conclusively the source of π-orbital distortion, experimental inconsistencies remain.

The phenyl group in (3) is planar and is rotated by 19° from a noncrystallographic mirror plane passing through the molecule. Equivalent distances and angles are internally consistent. The five-membered triazolo ring is in an envelope conformation. The closest intramolecular contacts of significance are H(11b)···H(14b), H(12b)···H(14b) and H(14a)···H(21) of 2·62, 2·65 and 2·59 Å. There are seven intermolecular contacts between 2·32 and 2·60 Å.

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Dimethyl *rel*-(1*R*,4*S*,4a*R*)-2,3,4,4a-Tetrahydro-1,4-methano-1*H*-benzocycloheptene-5,6-dicarboxylate, C₁₆H₁₈O₄

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Abstract. $M_r = 274.32$, monoclinic, $P2_1/c$, $a = 7.659$ (1), $b = 10.833$ (3), $c = 16.867$ (5) Å, $\beta = 96.04$ (2)°, $V = 1391.7$ (6) Å³, $Z = 4$, $D_x = 1.309$ g cm⁻³, $\lambda(Cu\ K\alpha) = 1.54178$ Å, $\mu = 7.77$ cm⁻¹, $F(000) = 584$, room temperature, $R = 0.044$ for 1566 unique reflections with $I > 3\sigma(I)$. The cycloheptatriene ring is in a distorted boat conformation. The two CCOOCH₃ moieties are planar, exhibit extended conformations, and make an interplanar angle of 94·3 (7)°. The norbornane system is slightly twisted because of fusion to the seven-membered ring.

Introduction. The cycloadditions of dimethyl acetylene-dicarboxylate (DMAD) to the three isomers of isodi-cyclopentadiene, (1) to (3), have been studied (Paquette & Carr, 1980; Subramanyam, Bartlett, Iglesia, Watson & Galloy, 1982; Bartlett & Wu, 1984). The diene (3) isomer reacts slowly with DMAD at 253 K to give only one product, (4), in good yield. Unlike the cycloadducts of DMAD with isomers (1) and (2), compound (4) is thermally labile due to its *trans*-fused bicyclic nature. When heated in solution to temperatures above 373 K, compound (4) quantitatively undergoes a norbornadiene–cycloheptatriene-type rearrangement (Herndon & Lowry, 1964; Lustgarten &

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Richey, 1974) to compound (5), the structure of which was established by NMR and X-ray diffraction techniques. The structure analysis revealed that one of the substituted ethylene-bridged C atoms has undergone a change in configuration during rearrangement. This result, together with the kinetic feature of this rearrangement, $\Delta H = 125\cdot2$ kJ mol^{-1}, $\Delta S = -47\cdot5$ J mol^{-1} K^{-1}, no solvent effect (Bartlett & Wu, 1984), supports a concerted mechanism: a preceding $[\sigma2a + \pi2s]$ sigmatropic process followed by a $[4s + \sigma2s]$ disrotatory electrocyclic ring opening.
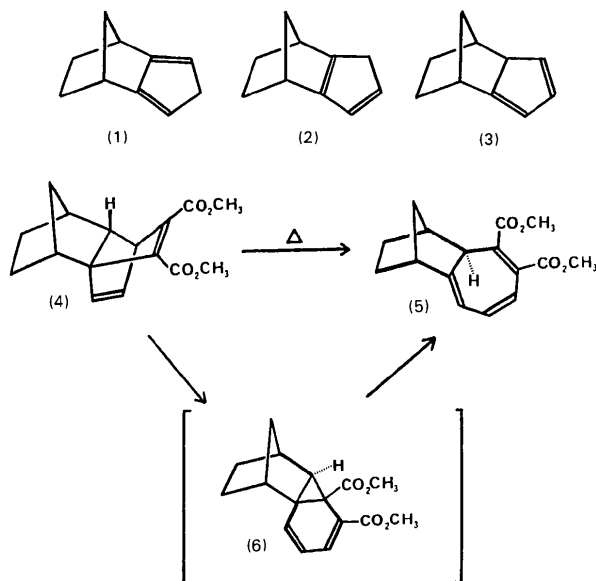
Experimental. Crystal $0\cdot50 \times 0\cdot42 \times 0\cdot40$ mm, Syntex $P2_1$ diffractometer, θ–2θ scan, variable scan rate, monochromated Cu $K\alpha$ radiation; lattice parameters from least squares on angular data for 15 reflections (systematic absences $l = 2n+1$ for $h0l$ and $k = 2n+1$ for $0k0$); 1896 independent reflections, $2\theta_{max} = 120°$ ($0 \leq h \leq 8$, $0 \leq k \leq 11$, $-17 \leq l \leq 17$), 1566 with $I > 3\sigma(I)$; monitored reflection showed no significant change in intensity; Lorentz and polarization corrections, no absorption correction; direct methods ($MULTAN78$; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms; 16 H atoms were located by difference Fourier synthesis, the positions of two H atoms were calculated; full-matrix least-squares refinement, C and O atoms refined anisotropically, H-atom positions and thermal parameters constrained; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, $R = 0\cdot044$, $R_w = 0\cdot065$, $S = 3\cdot3$ (181 parameters), $(\Delta/\sigma)_{av} = 0\cdot013$, $(\Delta/\sigma)_{max} = 0\cdot038$, highest peak in final difference Fourier map $0\cdot22$ e Å^{-3}; $XRAY76$ (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all computations; atomic scattering factors for C and O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Atomic

Table 1. Atomic positional parameters ($\times 10^4$) and U_{eq} values (Å$^2 \times 10^3$) for compound (5)

$$U_{eq} = \tfrac{1}{3}|U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha|.$$

	x	y	z	U_{eq}
C(1)	13936 (4)	3648 (3)	7113 (2)	67 (2)
C(2)	12877 (3)	2567 (3)	7365 (2)	56 (2)
C(3)	11556 (4)	1964 (3)	6965 (2)	69 (2)
C(4)	10693 (4)	919 (3)	7265 (2)	65 (2)
C(5)	10447 (3)	697 (3)	8035 (2)	56 (2)
C(6)	10908 (3)	1531 (2)	8702 (1)	46 (2)
C(7)	12314 (3)	2289 (2)	8768 (1)	44 (1)
C(8)	13697 (3)	2187 (2)	8188 (1)	45 (2)
C(9)	15276 (3)	3073 (2)	8305 (1)	53 (2)
C(10)	16572 (3)	2680 (3)	7712 (2)	63 (2)
C(11)	15690 (4)	3092 (3)	6899 (2)	73 (2)
C(12)	14533 (4)	4252 (3)	7917 (2)	70 (2)
C(13)	9727 (3)	1546 (3)	9360 (2)	53 (2)
O(131)	9939 (3)	2193 (2)	9936 (1)	90 (2)
O(132)	8427 (2)	746 (2)	9241 (1)	67 (1)
C(14)	7236 (3)	692 (3)	9853 (2)	78 (2)
C(15)	12731 (3)	3141 (2)	9459 (1)	50 (2)
O(152)	13793 (3)	2905 (2)	10009 (1)	77 (1)
O(151)	11890 (2)	4213 (2)	9360 (1)	61 (1)
C(16)	12322 (5)	5119 (3)	9979 (2)	91 (3)

positional parameters and U_{eq} values are listed in Table 1 while Tables 2 and 3 give bond lengths and selected valence and torsion angles. Force-field calculations were performed with a modified $MMPI$ program of Allinger (1975). The two COOCH$_3$ side chains of the 1,3,5-cycloheptatriene ring in compound (5) were replaced with H atoms. The calculated distances and angles are included in Tables 2 and 3.*

Discussion. Fig. 1 is an $ORTEP$ drawing (Johnson, 1971) of compound (5). Cycloheptatriene systems display a flexible boat-shaped conformation which is easily influenced by ring substitution (Stegemann & Lindner, 1979; Lambert, Durham, Lepoutere & Roberts, 1965; Gunther, Gorlitz & Meisenheimer, 1974; Davis & Tulinsky, 1966). In compound (5) the cycloheptatriene system is in a slightly distorted boat conformation with the C(4)–C(5) bond representing the stern. A force-field calculation with the two COOCH$_3$ side chains in compound (5) replaced by H atoms gave reasonable agreement with the X-ray values. The parameters obtained from the calculation are given in Tables 2 and 3. These tables also present the values for an isolated 1,3,5-cycloheptatriene system (Kao & Allinger, 1977), the experimental values for the 1,3,5-cycloheptatriene (Stegemann & Lindner, 1979) and a thujic acid derivative (Davis & Tulinsky, 1966). Compound (5) and the calculated model show standard deviations of $0\cdot01$ Å in distances and $2°$ in valence angles.

* Lists of H-atom coordinates, anisotropic thermal parameters, selected valence and torsion angles, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39562 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å)

	(5)	(5c)*	CHT(KA)*	Steg.*	Davis*
C(1)–C(2)	1·511 (5)	1·514			
C(1)–C(11)	1·549 (5)	1·536			
C(1)–C(12)	1·532 (5)	1·535			
C(2)–C(3)	1·327 (4)	1·347	1·348	1·336	1·322
C(2)–C(8)	1·519 (4)	1·504	1·502	1·497	1·515
C(3)–C(4)	1·430 (5)	1·457	1·462	1·475	1·458
C(4)–C(5)	1·353 (5)	1·358	1·355	1·357	1·338
C(5)–C(6)	1·457 (4)	1·460	1·462	1·466	1·476
C(6)–C(7)	1·350 (3)	1·351	1·348	1·338	1·337
C(6)–C(13)	1·504 (4)	—	—	—	—
C(7)–C(8)	1·520 (3)	1·500	1·502	1·467	1·516
C(7)–C(15)	1·495 (3)	—			
C(8)–C(9)	1·540 (3)	1·543			
C(9)–C(10)	1·541 (4)	1·543			
C(9)–C(12)	1·518 (4)	1·539			
C(10)–C(11)	1·530 (5)	1·542			
C(13)–O(131)	1·195 (4)	—			
C(13)–O(132)	1·319 (3)	—			
O(132)–C(14)	1·449 (4)	—			
C(15)–O(152)	1·195 (3)				
C(15)–O(151)	1·330 (3)	—			
O(152)–C(16)	1·446 (4)	—			

* (5c) is the force-field calculation for compound (5) with side chains replaced by H; CHT(KA) is the force-field calculation for 1,3,5-cycloheptatriene by Kao & Allinger (1977); Steg. represents the cycloheptatriene ring from 2,5-dimethyl-3,4-diphenyl-1,3,5-cycloheptatriene (Stegemann & Lindner, 1979); Davis represents the cycloheptatriene taken from the thujic acid derivative (Davis & Tulinsky, 1966).

Table 3. Selected valence angles (°) and torsion angles (°)

	(5)	(5c)*	CHT(KA)*	Steg.*	Davis*
C(2)C(1)C(11)	105·6†	107·7			
C(2)C(1)C(12)	101·6	99·7			
C(11)C(1)C(12)	100·8	103·9			
C(1)C(2)C(3)	129·9	126·1			
C(1)C(2)C(8)	106·5	107·2			
C(3)C(2)C(8)	123·4	126·6	121·6	122·8	123·9
C(2)C(3)C(4)	124·5	123·3	124·1	121·0	127·3
C(3)C(4)C5)	126·6	125·3	125·7	125·7	125·6
C(4)C(5)C(6)	125·7	126·7	125·7	124·5	124·7
C(5)C(6)C(7)	124·6	125·2	124·1	121·7	127·2
C(5)C(6)C(13)‡	117·4	116·5	—	—	—
C(7)C(6)C(13)‡	118·0	118·3	—	—	—
C(6)C(7)C(15)‡	122·9	118·6			
C(8)C(7)C(15)‡	116·1	117·1			
C(2)C(8)C(7)	108·6	109·2	111·5	108·8	108·2
C(2)C(8)C(9)	101·1	99·7			
C(7)C(8)C(9)	117·6	114·8			
C(8)C(9)C(10)	107·2	109·4			
C(8)C(9)C(12)	102·4	103·3			
C(10)C(9)C(12)	101·0	101·9			
C(9)C(10)C(11)	104·3	102·8			
C(1)C(11)C(10)	102·5	102·3			
C(1)C(12)C(9)	94·9	92·1			
C(2)C(3)C(4)C(5)	31·9 (5)	32·7		41·7	
C(3)C(4)C(5)C(6)	4·7 (5)	0·7		−2·5	
C(4)C(5)C(6)C(7)	−34·5 (4)	−32·9		−38·0	
C(5)C(6)C(7)C(8)	−9·0 (4)	−3·6		0·0	
C(6)C(7)C(8)C(2)	66·8 (3)	58·9		65·9	
C(7)C(8)C(2)C(3)	−63·0 (3)	−60·9		−66·4	
C(8)C(2)C(3)C(4)	2·6 (5)	4·7		0·0	

* See Table 2 for column headings.
† E.s.d. 0·2–0·3°.
‡ C(13) and C(15) replaced by H in (5c).

Bond alternation is observed in all cases with the double bonds in compound (5) ranging from 1·327 (4) to 1·353 (5) Å and the two $C(sp^2)–C(sp^2)$ single bonds being 1·430 (5) and 1·457 (4) Å. The C(3)–C(4) value of 1·430 (5) Å is significantly shorter than any of the calculated or observed values while the C(2)–C(3) experimental values are consistently shorter than those obtained by calculation. Variations in the experimental values can be related to differences in substitution patterns. The interplanar angles α = 52·0° [between C(7)C(8)C(2) and C(2)C(3)C(6)C(7)] and β = 27·6° [C(3)C(4)C(5)C(6) and C(2)C(3)C(6)C(7)] can be compared with the values of 52·6 and 34·3° (Stegemann & Lindner, 1979) and 47·9 and 24·4° (Davis & Tulinsky, 1966).

The two $CCOOCH_3$ groups exhibit extended conformations with one group coplanar with the C(6)–C(7) double bond [C(7)C(6)C(13)O(131) = 0·7 (6)°] and the other almost perpendicular [C(6)C(7)C(15)-O(151) = −85·7 (6)°]. The angle between the two planes is 94·3 (7)°. The interactions of the carbonyl groups with the cycloheptatriene π system probably account for some of the discrepancies between observed and calculated values. The six-membered ring of the norbornane system normally exists in a perfect boat conformation due to the bridging methylene group; however, the fusion of the seven-membered ring imparts a slight twist to the boat conformation. This is reflected in small variations of usually equivalent torsion angles [e.g. −68·2 (6) and 74·0 (6)° for C(2)C(8)C(9)C(10) and C(8)C(2)C(1)C(11)]. The shortest intramolecular contacts (calculated and observed) are 2·39, 2·41, and 2·58 Å for H(10a)···H(8), H(12b)···H(11b), and H(12b)···H(10b). There are three H···H intermolecular contacts of less than 2·6 Å.
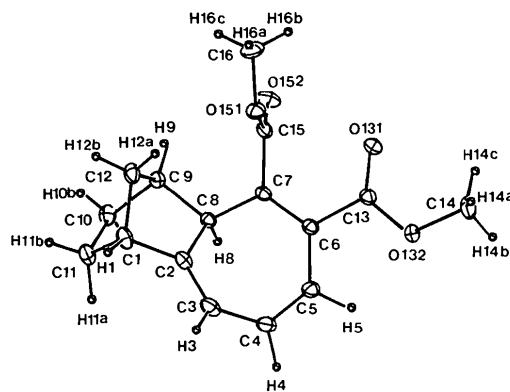
Fig. 1. ORTEP drawing of compound (5). Thermal ellipsoids are drawn at the 35% probability level.

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The Preferred Rotational Orientation of Equatorial and Axial Carboxyl Groups and Their Influence on the Cyclohexane Ring Geometry. Structures of Two Cyclohexanecarboxylic Acids: *cis*-1,3-Cyclohexanedicarboxylic Acid (I) and *trans*-1,3-Cyclohexanedicarboxylic Acid (II), $C_8H_{12}O_4$

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Abstract. (I): $M_r = 172 \cdot 18$, triclinic, $P\bar{1}$, $a = 5 \cdot 340$ (2), $b = 6 \cdot 558$ (1), $c = 13 \cdot 834$ (1) Å, $\alpha = 104 \cdot 54$ (1), $\beta = 96 \cdot 36$ (2), $\gamma = 69 \cdot 64$ (2)°, $V = 439 \cdot 5$ Å^3, $Z = 2$, $D_x = 1 \cdot 305$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 113$ mm^{-1}, $F(000) = 184$, $T \simeq 293$ K, $R = 0 \cdot 044$ for 1634 observed reflections $[I > 2 \cdot 5\sigma(I)]$. (II): $M_r = 172 \cdot 18$, triclinic, $P\bar{1}$, $a = 5 \cdot 301$ (1), $b = 6 \cdot 192$ (3), $c = 13 \cdot 311$ (2) Å, $\alpha = 102 \cdot 79$ (4), $\beta = 97 \cdot 20$ (1), $\gamma = 90 \cdot 50$ (4)°, $V = 422 \cdot 4$ Å^3, $Z = 2$, $D_x = 1 \cdot 359$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 117$ mm^{-1}, $F(000) = 184$, $T \simeq 293$ K, $R = 0 \cdot 054$ for 1671 observed reflections $[I > 2 \cdot 5\sigma(I)]$. The crystal of (I) consists of infinite chains of molecules along [201]. In each chain the molecules are held together around centres of symmetry by approximately linear hydrogen bonds of 2·664 and 2·648 Å. The carbonyl O atoms of the equatorial carboxyl groups are twisted away from the C_β-eclipsed position by 21·3 and 15·5°. The average C—C bond distance, C—C—C bond angle and C—C—C—C torsion angle in the ring are 1·525 Å, 110·9° and 56·4°, respectively. The cyclohexane ring is very regular: no single distance or angle deviates more that 3σ from its average ring value. No significant local influence of an equatorial carboxyl group on the geometry of the cyclohexane ring can be established. The crystal of (II) consists of infinite chains of molecules along [$\bar{1}11$]. In each chain the molecules are held together around centres of symmetry by approximately linear hydrogen bonds of 2·666 and 2·686 Å. The carbonyl O atom of the equatorial and axial carboxyl group is twisted away from the C_β-eclipsed position by 5·2 and 5·4°, respectively. The average C—C bond distance, C—C—C bond angle and C—C—C—C torsion angle in the ring are 1·524 Å, 111·4° and 55·0°, respectively. Flattening of the cyclohexane ring at the axial carboxyl side of the ring, enlarging of the C_α—C_β—C_γ angle, elongation of the C_α—C_β bonds and shortening of the C_β—C_γ bonds is observed. These effects on the ring parameters have been observed as well in several other structures containing an axial carboxyl group. The analysis (again) illustrates that there is no difference between the rotational orientation of an axial and an equatorial carboxyl group in cyclohexanecarboxylic acids: both prefer the synperiplanar C_β—C_α—C=O arrangement.