (3)
C(21)—O(22)—C(22)	117·2 (3)	O(22)—C(22)—C(23)	109·9 (3)
C(2)—C(31)—O(31)	125·7 (3)	C(2)—C(31)—O(32)	108·3 (3)
O(31)—C(31)—O(32)	126·0 (3)	C(31)—O(32)—C(32)	116·2 (3)
O(32)—C(32)—C(33)	107·2 (3)		

Symmetry operator (i): 0·5—x, 1·5—y, z.

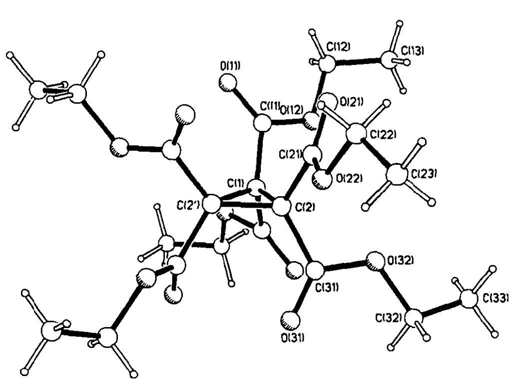

Fig. 1. The title molecule in the crystal, showing the numbering scheme of the asymmetric unit.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43951 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

That there is steric crowding among the ester groups is evident from the exocyclic CC bond distances and geminal intersubstituent angles. The different bond lengths between a ring C and the corresponding ester C (1·515 Å) are very similar. In unstrained molecules, in 1,1-cyclopropanedicarboxylic acid (Meester, Schenk & MacGillavry, 1971), *cis*- and *trans*-1,2-cyclopropanedicarboxylic acid (Schrumpf & Jones, 1987*d*), and 1-cyanocyclopropanecarboxylic acid (Jones & Schrumpf, 1987*b*), the bond lengths are between 1·480 and 1·490 Å. Thus, the lengthening of this bond in the hexaester absorbs some of the strain between the carbonyl oxygen atoms, which are in a *syn* position relative to the ring, as is usual.

The angles between geminal substituents, C(11)C(1)C(11$^{\rm i}$) and C(21)C(2)C(31), are 111·3 and 112·3°, respectively. In comparison, in the 1,1-diacid and the 1-cyanoacid, these angles are 118·3 (2), 118·4 (2) (Meester *et al.,* 1971) and 117·1 (3)° (Jones & Schrumpf, 1987*b*). Forcing geminal ethoxycarbonyl groups together appears to be energetically less severe than the carbonyl oxygen interaction for vicinal ethoxycarbonyl groups, because torsional relaxation of the former is efficient.

There are other small but systematic bond-distance differences in comparison with similar molecules. Whereas the average ester C—O single-bond length in the molecules ETDC, ETSC and ETNC with only one ester group is 1·310 Å and in ETTC 1·315 Å, these bonds are longer in the hexaester by 2–3 e.s.d.'s [$r(\mathrm{CO})_{\mathrm{av}}$ = 1·326 Å]. The average of the angles C(1)-C(11)O(11), C(2)C(21)O(21) and C(2)C(31)O(31) (125·9°) is noteworthy. In ETTC, the average is 122·8°, and the average in ETDC, ETSC and ETNC is 123·1°. Thus, the main centre of steric repulsion is the three carbonyl O atoms on either side of the cyclopropane ring. This strain is relaxed over several internal coordinates.

The atoms of the ester moieties C—C(=O)—O—C are nearly coplanar, with dihedral angles C(1)C(11)O(12)-C(12) 176·2, C(2)C(21)O(22)C(22) 179·2 and C(2)-C(31)O(32)C(32) 173·5°. However, the dihedral angles about the C(alkyl)—O single bonds vary more, being 146, 151 and 162°, respectively. The CC single-bond lengths C(12)C(13) (1·445), C(22)C(23) (1·417) and C(32)C(33) (1·468 Å) not only differ widely, but are also outside normal values for CC single bonds. We attribute this to libration effects arising from the high flexibility of the chain end atoms C(13), C(23) and C(33), for which substantially larger displacement parameters are found than for the 'inner' atoms C(12), C(22) and C(32). A riding-model libration correction (Johnson, 1970) gave C(12)C(13) 1·477, C(22)C(23) 1·469 and C(32)C(33) 1·499 Å, which is more reasonable in view of experimental CC bond-length ranges reported so far; such corrections are usually somewhat underestimated.

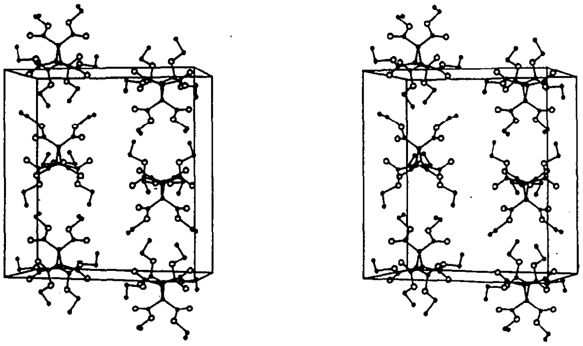

Fig. 2. Stereo packing diagram viewed approximately along the *y* axis; *x* horizontal, *z* vertical.

The molecules in the crystal are conformationally chiral, although the whole structure (Fig. 2) is that of the conformational racemate. The other possible structure, with the carbonyl oxygens above and below the ring plane pointing in the same direction with respect to the C_3 operation, *i.e.* the C_{3h} structure with the cyclopropane ring as the mirror plane, is not observed.

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