that found in N^1,N^2-diphenylformamidine (Anulewicz *et al.*, 1987), where a different H-bond pattern was also found. The molecules of this formamidine form H-bonded dimers; such a dimerization is possible owing to the location of the lone pair at N^2 and the N^1—H donor on the same side of the molecule. In the present di(p-tolyl)acetamidine the lone pair at N^2 and the N^1—H are situated on opposite sides of the molecule, leading to a different pattern of H bonds in the crystal. The molecular packing is shown in Fig. 2. An intermolecular hydrogen bond between the molecules related by a glide plane [N(1)···N(2^i) 3·196 (4), H(1)···N(2^i) 2·38 (4) Å, N(1)—H(1)···N(2^i) 170 (2)°; (i) x, 0·5−y, −0·5+z] joins the molecules into infinite chains parallel to **c**. According to its ΔHA parameters (Jaskólski, 1982*b*), this hydrogen bond can be considered as medium weak (ΔHA = 12·5).

According to Sohàr (1967), solid N,N'-diphenylacetamidine shows an IR spectrum indicating the formation of a cyclic dimeric structure. The X-ray analysis of di-p-tolylacetamidine shows a different H-bond pattern and does not confirm the rule drawn from inspection of the IR spectrum.

As can be seen in Fig. 2, the *E,Z* configuration of the molecules makes possible the formation of infinite chains joined by hydrogen bonds.

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Structure of *rel*-(1*S*,2*S*,3*S*,6*S*,7*R*)-6-Acetoxy-5-bromo-1,2-dimethoxycarbonyl-3,7-dimethylcyclohept-4-ene

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Abstract. Dimethyl *rel*-(1*S*,2*S*,3*S*,6*S*,7*R*)-6-acetoxy-5-bromo-1,2-dimethoxycarbonyl-3,7-dimethylcyclohept-4-ene-1,2-dicarboxylate, $C_{15}H_{21}BrO_6$, M_r = 377·24, monoclinic, $P2_1/n$, a = 26·004 (2), b = 7·746 (1), c = 8·540 (3) Å, β = 98·90 (1)°, V = 1699·5 Å^3, Z = 4, D_x = 1·474 Mg m^{-3}, λ(Mo $K\bar{\alpha}$) =

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0·71069 Å, $\mu = 1{\cdot}75$ mm^{-1}, $F(000) = 776$, room temperature, final $R = 0{\cdot}035$ for 1632 observed reflections. The crystal structure of the title compound (III) allows unambiguous determination of the relative (1*S*,2*S*,3*S*,6*S*,7*R*) configurations of the chiral centers present in the molecule. Surprisingly large angles within the ring have been determined. The cycloheptene ring adopts a 'pseudo-chair' conformation.

Introduction. The title compound is a potential precursor of the partial structural unit R^1CH(Me)CH(OH)CH(Me)CH(OH)CH(Me)R^2 found in many important natural products (Kishi, 1980). The configuration at the carbon which holds the acetate group was unknown. Investigation was therefore undertaken to determine this configuration as well as to ascertain the rest of the structure and its conformation.

Experimental. The Diels–Alder product (I) (Fig. 1) which is readily available (Petrov & Sopov, 1955) from the addition of dimethyl fumarate to *trans-trans*-2,4-hexadiene was converted [$CHBr_3$, NaOH, $(C_2H_5)_3N^+.CH_2C_6H_5Cl^-$, 273→298 K, 65% yield (Davalian, Garratt, Koller & Mansuri, 1980; Makosza & Wawrzyniewicz, 1969)] into the dibromocyclopropane derivative (II) (m.p. 363–364 K). Solvolysis (Reese & Shaw, 1970) (CH_3COOH, AgOAc, reflux, 5 d) of (II) (Fig. 1) gave, after recrystallization in hexane, the title compound (III) (m.p. 360–361 K) in 71% yield, plus two unidentified isomers (6% and 2% respectively).

Spherical crystal: 0·3 mm; Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Mo $K\bar{\alpha}$ radiation, lattice parameters determined from 25 high-angle reflections; $\omega/2\theta$ scan technique; $2\theta_{max} = 50°$; $-30 \le h \le 30$, $0 \le k \le 9$, $0 \le l \le 8$; one standard reflection monitored every 90 reflections showed no significant deterioration in intensity; 2835 unique measured reflections, 1632 observed with $F \ge 2\sigma(F)$. Spherical absorption applied. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refinement was performed with block-diagonal least squares based on *F* with *XTAL* (Stewart & Hall, 1985) and *PLUTO* (Motherwell & Clegg, 1978). Weights based on counting statistics. $R = 0{\cdot}035$; $wR = 0{\cdot}027$; $S = 2{\cdot}259$; max. $\Delta/\sigma = 1{\cdot}7$ [*z* of H(21C); 0·08 for non-H atoms]; and average $\Delta/\sigma = 0{\cdot}8$; max. and min. electron densities in final difference map −0·12 to 0·73 e Å^{-3}; H atoms all calculated and refined with isotropic thermal factors except for the last two cycles; all non-H atoms refined anisotropically.

Table 1. *Fractional coordinates and equivalent B's for nonhydrogen atoms of the title compound with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
C(1)	0·1361 (1)	0·3268 (5)	0·7703 (4)	2·51
C(2)	0·1565 (1)	0·2688 (5)	0·9421 (4)	2·63
C(3)	0·1121 (1)	0·2231 (5)	1·0367 (4)	3·17
C(4)	0·0875 (2)	0·0502 (5)	0·9868 (4)	3·58
C(5)	0·0656 (2)	0·0091 (5)	0·8438 (5)	3·65
C(6)	0·0594 (1)	0·1157 (5)	0·6954 (5)	3·30
C(7)	0·1109 (1)	0·1859 (5)	0·6555 (4)	3·02
C(8)	0·1786 (1)	0·4114 (5)	0·6973 (4)	3·23
O(9)	0·2248 (1)	0·3853 (4)	0·7349 (3)	4·60
O(10)	0·1593 (1)	0·5178 (3)	0·5790 (3)	3·81
C(11)	0·1970 (2)	0·6091 (6)	0·5028 (5)	4·57
C(12)	0·1908 (1)	0·4078 (5)	1·0284 (4)	3·05
O(13)	0·2306 (1)	0·3837 (4)	1·1163 (3)	4·10
O(14)	0·1696 (1)	0·5657 (3)	0·9981 (3)	3·65
C(15)	0·2012 (2)	0·7123 (6)	1·0572 (5)	5·07
C(16)	0·1296 (2)	0·2166 (6)	1·2139 (4)	4·95
Br(17)	0·04057 (2)	−0·22482 (6)	0·80831 (7)	6·51
O(18)	0·0273 (1)	0·2651 (3)	0·7142 (3)	3·70
C(19)	−0·0248 (1)	0·2376 (6)	0·6954 (4)	4·01
O(20)	−0·0443 (1)	0·1015 (4)	0·6656 (3)	4·98
C(21)	−0·0533 (2)	0·4013 (6)	0·7163 (6)	6·41
C(22)	0·1476 (2)	0·0373 (5)	0·6321 (5)	4·32

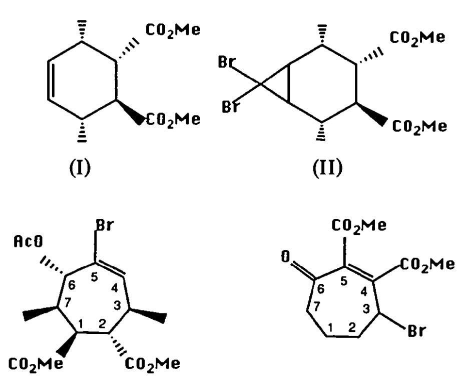

Fig. 1. Molecular formulae.

Discussion. Fig. 1 shows the molecular structure and atomic numbering. Final parameters and B_{eq} values are given in Table 1, bond lengths and angles in Table 2(*a*,*b*).* The relative chirality represented on the molecular scheme (III) of Fig. 1 is confirmed by the crystal structure shown in Fig. 2. Unusually large values of intramolecular distances and angles within the cycloheptene ring are observed. The same observation was also reported for BCMXP (Atwood, Williams, Garner & Cone, 1974), the most similar cycloheptene derivative among five entries (refcodes: BCHPPD, BCMXHP, CHEBAR, CHPTPT, CLMEPT) retrieved from the 1988 Cambridge Crystal Structure Data Base (Allen *et al.*, 1979).

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51226 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular geometry*

(*a*) Bond lengths (Å) with e.s.d.'s in parentheses

	(III)	BCMXHP*		(III)	BCMXHP*
C(1)–C(2)	1·547 (5)	1·519 (5)	C(6)–O(18)	1·450 (5)	
C(1)–C(7)	1·544 (5)	1·531 (5)	C(7)–C(22)	1·528 (6)	
C(1)–C(8)	1·501 (5)		C(8)–O(9)	1·212 (4)	
C(2)–C(3)	1·549 (5)		C(8)–O(10)	1·340 (5)	
C(2)–C(12)	1·515 (5)		O(10)–C(11)	1·443 (5)	
C(3)–C(4)	1·516 (6)	1·499 (4)	C(12)–O(13)	1·195 (4)	
C(3)–C(16)	1·512 (5)		C(12)–O(14)	1·350 (5)	
C(4)–C(5)	1·304 (5)	1·339 (4)	O(14)–C(15)	1·446 (5)	
C(5)–C(6)	1·500 (6)	1·511 (4)	O(18)–C(19)	1·356 (4)	
C(5)–Br(17)	1·933 (4)	1·978 (4)	C(19)–O(20)	1·180 (5)	
C(6)–C(7)	1·532 (5)	1·491 (5)	C(19)–C(21)	1·493 (6)	

(*b*) Valence angles (°) with e.s.d.'s in parentheses

	(III)	BCMXHP*		(III)	BCMXHP*
C(2)–C(1)–C(7)	116·5 (3)	115·4 (3)	C(1)–C(7)–C(6)	114·2 (3)	113·6 (3)
C(2)–C(1)–C(8)	110·7 (3)		C(1)–C(7)–C(22)	113·8 (3)	
C(7)–C(1)–C(8)	108·2 (3)		C(6)–C(7)–C(22)	110·3 (3)	
C(1)–C(2)–C(3)	112·8 (3)	118·0 (3)	C(1)–C(8)–O(9)	125·5 (3)	
C(1)–C(2)–C(12)	110·2 (3)		C(1)–C(8)–O(10)	111·6 (3)	
C(3)–C(2)–C(12)	109·8 (3)		O(9)–C(8)–O(10)	122·9 (4)	
C(2)–C(3)–C(4)	111·8 (3)	117·5 (3)	C(8)–O(10)–C(11)	116·1 (3)	
C(2)–C(3)–C(16)	113·3 (3)		C(2)–C(12)–O(13)	125·6 (4)	
C(4)–C(3)–C(16)	107·5 (3)		C(2)–C(12)–O(14)	111·0 (3)	
C(3)–C(4)–C(5)	125·6 (4)	126·73 (23)	O(13)–C(12)–O(14)	123·4 (3)	
C(4)–C(5)–C(6)	129·1 (4)	126·13 (23)	C(12)–O(14)–C(15)	116·8 (3)	
C(4)–C(5)–Br(17)	117·6 (3)		C(6)–O(18)–C(19)	116·3 (3)	
C(6)–C(5)–Br(17)	113·2 (3)		O(18)–C(19)–O(20)	123·6 (4)	
C(5)–C(6)–C(7)	113·6 (3)	117·2 (3)	O(18)–C(19)–C(21)	111·0 (3)	
C(5)–C(6)–O(18)	109·5 (3)		O(20)–C(19)–C(21)	125·4 (3)	
C(7)–C(6)–O(18)	106·3 (3)				

(*c*) Torsion angles (°) with e.s.d.'s in parentheses including atoms of the seven-membered ring

				(III)	BCMXHP*
C(7)	C(1)	C(2)	C(3)	−70·1 (3)	−43·2 (2)
C(2)	C(1)	C(7)	C(6)	67·4 (3)	−38·3 (2)
C(1)	C(2)	C(3)	C(4)	75·0 (4)	70·7 (3)
C(2)	C(3)	C(4)	C(5)	−58·3 (3)	−18·0 (2)
C(3)	C(4)	C(5)	C(5)	0·7 (3)	−10·7 (2)
C(4)	C(5)	C(6)	C(7)	55·7 (3)	−32·8 (2)
C(5)	C(6)	C(7)	C(1)	−69·7 (4)	78·9 (3)

(*d*) Distances (Å) to the least-squares plane

Equation of the plane: $9{\cdot}52\,(6)\,X-7{\cdot}12\,(7)\,Y+0{\cdot}67\,(1)=0{\cdot}19\,(1)$.
Distances to the plane from atoms:

In the plane		Out of the plane	
C(2)	0·018 (5)	C(1)	−0·704 (5)
C(3)	−0·015 (6)	C(4)	0·947 (7)
C(6)	0·016 (5)	C(5)	0·934 (7)
C(7)	−0·019 (5)		

* Atwood, Williams, Garner & Cone (1974).

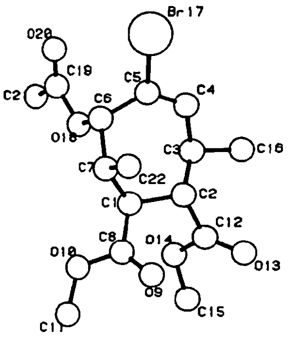

Fig. 2. *PLUTO* perspective view and atom numbering.

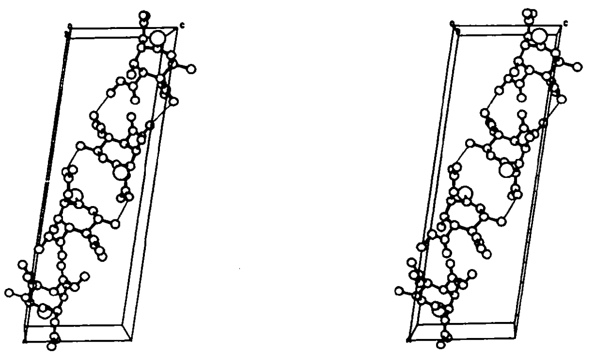

Fig. 3. Stereoview of the molecules as packed into the unit cells: projection in the *ac* plane.

The configuration of the ring is highly dependent on steric hindrances induced by the substituents. Nevertheless, it adopts a 'chair-like' conformation as can be deduced from Table 2(*d*) and Fig. 2: C(4) and C(5) are above the least-squares plane [C(2), C(3), C(6), C(7)], whereas C(1) is under; the double bond C(4)–C(5) is mostly parallel to it. This observation is also confirmed by the alternance of the torsion angles given in Table 2(*c*). The shortest contact distance C(2)···O(20) is 3·115 (3) Å and governs the packing by dimer associations of molecules shown in Fig. 3.

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Structure of Methyl 4-Methoxy-2,6-dimethylbenzoate

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Abstract. $C_{11}H_{14}O_3$, M_r = 194·23, m.p. 329–330 K, monoclinic, $P2_1/c$, a = 13·455 (5), b = 11·692 (2), c = 6·851 (3) Å, β = 102·48 (3)°, V = 1052·3 (6) Å^3, Z = 4, D_x = 1·226 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 0·083 mm^{-1}, $F(000)$ = 416, T = 293 K, final R = 0·050 for 1407 independent reflections with $F > 2\sigma(F)$. The methoxycarbonyl group is rotated by 64° with respect to the benzene-ring plane, a finding which is relevant to a recent ^{13}C NMR study [Dell'Erba, Sancassan, Novi, Petrillo, Mugnoli, Spinelli, Consiglio & Gatti (1988). *J. Org. Chem.* **53**, 3564–3568]. Even with this rotation, the O atoms of the methoxycarbonyl group have close contacts with the *ortho*-C atoms.

Introduction. A recent ^{13}C NMR study (Dell'Erba *et al.*, 1988) has shown that the effect of 4-*X* substituents on the carbonyl-C-atom chemical shift in methyl 4-*X*-benzoates and in methyl 2,6-dimethyl-4-*X*-benzoates is very similar, in spite of an expected steric inhibition to conjugation between the COOMe group and the aromatic ring in the latter series of compounds. To rationalize the observed spectroscopic behaviour, definite structural information on the relevant benzoates seemed necessary; as a first step, the crystal structure of the title compound has been determined.

Experimental. The compound (Kuhn & Corwin, 1948) was crystallized by slow evaporation from a diethyl ether solution. A crystal ground to a sphere (r 0·18 mm) was sealed in a thin glass capillary and used to collect data on a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, ω/θ scan mode, scan width 1·5°, scan speed 1–10° min^{-1}, θ range 2·5–27·5°; unit cell from 25 reflections, $16 < \theta < 19°$, least-squares refinement; max. $(\sin\theta)/\lambda$ 0·65 Å^{-1}; 2415 unique reflections collected with h −17 to 17, k 0 to 15, l 0 to 8; two check reflections monitored every one hour to test the crystal stability, and three to test the crystal orientation; no absorption correction applied (μr 0·015); $P2_1/c$ from systematic absences; 1407 reflections with $F > 2\sigma(F)$ considered observed. Crystal-structure solution and refinement with *SHELX*76 (Sheldrick, 1976); E map calculated with 405 largest E values ($E \geq 1·2$); full-matrix anisotropic least squares on F for 14 non-H atoms; H atoms located on difference maps and included in structure-factor calculations with an isotropic temperature factor equal to U_{eq} of the bonded C atom; 127 parameters refined minimizing $\sum w(\Delta F)^2$ with weights $w = [\sigma^2(F) + 0·009F^2]^{-1}$; R = 0·050, wR = 0·068 for 1407 observed reflections, S = 0·882, $(\Delta/\sigma)_{max}$ 0·003,

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