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The Structures of Ethyl 1,4,5-*exo*-Trimethyl-7-oxo-2,3-diphenylbicyclo[2.2.1]hept-2-ene-5-*endo*-carboxylate (*A*) and Ethyl 1,4-Dimethyl-7-oxo-2,3-diphenylbicyclo[2.2.1]hept-2-ene-5-*endo*-carboxylate (*B*)

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Abstract

Crystals of $C_{25}H_{26}O_3$ (*A*) are triclinic, space group $P\bar{1}$, with $a = 9{\cdot}197$ (2), $b = 10{\cdot}357$ (2), $c = 11{\cdot}086$ (3) Å, $\alpha = 94{\cdot}07$ (2), $\beta = 98{\cdot}21$ (3), $\gamma = 90{\cdot}82$ (2)°, $V = 1042{\cdot}2$ Å^3, $Z = 2$, $D_{\rm obs} = 1{\cdot}19$, $D_{\rm calc} = 1{\cdot}198$ Mg m^{-3} and μ(Cu $K\alpha$) = 0·661 mm^{-1}; R = 6·2% for 2525 significant reflections. Crystals of $C_{24}H_{24}O_3$ (*B*) are monoclinic, space group $P2_1/a$, with $a = 11{\cdot}584$ (2), $b = 11{\cdot}315$ (2), $c = 15{\cdot}900$ (4) Å, $\beta = 104{\cdot}02$ (2)°, $V = 2022{\cdot}4$ Å^3, $Z = 4$, $D_{\rm obs} = 1{\cdot}19$, $D_{\rm calc} = 1{\cdot}185$ Mg m^{-3} and μ(Mo $K\alpha$) = 0·081 mm^{-1}; R = 4·2% for 1990 significant reflections. The steric strain introduced by the bulky substituents on the norbornenone system is discussed. In addition, a possible relationship between the orientation of the ester function and the anisochrony of its *O*-methylene protons is brought out.

Introduction

The X-ray crystallographic investigations of the title compounds were undertaken in order to verify the hypothesis (Bhaskara Reddy, 1976) that the greater anisochrony exhibited by the *O*-methylene protons of compound *A*, which was in apparent violation of a heuristic developed by Binsch (1973), could have arisen, in part, due to a tilt in the ester axis, C(5)—C(10) (Fig. 1), towards the phenyl rings, caused by changing the substituent from H to methyl at C(5).

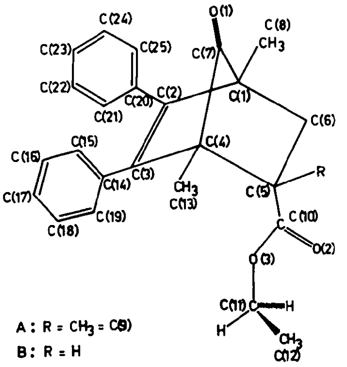

Fig. 1. Numbering of the atoms.

The heuristic developed by Binsch (1973) was for ethanes of the type $XYZCCu_Au_Bu$ and did not take into account possible cyclic connectivity among the ligands *X*, *Y*, *Z*. That it would be violated if such connectivity existed is demonstrated by the compounds *A* and *B*.

Experimental

Preliminary Weissenberg photographs indicated the monoclinic space group $P2_1/a$ for *B* and the triclinic space group $P1$ or $P\bar{1}$ for *A*. Intensity data were collected on a CAD-4 diffractometer with Cu $K\alpha$ and Mo $K\alpha$ radiations for *A* and *B* respectively. The total numbers of reflections collected for *A* and *B* were 3107

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and 2717 respectively, of which 2525 and 1990 were significant $[|F_o| > 2\sigma(|F_o|)]$.

Structure solution and refinement

Both structures *A* and *B* were solved by direct methods (structure *A* in $P\bar{1}$) using the programs *MULTAN* (Germain, Main & Woolfson, 1971) and *SHELX* (Sheldrick, 1976) respectively. During the refinement of structure *A*, the isotropic temperature factors of the ethyl-group atoms were found to be very high (B = 11·0 and 11·2 Å^2 for the methylene and the methyl carbons respectively). In addition, the bond lengths involving these atoms were abnormal (C—O = 1·59 and C—C = 1·27 Å) compared with the values of 1·459 (5) and 1·470 (8) Å for the corresponding bonds in 5-ethoxycarbonyl-3,4′-diethyl-4,3′,5′-trimethyl-2,2′-dipyrrolyl ketone (5-ethoxycarbonyl compound hereafter) (Sheldrick, Becker & Engel, 1978). Disorder was therefore suspected and a difference Fourier map (omitting the ethyl carbons) revealed, in addition to the methylene and methyl carbons at their original positions, a peak separated by 1 Å from the methylene carbon. This was taken to be another position for the methylene carbon [C(11)]. Based on the ratio of peak strengths, occupanices of 0·4 and 0·6 were assigned to these two positions, keeping the isotropic temperature factor fixed at 6·5 Å^2. The rest of the atoms were treated anisotropically and, when the R factor was 10·2%, a difference Fourier map revealed all the H atoms, except those of the ethyl group, at stereochemically meaningful positions. Refinement, including these 21 H atoms (with isotropic temperature factors)

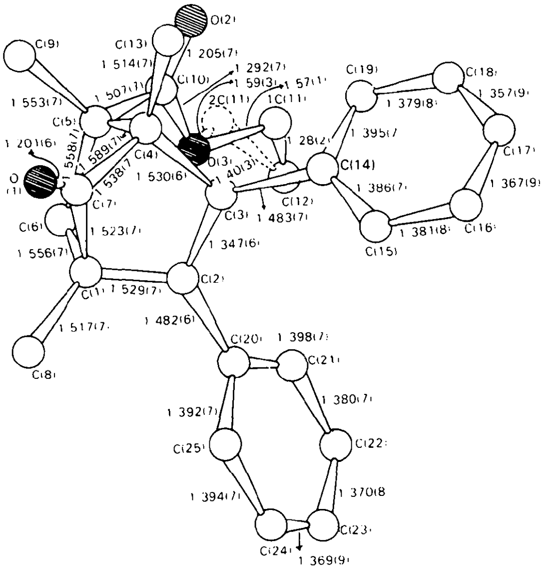

Fig. 2. Bond lengths (Å) involving the non-hydrogen atoms, with e.s.d.'s in parentheses (structure *A*).

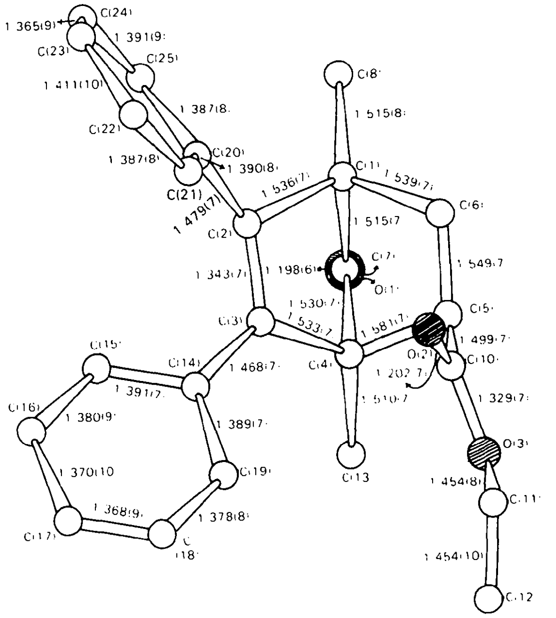

Fig. 3. Bond lengths involving the non-hydrogen atoms, with e.s.d.'s in parentheses (structure *B*).

Table 1. *Final fractional positional parameters* (×10^4) *and equivalent isotropic thermal parameters for non-hydrogen atoms in structure A*

E.s.d.'s are in parentheses.

	x	y	z	B_{eq} (Å^2)*
C(1)	2594 (5)	296 (5)	6333 (4)	3·12
C(2)	2563 (5)	1734 (5)	6099 (4)	2·89
C(3)	2942 (5)	2434 (4)	7172 (4)	2·80
C(4)	3217 (5)	1510 (5)	8194 (4)	3·06
C(5)	1701 (5)	805 (5)	8307 (4)	3·36
C(6)	1272 (5)	62 (5)	7031 (5)	3·66
C(7)	3826 (5)	417 (5)	7412 (4)	3·26
C(8)	2753 (6)	−715 (5)	5304 (5)	4·10
C(9)	1911 (7)	−170 (6)	9315 (5)	4·66
C(10)	624 (6)	1798 (6)	8656 (5)	4·01
1C(11)	−1294 (12)	3299 (12)	8082 (11)	6·59
2C(11)	−1939 (27)	2478 (22)	8174 (20)	6·28
C(12)	−2435 (16)	3309 (14)	7271 (13)	11·97
C(13)	4204 (6)	1957 (5)	9367 (5)	4·12
C(14)	3185 (5)	3856 (5)	7363 (4)	3·00
C(15)	3892 (6)	4500 (5)	6550 (5)	4·21
C(16)	4205 (7)	5813 (6)	6738 (6)	5·03
C(17)	3807 (8)	6508 (6)	7729 (6)	4·94
C(18)	3087 (7)	5900 (6)	8522 (5)	4·65
C(19)	2762 (6)	4589 (5)	8354 (5)	3·91
C(20)	1996 (5)	2219 (5)	4900 (4)	3·04
C(21)	794 (5)	3035 (5)	4814 (4)	3·55
C(22)	214 (6)	3487 (6)	3711 (5)	4·43
C(23)	814 (7)	3144 (6)	2675 (5)	4·55
C(24)	2001 (7)	2355 (6)	2738 (5)	4·53
C(25)	2598 (6)	1880 (5)	3843 (4)	3·90
O(1)	4954 (4)	−153 (4)	7605 (4)	4·52
O(2)	721 (5)	2359 (5)	9656 (4)	5·65
O(3)	−408 (6)	2055 (7)	7794 (4)	6·65

* $B_{eq} = (B_1B_2B_3)^{1/3}$.

Table 2. *Final fractional positional parameters* (×10^4) *and equivalent isotropic thermal parameters for non-hydrogen atoms in structure B*

E.s.d.'s are in parentheses.

	x	y	z	B_{eq}*
C(1)	3202 (4)	1920 (4)	3249 (3)	4·19
C(2)	2488 (4)	2631 (4)	2475 (3)	3·99
C(3)	2276 (4)	3714 (4)	2751 (3)	3·77
C(4)	2856 (4)	3802 (4)	3721 (3)	3·82
C(5)	4247 (4)	3738 (4)	3827 (3)	4·20
C(6)	4449 (5)	2491 (5)	3491 (3)	4·68
C(7)	2678 (4)	2503 (5)	3928 (3)	4·22
C(8)	3190 (5)	581 (5)	3207 (4)	5·88
C(10)	4712 (4)	4718 (5)	3366 (4)	4·67
C(11)	5253 (7)	6748 (6)	3434 (5)	7·21
C(12)	4819 (7)	7810 (6)	3768 (5)	8·18
C(13)	2411 (5)	4695 (5)	4276 (3)	4·82
C(14)	1599 (4)	4676 (4)	2236 (3)	4·05
C(15)	544 (5)	4436 (5)	1621 (4)	5·34
C(16)	−96 (5)	5335 (6)	1133 (4)	6·65
C(17)	288 (6)	6483 (6)	1249 (4)	6·63
C(18)	1324 (6)	6744 (5)	1848 (4)	6·09
C(19)	1964 (5)	5850 (5)	2338 (4)	5·03
C(20)	2300 (4)	2202 (4)	1573 (3)	4·46
C(21)	2873 (5)	2783 (5)	1016 (4)	5·49
C(22)	2779 (6)	2371 (6)	182 (4)	6·77
C(23)	2107 (6)	1378 (6)	−116 (4)	6·87
C(24)	1529 (5)	815 (5)	423 (4)	5·77
C(25)	1624 (5)	1216 (6)	1263 (4)	6·77
O(1)	2250 (4)	2083 (4)	4476 (3)	5·66
O(2)	4927 (4)	4738 (4)	2667 (3)	6·52
O(3)	4835 (4)	5716 (3)	3821 (3)	5·82

* $B_{eq} = (B_1B_2B_3)^{1/3}$.

Table 3. *Fractional coordinates* (×10^3) *for hydrogen atoms for structure A, with their isotropic temperature factors*

E.s.d.'s are given in parentheses. The temperature factor is of the form: $T = \exp(-B \sin^2 \theta/\lambda^2)$.

	Bonded to	x	y	z	B (Å^2)
H(1)	C(6)	114 (7)	−96 (6)	724 (6)	7·6 (1·5)
H(2)	C(6)	25 (6)	45 (5)	656 (5)	4·2 (1·1)
H(3)	C(8)	185 (7)	−65 (6)	453 (5)	7·2 (1·6)
H(4)	C(8)	363 (7)	−55 (7)	490 (6)	5·8 (1·3)
H(5)	C(8)	277 (7)	−169 (6)	569 (5)	6·5 (1·5)
H(6)	C(9)	275 (7)	−91 (6)	904 (6)	6·0 (1·6)
H(7)	C(9)	209 (6)	27 (6)	1013 (5)	5·2 (1·3)
H(8)	C(9)	109 (8)	−77 (7)	927 (6)	6·9 (1·8)
H(9)	C(13)	459 (7)	123 (7)	985 (6)	6·9 (1·5)
H(10)	C(13)	513 (8)	241 (7)	929 (6)	8·4 (1·7)
H(11)	C(13)	370 (6)	249 (6)	992 (5)	4·9 (1·4)
H(12)	C(15)	418 (7)	395 (6)	576 (6)	7·6 (1·6)
H(13)	C(16)	488 (10)	626 (9)	612 (8)	11·7 (2·6)
H(14)	C(17)	404 (6)	744 (6)	790 (5)	5·1 (1·4)
H(15)	C(18)	289 (7)	633 (6)	918 (6)	6·7 (1·7)
H(16)	C(19)	220 (5)	422 (5)	893 (4)	3·3 (1·0)
H(17)	C(21)	43 (5)	333 (4)	550 (4)	2·4 (0·9)
H(18)	C(22)	−50 (8)	406 (7)	375 (6)	9·0 (2·0)
H(19)	C(23)	49 (7)	337 (6)	198 (6)	6·6 (1·5)
H(20)	C(24)	242 (6)	217 (5)	199 (5)	5·2 (1·2)
H(21)	C(25)	354 (7)	125 (6)	396 (6)	6·0 (1·4)

Table 4. *Fractional coordinates* (×10^3) *for hydrogen atoms in structure B, with their isotropic temperature factors*

E.s.d.'s are given in parentheses. The temperature factor is of the form: $T = \exp(-B \sin^2 \theta/\lambda^2)$.

	Bonded to	x	y	z	B (Å^2)
H(1)	C(5)	459 (3)	380 (3)	440 (3)	3·7 (0·9)
H(2)	C(6)	478 (4)	255 (4)	298 (3)	5·3 (1·0)
H(3)	C(6)	496 (4)	202 (4)	397 (3)	6·9 (1·3)
H(4)	C(8)	369 (5)	33 (5)	379 (4)	8·6 (1·6)
H(5)	C(8)	235 (5)	26 (5)	305 (4)	7·6 (1·4)
H(6)	C(8)	356 (4)	32 (4)	268 (3)	5·8 (1·1)
H(7)	C(11)	494 (6)	672 (6)	278 (5)	13·1 (2·1)
H(8)	C(11)	616 (8)	668 (7)	364 (6)	15·9 (2·7)
H(9)	C(12)	495 (12)	719 (10)	422 (9)	24·8 (5·1)
H(10)	C(12)	505 (6)	848 (6)	343 (5)	10·8 (2·0)
H(11)	C(12)	392 (6)	771 (6)	363 (5)	11·1 (1·9)
H(12)	C(13)	263 (4)	553 (4)	426 (3)	6·5 (1·3)
H(13)	C(13)	148 (5)	471 (5)	412 (4)	7·4 (1·4)
H(14)	C(13)	269 (5)	452 (5)	486 (4)	7·5 (1·4)
H(15)	C(15)	26 (4)	360 (4)	152 (3)	6·3 (1·2)
H(16)	C(16)	−89 (7)	514 (6)	65 (6)	13·1 (2·3)
H(17)	C(17)	−1 (4)	712 (4)	94 (3)	6·6 (1·3)
H(18)	C(8)	172 (5)	754 (5)	204 (4)	8·4 (1·5)
H(19)	C(19)	267 (4)	604 (4)	279 (3)	5·0 (1·1)
H(20)	C(21)	341 (4)	353 (4)	123 (3)	5·5 (1·1)
H(21)	C(22)	317 (8)	288 (7)	−31 (6)	14·0 (2·7)
H(22)	C(23)	206 (7)	108 (6)	−72 (5)	9·1 (2·1)
H(23)	C(24)	110 (5)	7 (5)	23 (4)	7·4 (1·4)
H(24)	C(25)	127 (5)	85 (4)	161 (4)	7·6 (1·4)

and with anisotropic temperature factors for the non-hydrogen atoms (including the disordered ones), resulted in a final R factor of 6·2%.* The final refined occupancies of the disordered positions are 0·65 and 0·35 for 1C(11) and 2C(11) respectively. Structure B does not show any disorder in the ester function. The final R value for this structure is 4·2%.* The block-diagonal least-squares refinement program used was that of Shiono (1968), modified by B. S. Reddy for an IBM 360/44 computer. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(|F_o|)$. Figs. 2 and 3 show the bond lengths involving the non-hydrogen atoms in structures A and B respectively. Tables 1 and 2 give the final positional parameters for the non-hydrogen atoms, and Tables 3 and 4 the positional and thermal parameters for the H atoms in structures A and B respectively. Table 5 gives the bond angles involving the non-hydrogen atoms.

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* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms, for both compounds, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35752 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Bond angles (°) involving the non-hydrogen atoms for structures A and B*

The e.s.d.'s are given in parentheses.

	A	*B*		*A*	*B*		*A*	*B*
C(2)–C(1)–C(6)	105·3 (4)	105·8 (4)	C(4)–C(5)–C(10)	109·4 (4)	113·1 (4)	C(3)–C(14)–C(15)	119·6 (4)	120·4 (5)
C(2)–C(1)–C(7)	96·4 (4)	96·4 (4)	C(6)–C(5)–C(10)	115·4 (4)	113·9 (4)	C(3)–C(14)–C(19)	122·8 (4)	122·4 (5)
C(2)–C(1)–C(8)	120·2 (4)	119·3 (4)	C(4)–C(5)–C(9)	110·8 (4)	–	C(15)–C(14)–C(19)	117·6 (4)	117·2 (5)
C(6)–C(1)–C(7)	99·2 (4)	98·8 (4)	C(9)–C(5)–C(10)	107·9 (4)	–	C(14)–C(15)–C(16)	121·0 (5)	120·9 (5)
C(6)–C(1)–C(8)	115·1 (4)	115·4 (4)	C(6)–C(5)–C(9)	109·9 (4)	–	C(15)–C(16)–C(17)	120·4 (6)	120·4 (6)
C(7)–C(1)–C(8)	117·2 (4)	117·7 (4)	C(1)–C(6)–C(5)	105·0 (4)	105·0 (4)	C(16)–C(17)–C(18)	119·5 (6)	119·9 (6)
C(1)–C(2)–C(3)	108·7 (4)	108·9 (4)	C(1)–C(7)–C(4)	99·3 (4)	99·5 (4)	C(17)–C(18)–C(19)	121·2 (6)	119·7 (6)
C(1)–C(2)–C(20)	123·3 (4)	122·0 (4)	C(1)–C(7)–O(1)	131·1 (4)	130·8 (5)	C(18)–C(19)–C(14)	120·3 (5)	121·8 (5)
C(3)–C(2)–C(20)	127·5 (4)	128·2 (5)	C(4)–C(7)–O(1)	129·6 (4)	129·6 (5)	C(2)–C(20)–C(21)	119·1 (4)	118·7 (5)
C(2)–C(3)–C(4)	108·9 (4)	108·4 (4)	C(5)–C(10)–O(2)	123·4 (5)	125·3 (5)	C(2)–C(20)–C(25)	122·7 (4)	123·2 (5)
C(2)–C(3)–C(14)	123·8 (4)	123·9 (4)	C(5)–C(10)–O(3)	115·6 (5)	111·5 (4)	C(21)–C(20)–C(25)	118·1 (4)	118·1 (5)
C(4)–C(3)–C(14)	127·1 (4)	127·6 (4)	O(2)–C(10)–O(3)	121·0 (5)	123·2 (5)	C(20)–C(21)–C(22)	121·0 (5)	121·0 (5)
C(3)–C(4)–C(5)	108·2 (4)	107·0 (4)	C(10)–O(3)–C(11)	114·6 (9) [1C(11)] 118 (1·2) [2C(11)]	117·3 (5) –	C(21)–C(22)–C(23)	120·3 (5)	120·3 (6)
C(3)–C(4)–C(7)	95·5 (3)	96·1 (4)	O(3)–C(11)–C(12)	108 (1·0) [1C(11)] 101 (1·5) [2C(11)]	109·4 (6) –	C(22)–C(23)–C(24)	119·8 (5)	118·2 (6)
C(3)–C(4)–C(13)	119·1 (4)	120·2 (4)				C(23)–C(24)–C(25)	120·8 (5)	121·5 (6)
C(5)–C(4)–C(7)	97·0 (3)	96·9 (4)				C(24)–C(25)–C(20)	119·9 (5)	120·9 (5)
C(7)–C(4)–C(13)	115·1 (4)	115·7 (4)						
C(4)–C(5)–C(6)	103·4 (4)	103·8 (4)						

Discussion

There are two sets of equivalent bonds in the present structures: the C(1)—C(2) class consisting of the C(1)—C(2) and the C(3)—C(4) bonds and the C(1)—C(7) class comprising the C(1)—C(7) and C(4)—C(7) bonds. As can be seen from Figs. 2 and 3, the bonds belonging to the C(1)—C(2) class in structure *A* are equal in length (within the limits of experimental error) and are equal to the corresponding bonds in structure *B*. However, the bonds in the C(1)—C(7) category range from 1·515 (7) Å in structure *B* to 1·538 (7) Å in structure *A*. Such significant differences (at the 3σ level) between equivalent bonds have also been observed in the structure of a brendene derivative (Usha, 1980), where the substituents have again distorted the norbornane system.

The norbornenone moiety in *A* and *B* has some long bonds – the longest being C(4)—C(5) [1·589 (7) Å in *A* and 1·581 (7) Å in *B*]. Such long bonds between highly substituted C atoms are not uncommon. They have been found to occur in a tetracyclic diketone, 1·587 (3) Å (Przybylska, 1972), in a toxaphene component, 1·610 (3) Å (Swanson, Hope & Landrum, 1978), and in a few other cases. Whether this lengthening is solely due to the substituent effects or whether there are any contributions from electronic factors is not too well understood. C(4)—C(5) in *A*, where both C(4) and C(5) are fully substituted, is slightly, though not significantly, longer [1·589 (7) Å] than the corresponding bond in *B* [1·581 (7) Å] where C(5) has a H in place of the CH_3 in *A*. This does not give any conclusive evidence for the effect of substituents on the length of a bond. Moreover, there is a possibility of a through-space interaction (Hoffmann, 1971) between the C(2)—C(3) double bond and the apex carbonyl group in *A* and *B*. In this connection it may be observed that angles C(6)—C(1)—C(7) and C(5)—C(4)—C(7) are larger than C(2)—C(1)—C(7) and C(3)—C(4)—C(7) in both compounds (Table 5), indicating that the carbonyl group is bent towards the double bond. However, a correlation between such a through-space interaction and the presence of long bonds appears fortuitous.

All the bond angles within the norbornenone moiety of *A* are comparable with the corresponding values in *B*. As expected, the bridgehead angle has decreased considerably [99·3 (4)° for *A* and 99·5 (4)° for *B*] from the ideal value of 120·0° for a straight-chain ketone. As can be seen from the torsion angles (Table 6), the five-membered rings are in the envelope conformation and the six-membered ring is in the boat conformation. The pseudorotation angles, Δ, calculated by the method of Altona, Geise & Romers (1968), for the saturated five-membered rings in *A* and *B* are 28·4 and 33·7° respectively. For these two rings, φ_m (the maximum possible torsion angle) is 59·3 and −59·0° respectively. The twist in the norbornane system in these two structures falls into the *contra* category (Altona & Sundaralingam, 1970). The twist of the unsaturated arm is negligible, whereas the saturated arm shows some twist, the latter for *A* being significantly larger [2·9 (5)°] than that of *B* [1·1 (5)°]. This is probably due to the presence of an additional methyl group at C(5) in structure *A*.

The cis-stilbene moiety

The two phenyl rings attached to the double bond resemble *cis*-stilbene. The bond lengths in the phenyl

Table 6. *Torsion angles (°) within the norbornenone moiety for structures A and B*

	A	*B*		*A*	*B*		*A*	*B*
C(6)–C(1)–C(2)–C(3)	69·8 (5)	−69·7 (5)	C(4)–C(5)–C(6)–C(1)	4·3 (5)	−1·7 (5)	C(1)–C(2)–C(3)–C(4)	−1·2 (5)	1·1 (5)
C(1)–C(2)–C(3)–C(4)	−1·2 (5)	1·1 (5)	C(5)–C(6)–C(1)–C(7)	30·6 (4)	−32·7 (5)	C(2)–C(3)–C(4)–C(7)	33·1 (4)	−32·7 (5)
C(2)–C(3)–C(4)–C(5)	−66·1 (5)	66·5 (5)	C(6)–C(1)–C(7)–C(4)	−55·5 (4)	56·4 (4)	C(3)–C(4)–C(7)–C(1)	−51·7 (4)	51·4 (4)
C(3)–C(4)–C(5)–C(6)	61·2 (4)	−63·8 (5)	C(1)–C(7)–C(4)–C(5)	57·5 (4)	−56·5 (4)	C(4)–C(7)–C(1)–C(2)	51·2 (4)	−50·8 (4)
C(4)–C(5)–C(6)–C(1)	4·3 (5)	−1·7 (5)	C(7)–C(4)–C(5)–C(6)	−37·0 (4)	34·8 (4)	C(7)–C(1)–C(2)–C(3)	−31·6 (4)	31·4 (5)
C(5)–C(6)–C(1)–C(2)	−68·7 (4)	66·6 (5)						

rings range from 1·357 (9) Å in ring *α* (the ring closer to the ester group is designated *α* and the farther one, *β*) of structure *A* to 1·411 (10) Å in ring *β* of structure *B*. The terminal atoms of the benzene rings are greatly affected by thermal motion and the bonds emanating from them show the largest deviations from the normal length of 1·392 (4) Å for benzene (Cox, Cruickshank & Smith, 1958). The shortest and the longest phenyl-ring bonds mentioned above come under this category. The *α* and *β* rings have undergone different degrees of rotation about the C(3)–C(14) and C(2)–C(20) bonds, in order to maintain the Ph···Ph contacts to be the same as in 1,2-diphenylcyclopentene (Bernstein, 1975).

The ester group

The C(10)–O(2) bond of *A* and *B* [1·205 (7) and 1·202 (7) Å], though different from the normal value [1·233 (5) Å] recorded by Sutton (1965), agrees well with the value obtained for other ethyl esters; for instance, in the 5-ethoxycarbonyl compound, 1·206 (3) Å (Sheldrick *et al.*, 1978). The C(10)–O(3) length in *B* [1·329 (7) Å] agrees very well with that in the above-mentioned structure, 1·327 (4) Å. The ester group of structure *A* as mentioned earlier is disordered and makes any detailed discussion of the dimensions uncertain. The O(3)–C(11) bond of *B* [1·454 (8) Å] compares well with that in the 5-ethoxycarbonyl compound, 1·459 (5) Å. The CH_2–CH_3 length in *B* is shortened, but not significantly [1·45 (1) Å] relative to that in the 5-ethoxycarbonyl compound, 1·470 (8) Å.

In order to verify the hypothesis that the axis of the ester group in *A* would be tilted in a manner that would reposition the methylene protons in a region with a steeper gradient of the anisotropy locally originating in the phenyl rings, the distance between the methylene carbon and the centroid of the *α* phenyl ring was calculated [4·92 and 5·84 Å for 1C(11) and 2C(11) of *A* and 5·24 Å for C(11) of *B*]. However, the disorder in the CH_2 carbon of *A* and the subsequent large errors in the positional parameters prevented us from arriving at any direct conclusion regarding the above-mentioned hypothesis. However, there is some support for this assumption from the angle C(4)–C(5)–C(10), that for *A* [109·4 (4)°] being significantly smaller than that for *B* [113·1 (4)°] which implies that the ester group is pushed more towards the phenyl rings in *A* than in *B*.

The conformation of the ester group about the C(5)–C(10) bond in structure *A* is different from that in *B*. In *A*, the C(10)–O(3) bond is *cis* to the C(5)–C(6) bond, and in *B* the C(10)–O(2) bond is *cis* to it. The ester group in *A* was fixed in a conformation identical to that in *B* and this resulted in very short intermolecular contacts. Therefore, a rotation about the C(5)–C(10) bond has arisen mainly due to packing considerations.

Packing of the molecules in A and B

Figs. 4 and 5 show the packing of the molecules in structures *A* and *B*. The organization of the molecules in both these structures is such that the phenyl rings cluster around centres of symmetry. It is noteworthy that despite the several similarities in these two structures, they have crystallized in different space groups.

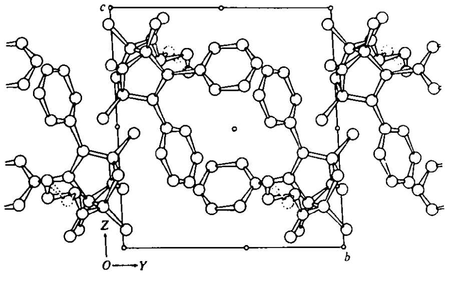

Fig. 4. Packing of the molecules viewed down the *a* axis (structure *A*).

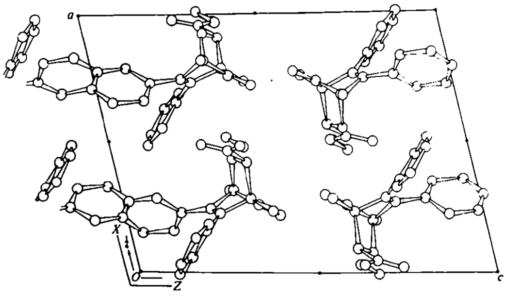

Fig. 5. Packing of the molecules viewed down the *b* axis (structure *B*).

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