© 2000 The Chemical Society of Japan

Molecular Structures of Methyl 5,6-Diaryl-1,2,4-trimethyl-7-oxobicyclo[2.2.1]hept-5-en-2-*endo*-carboxylates (aryl = phenyl or *o*-methoxyphenyl)

S. Natarajan Balasubrahmanyam,* Sunkada P. Rao,† Mohan M. Bhadbhade,††
C. Sudarsanakumar,††† and Bubbly K. Joseph†††

Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India

†Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India

††National Chemical Laboratory, Pune-400008, India

†††School of Pure & Applied Physics, Mahatma Gandhi University, Kottayam-686560, India

(Received April 26, 1999)

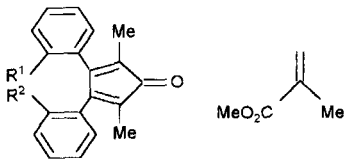
Structural assignments based on a reconstruction from the ^{1}H NMR dynamic behavior of the three 5,6-bis(substituted aryl)-7-oxo-5-norbornene-2-carboxylic esters named in the title have received confirmation from X-ray crystallographic studies. The specific structural features of these systems are compared among themselves and with those of 7-oxo-5,6-diphenyl-5-norbornene-2-carboxylic esters, analogues systems without substitution on the phenyl groups, which were studied earlier.

In the room temperature ^{1}H NMR spectra of dilute solutions in $CDCl_3$, the O–*Me*, C–*Me*, and aromatic *H* resonances of methyl 5,6-bis(2-methoxy phenyl)-1,2,4-trimethyl-7-oxobicyclo[2.2.1]hept-5-en-2-*endo*-carboxylate (**1**, synthesized in another connection)[1] are all seen as highly broadened envelopes. On nearing 220 K in VT-DNMR experiments, these resonances sharpened at apparently different rates[2] and the spectra became consistent with the presence of two unequally populated forms (ca. 10 : 1, as judged from the intensities of the components of the salient, duplexed methoxyphenyl and ester –O*Me* resonances; Figs. 4a and 4b).[2b]

Compound **1** was the major component in the mixture of products from the [4π+2π] cycloaddition of methyl methacrylate (**Ma**) to cyclopentadienone (**Cp1**) (Scheme 1). Since *endo*-esters are known to preponderate in such reactions,[3] an *endo* configuration was assumed for the ester function at C(2) in **1**. The temperature-variable behavior seemed to be attributable to hindered rotation of the magnetically highly anisotropic 2-methoxyphenyl groups, expected to prefer rotational conformations highly angled in relation to the C(5)–C(6) line in the forms detected at low temperature because coplanar arrangements would coincide with high barriers.[4] Two combinations with the methoxyphenyls in mutually opposed rotational orientations[5] [one methoxyphenyl rotated 'inward' (methoxy towards the *endo*-side), while the other is rotated 'outward' (methoxy towards the *exo*-side),[6] Structure **1**] were likely to be the largest and next-largest contributors to equilibrium at low temperature. The high disparity (10 : 1) in their stabilizations was thought to reflect likely large differences in the interactions (dipolar and steric) between the 'inward' and 'outward' rotated 'attitudes' of the *o*-methoxyphenyl group at C(6), proximal to the *endo*-ester function.[7]

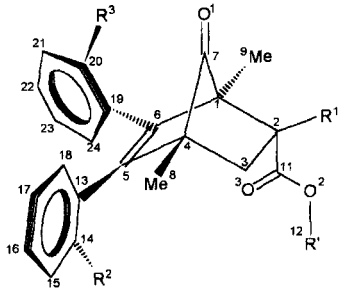
Support for this reconstruction was sought from the behavior of isomeric monomethoxyphenylated systems, **2** and **3**. The cycloaddition of **Ma** to the monomethoxyphenylated cyclopentadienone **Cp2** gave two easily separated components, labeled **A** and **B**, formed in the approximate ratio 2.6 : 1, together constituting about 80% of the weight of the total product.[8] While **A** and **B** could have been isomeric by virtue of a difference in configuration at C(2), their dynamic behavior appeared to be more compatible with *both* being *endo*-esters, regio-isomeric by way of location of the 2-methoxyphenyl group. The stabilization ratio in **A** was very similar to that in the bismethoxyphenylated case **1** (ca. 10 : 1; Figs. 4c and 4d),[2b] supporting not only the assignment of structure **2** (methoxyphenyl group at C(6), proximal to the *endo*-ester group), but also a possibility that the C(6) methoxyphenyl controls the attitude of the C(5) methoxyphenyl in the bismethoxyphenylated case.

The stabilization ratio was more equitable (ca. 10 : 7; Figs. 4e and 4f)[2b] in the case of **B**, consistent with the assignment of structure **3** to it, the 'inward' rotated methoxyphenyl, now at C(5), facing less steric interaction from the *endo*-ester than when at C(6). It seemed prudent to confirm through X-ray crystallography that all three products, **1**, **A**, and **B**, had the ester group in *endo*-orientation[9] at C(5) and that **A** and **B** were regio-isomeric [**A** having the *o*-methoxyphenyl group at C(6) and **B** at C(5)] before proceeding to attempt a full interpretation of the dynamic behavior of each of these



Ma

Cp1: R^1=R^2=OMe
Cp2: R^1=H; R^2=OMe



1: R^1=R'=Me; R^2=R^3=OMe
2: R^1=R'=Me; R^2=H; R^3=OMe (A)
3: R^1=R'=Me; R^2=OMe; R^3=H (B)
4: R^1=R^2=R^3=H; R'=Et
5: R^1=Me; R^2=R^3=H; R'=Et

Scheme 1.

systems.[10]

Experimental

Preparative: The bicyclic keto-esters **1**—**3** were prepared by the cycloaddition of methyl methacrylate (**Ma**) to cyclopentadienones **Cp**.[3,11] The latter can be prepared by dehydration of intermediate aldols from the condensation of diethyl ketone with appropriate benzils.[11]

2-Methoxy and 2,2′-dimethoxybenzils are long known, and were obtained in reported yields (respectively ca. 60 and ca. 40%) by following described procedures (benzoin condensation of 2-methoxybenzaldehyde or a mixture of 2-methoxybenzaldehyde and benzaldehyde followed by oxidation of formed benzoin to the benzil with copper sulphate-pyridine).[12] The intermediate benzoins were not obtained as crystalline materials and were oxidised to the benzils without purification.

2-Methoxybenzil: Mp 58—60 °C (reported[13] 59—60 °C; Ref. 12 reports the mp as 71—72 °C); IR (mineral oil mull) 1670, 1650, 1600 cm^{-1}; ^{1}H NMR (60 MHz; $CDCl_3$) δ = 3.6 (s, OMe *H*'s), 6.8—7.8 (m, 2-methoxyphenyl and phenyl ring *H*'s); integrated intensity ratio 1 : 3.

2,2′-Dimethoxybenzil: Mp 128—129 °C (reported[12] 128—129 °C).

3, 4- Di(2- methoxyphenyl)- 2, 5- dimethylcyclopentadienone Cp1: The intermediate aldols (cyclopentenolones), expected to be formed when a procedure described for the preparation of 'cyclone' (3,4-diphenyl-2,5-dimethylcyclopentadienone)[3] by the aldol condensation of diethyl ketone with benzil is applied to 2,2′-dimethoxy- and 2-methoxybenzils, could not be isolated as crystalline materials. Acid-catalysed dehydration by warming the crude product from 2,2′-dimethoxybenzil in acetic anhydride containing a few drops of conc. sulphuric acid gave, however, 3,4-di(2-methoxyphenyl)-2,5-dimethylcyclopentadienone **Cp1** as a bright-red crystalline solid, recrystallisable from ethyl acetate as red square prisms.[14] Yield (from 2,2′-dimethoxybenzil) 76%; mp 136—138 °C; IR (mineral oil mull) ν_{max} 1700 (keto C=O), 1600 (aromatic C=C), 1580 (cyclopentenone C=C) cm^{-1} (OH band absent); ^{1}H NMR ($CDCl_3$, 60 MHz) δ = 7.5—6.8 (m, C(3) and C(4) 2-methoxyphenyl *H*'s), 3.7 (s, OMe *H*'s) and 2.1 (s, C(2) and C(3) Me *H*'s) ppm ex-TMS (integrated intensity ratio: ca. 4 : 3 : 3).

Found: C, 78.35; H, 6.5%. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29%.

A [4π+2π] Cyclodimer of 3-(2-Methoxyphenyl)-4-phenyl-2, 5-dimethylcyclopentadienone Cp2: A similar acid-catalysed dehydration of the material from 2-methoxybenzil gave a colorless product recrystallisable from ethyl acetate–hexane: Mp 150 °C. While its main IR bands (mineral oil mull: 1770, 1690, 1600, 1580 cm^{-1}) were at positions closely similar to those of its symmetrically dimethoxylated analogue **Cp1**, its NMR spectrum clearly indicated it to be one of the three possible isomeric [4π+2π] cyclodimers of 3-(2-methoxyphenyl)-4-phenyl-2,5-dimethylcyclopentadienone **Cp2**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 7.3—6.2 (m, C(2), C(3), C(8), and C(9) 2-methoxyphenyl and phenyl *H*'s), 3.9 and 3.85 (2s, –OMe *H*'s) and 1.75, 1.52, 1.17 and 0.6 (4s, C(1), C(4), C(6), and C(7) Me *H*'s) ppm ex-TMS [integrated intensity ratio: ca. 6 : 6 lines of intensity 1 consistent with one of the structures: 1,4,6,7-tetramethyl-5,10-dioxo-2 or 3, 8 or 9-di(2-methoxy-phenyl)-8,9 or 2,3-diphenyltricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene]. Found: C, 83.12; H 6.37%. Calcd for $C_{40}H_{34}O_4$: C, 83.60; H, 6.26%.

Methyl 5,6-Bis(2-methoxyphenyl)-1,2,4-trimethyl-7-oxobicyclo[2.2.1]hept-5-en-2-*endo*-carboxylate (1): Heating under reflux (2 h) a ca. 20% w/v toluene solution of a ca. 1 : 2 molar mixture of **Cp1** with methyl methacrylate (**Ma**) gave the norbornenone ester **1** as the major product: Yield 88%; colorless plates from ethyl acetate; mp 155—156 °C; ν_{max} (mineral oil mull) 1770 (norbornenone C=O), 1730 (ester C=O), 1590 (aromatic C=C), 1580 (norbornene C=C) cm^{-1}; this product exhibited temperature-dependent, unequally populated two-site exchange behaviour[15] in ^{1}H NMR with a population ratio of ca. 10.1 (Figs. 4a and 4b).[2b]

Found: C, 74.13; H, 6.69%. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71%.

M_w by HRMS: Found: *m/z* 420.1917. Calcd for $C_{26}H_{28}O_5$: M, 420.1937.

Methyl 5-Phenyl-6-(2-methoxyphenyl)-1,2,4-trimethyl-7-oxobicyclo[2.2.1]hept-5-en-2-*endo*-carboxylate (2) and Methyl 5-(2-Methoxyphenyl)-6-phenyl-1,2,4-trimethyl-7-oxo-bicyclo[2.2.1]-hept-5-en-2-*endo*-carboxylate (3): On the assumption that the cyclodimer derived from 3-(2-methoxyphenyl)-4-phenyl-2,5-dimethylcyclopentadienone (**Cp2**) would be thermally monomerisable and that the monomeric form would undergo [4π+2π] cycloaddition, the dimeric product of **Cp2** was subjected to the conditions of cycloaddition of methyl methacrylate. The product was a mixture of two major components (TLC test) which, together, accounted for about 90% by weight of the total product.[16] The material to crystallize out first as colorless needles during an attempted fractional crystallization from ethanol, labelled **A**, has now been shown to have structure **2**: Mp 172—173 °C; ν_{max} (mineral oil mull) 1767 (norbornenone C=O), 1725 (ester C=O), 1590 (aromatic C=C), 1580 (norbornene C=C) cm^{-1}.

Found: C, 77.07; H, 7.17%. Calcd for $C_{25}H_{26}O_4$: C, 76.89; H, 6.71%.

M_w by HRMS: Found: *m/z* 390.1816. Calcd for $C_{25}H_{26}O_4$: M, 390.1831.

The second crop, also colorless, labelled **B** (**A/B** ratio ≈ 2.6 : 1), had infrared absorption different from **A** in the 'fingerprint region', and has now been shown to have structure **3**: Mp 100—101 °C; ν_{max} (mineral oil mull) 1773 (norbornenone C=O), 1734 (ester C=O), 1590 (aromatic C=C), 1578 (norbornene C=C) cm^{-1}.

Found: C, 77.13; H, 6.81%. Calcd for $C_{25}H_{26}O_4$: C, 76.89; H, 6.71%.

M_w by HRMS: Found: *m/z* 390.1852. Calcd for $C_{25}H_{26}O_4$: M,

Table 1. Crystallographic Data Collection and Refinement Parameters for **1**, **A**, and **B**

System	**1**	**A**	**B**
Molecular formula	$C_{26}H_{28}O_5$	$C_{25}H_{26}O_4$	$C_{25}H_{26}O_4$
M_r	420.48	390.458	390.458
Crystal shape	Plates	Short needles	Long needles
and color	Colorless	Colorless	Colorless
Crystal size/mm	$0.07 \times 0.2 \times 0.5$	$0.6 \times 0.4 \times 0.2$	$0.4 \times 0.3 \times 0.2$
Crystal System	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	9.829(1)	14.686(2)	8.935(5)
b/Å	22.565(4)	10.088(3)	9.035(2)
c/Å	10.949(3)	14.465(2)	14.016(3)
α/°	90	90	107.13(2)
β/°	113.03(2)	97.50(1)	95.42(3)
γ/°	90	90	77.82(3)
V/Å^3	2234.9(8)	2124.5	1056.3
Z	4	4	2
D_x/g cm^{-3}	1.250	1.219	1.226
μ/mm^{-1}	6.9	8.8	8.8
Angle range for data collection/°	$4 \leq 2\theta \leq 75$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 46$
Index ranges/°	$0 \leq h \leq 12$ $0 \leq k \leq 28$ $-13 \leq l \leq +12$	$-17 \leq h \leq +17$ $0 \leq k \leq 11$ $0 \leq l \leq 16$	$-9 \leq h \leq +9$ $-9 \leq k \leq +9$ $0 \leq l \leq 16$
Diffraction angle θ_{max}/°	24.5	22.5	22.5
Reflections observed	4939	3714	2940
Reflections used	4600	2136	2009
under criterion	$[\lvert I_o\rvert \geq 2\sigma\lvert I_o\rvert]$	$[\lvert F_o\rvert \geq 3\sigma\lvert F_o\rvert]$	$[\lvert F_o\rvert \geq 3\sigma\lvert F_o\rvert]$
No. of parameters	392	366	366
$F(000)$	896	832	416
$(\Delta/\sigma)_{max}$	< 0.03	< 0.03	< 0.03
$\Delta\rho_{max}$/e Å^{-3}	0.43	0.35	0.30
$\Delta\rho_{min}$/e Å^{-3}	−0.65	−0.28	−0.25
Refinement	On $\lvert I\rvert$	On $\lvert F\rvert$	On $\lvert F\rvert$
Final R	0.064	0.070	0.067
Weighted R (wR)	0.169	0.083	0.066
Goodness of fit s	1.05	1.20	1.40

390.1831.

While product **A** resembled **1** and exhibited temperature-dependent two-site exchange behavior[15] in ^{1}H NMR with a population ratio of 10 : 1, the population ratio in **B** was 10 : 7 (compare Figs. 4c and 4e).[2b]

Crystallographic: Good-sized crystals, suitable for single-crystal X-ray analysis, were selected from crops grown by slow evaporation of methanol solutions of **1**, **A**, and **B**. Preliminary Weissenberg photographs indicated the monoclinic space group for **1** and **A** ($P2_1/c$ and $P2_1/n$, respectively) and the triclinic space group for **B** (confirmed as $P\bar{1}$). Intensity data were collected with an Enraf–Nonius CAD-4 diffractometer using Ni filtered Cu $K\alpha$ radiation (λ = 1.54180 Å) for **1** and graphite-filtered Mo $K\alpha$ radiation (λ = 0.71069 Å) for **A** and **B** employing the $\omega/2\theta$ mode at a scan speed of 1 ° min^{-1}. Stability and orientation were monitored every 3600 s of data collection by measuring three standard reflections and the orientation was checked at every 400th reflection. No significant fluctuations in intensity were observed. Intensity data have been corrected for Lorentz and polarization effects, but not for absorption. Crystallographic data collection and refinement parameters are gathered in Table 1.

The structures were solved using direct methods, MULTAN-78[17a] for **A**, an earlier version of MULTAN[17b] for **B**, and the SHELXL package[17c] for **1**. The results of refinement are included in Table 1. All non-hydrogen atoms (31 in **1** and 29 in **A** and **B**) were located in the E-maps using the SHELXL default options for **1**, the phase set having the highest figure of merit for **A** and the second best figure of merit for **B**.[18] A block-diagonal least-squares refinement of these locations (SHELXL package for **1** and the SFLS program[18b] for **A** and **B**), after including isotropic and then anisotropic temperature factors, led to first-stage low values for the R-indices. Difference Fourier maps computed at this stage revealed the 28 hydrogen atoms in **1** and the 26 hydrogen atoms in **A** and **B** at stereochemically meaningful positions. Inclusion of the hydrogen locations, together with their isotropic temperature factors, led to the second-stage lowering of the R-indices. Full-matrix, least-squares refinement for reflections with $|F_o| \geq 3\sigma(|F_o|)$, carried out with SHELX93 using the weighting scheme $\omega = 1/[\sigma^2(|F_o|)^2 + (0.0996p)^2 + 0.8143p]$, where $p = [(|F_o|)^2 + 2|F_c|^2/3$ for **1**, $\omega = 1.48/[\sigma(|F_o|)^2 + 0.09|F_o|^2$ for **A** and $\omega = 1.62/[\sigma(|F_o|)^2 + 0.002|F_c|^2]$ for **B**, lowered the R-indices to the final values given in Table 1.

The anisotropic temperature factors of the non-hydrogen atoms, the final factional positional and equivalent isotropic displacement parameters of both non-hydrogen and hydrogen atoms, bond lengths

Table 2. Select Parameters for Comments on the Structural Features of Norbornenone Esters **1**, **2**, and **3** and Comparison with Systems **4** and **5**

System No.	**1**	**2**	**3**	**4**[a)]	**5**[a)]
	Bis(methoxyphenyl)	C(6)-Monomethoxyphenyl	C(5)-Monomethoxyphenyl	Diphenyl (ethyl esters) C(5)–H	C(5)–Me
1) Dispositions of the aryl rings:					
a) Aryl ring at C(5): torsion angles (°)					
C(6)–C(5)–C(13)–C(14)	130.2(2)	48.5(7)	−119.3(6)	−57.7(8)	51.8(7)
Aryl ring at C(6): torsion angles (°)					
C(2)–C(6)–C(19)–C(20)	93.8(2)	−74.5(7)	51.7(7)	−41.2(8)	39.2(7)
b) Other torsion angles (°):					
C(4)–C(5)–C(6)–C(1)	0.1(2)	−0.5(5)	0.6(5)	−1.2(5)	1.1(5)
C(13)–C(5)–C(6)–C(19)	−0.7(2)	5.3(8)	6.6(7)	12.6(8)	−14.1(7)
2) a) Bond lengths (Å) within the norbornene moiety (single bonds):					
C(4)–C(5)	1.527(2)	1.539(6)	1.527(6)	1.536(7)	1.529(7)
C(4)–C(7)	1.537(2)	1.520(7)	1.524(6)	1.515(7)	1.523(7)
C(4)–C(3)	1.546(2)	1.563(7)	1.546(6)	1.539(7)	1.556(7)
C(6)–C(1)	1.531(2)	1.543(6)	1.526(6)	1.533(7)	1.530(6)
C(1)–C(2)	1.583(2)	1.567(7)	1.588(6)	1.581(7)	1.589(7)
C(1)–C(7)	1.537(2)	1.545(7)	1.517(6)	1.530(7)	1.538(7)
C(2)–C(3)	1.559(2)	1.558(8)	1.556(7)	1.549(7)	1.558(7)
b) Bond lengths (Å) within the norbornene moiety (double bond):					
C(5)–C(6)	1.353(2)	1.331(6)	1.341(6)	1.343(7)	1.347(6)
c) Non-bonded distances (calculated; Å):					
C(4)···C(1)	2.34	2.33	2.32	2.33	2.33
C(13)···C(19)	3.14	3.13	3.08	3.17	3.16
3) a) Bond angles (°) within the norbornene moiety:					
C(5)–C(4)–C(3)	107.8(1)	106.2(4)	107.1(4)	105.8(4)	105.3(4)
C(5)–C(4)–C(7)	95.7(1)	96.9(4)	96.0(3)	96.4(4)	96.4(4)
C(3)–C(4)–C(7)	98.5(1)	98.6(4)	98.2(3)	98.8(4)	99.2(4)
C(4)–C(5)–C(6)	108.4(1)	108.1(4)	108.3(4)	108.9(4)	108.7(4)
C(5)–C(6)–C(1)	109.1(1)	109.9(4)	109.1(4)	108.4(4)	108.9(4)
C(6)–C(1)–C(2)	109.4(1)	107.5(4)	107.1(3)	107.0(4)	108.2(4)
C(6)–C(1)–C(7)	95.2(1)	95.3(4)	96.0(3)	96.1(4)	95.5(4)
C(2)–C(1)–C(7)	96.8(1)	96.8(4)	97.8(3)	96.9(4)	97.0(3)
C(1)–C(2)–C(3)	103.4(1)	104.5(4)	102.8(3)	103.8(4)	103.4(4)
C(4)–C(3)–C(2)	105.2(1)	104.2(4)	105.4(4)	105.0(4)	105.0(4)
C(4)–C(7)–C(1)	98.9(1)	99.1(4)	99.5(3)	99.5(4)	99.3(4)
b) External angles (°)					
C(6)–C(5)–C(13)	126.9(1)	128.1(4)	126.2(4)	128.2(5)	127.5(4)
C(5)–C(6)–C(19)	127.3(1)	126.7(4)	125.7(4)	127.6(4)	127.1(4)
4) Magnitudes of torsion angles (°) within rings **S** & **U** of the norbornene moiety (see Fig. 3):					
S–C(3)–C(2)–C(1)–C(7) (**a**)	36.9(1)	36.1(5)	34.7(4)	34.8(4)	37.0(4)
S–C(2)–C(3)–C(4)–C(7) (**c**)	31.6(2)	32.2(5)	33.1(4)	32.7(5)	30.6(4)3
a−**c** differences	5.3 (**a** > **c**)	3.9 (**a** > **c**)	1.6 (**a** > **c**)	2.1 (**a** > **c**)	6.4 (**a** > **c**)
U–C(5)–C(6)–C(1)–C(7) (**a**′)	33.1(1)	32.2(5)	31.8(4)	32.7(5)	33.1(4)
U–C(6)–C(5)–C(4)–C(7) (**c**′)	32.9(1)	32.2(4)	32.7(4)	31.4(5)	31.6(4)
a′−**c**′ differences	+0.2 (**a**′ > **c**′)	0.0 (**a**′ = **c**′)	−0.9 (**a**′ < **c**′)	+1.3 (**a**′ > **c**′)	+1.5 (**a**′ > **c**′)
Twist designation	*contra* (+,−)	(+,0)	*synchro* (+,+)	*contra* (+,−)	*contra* (+,−)

Table 2. (Continued)

System No.	1 Bis(methoxyphenyl)	2 C(6)-Monomethoxyphenyl	3 C(5)-Monomethoxyphenyl	4[a] Diphenyl (ethyl esters) C(5)–H	5[a] Diphenyl (ethyl esters) C(5)–Me
5) Tilt of the C(4)–C(7)–C(1) plane:					
M(5,6)–M(1,4)–C(7) angle (θ_1;°)	123.52	126.13	124.79	125.3	124.7
M(2,3)–M(1,4)–C(7) angle (θ_2;°)	120.66	120.42	121.30	121.4	121.6
Tilt angles ($\theta_1 - \theta_2$; °)	+3.06	+5.71	+3.49	+3.9	+3.1
6) Disposition of the endo ester group at C(2):					
a) C(3)–C(2)–C(11)=O(3) torsion angles (°)	−32.5(3)	3.7(9)	−1.5(7)	19.6(8)	172.3(5)
b) C(1)–C(2)–C(11) bond angles (°)	115.3(1)	111.9(4)	111.5(4)	113.1(4)	109.4(4)
c) C(3)–C(2)–C(11) bond angles (°)	110.0(1)	111.9(5)	111.3(4)	113.9(4)	115.4(4)
d) C(11)–C(2)–C(Me) bond angles (°)	106.7(1)	106.6(5)	109.4(4)	—	107.9(4)

a) Data taken from Ref. 21.

and bond angles not involving and involving hydrogen atoms constitute the data placed in deposit.[19]

Perspective (ORTEP)[20] views of the molecular structures of the three compounds are reproduced in Figs. 1a, 1b, and 1c and packing diagrams are depicted in Figs. 2a, 2b, and 2c. Select parameters pertinent to the comments given below, taken from data in deposit,[19] have been assembled in Table 2 in an itemized manner for quick reference. Included in the table, for purposes of comparison, are parameters pertinent to the norbornenone *ethyl* esters **4** and **5**, both without any substitution on the phenyl rings, studied earlier.[21]

Results and Discussion

The crystallographic results immediately confirmed that all three products were norbornenone esters with the ester group in *endo*-configuration at C(2). **A**, the lower melting isomer showing a higher population disparity, has the *o*-methoxyphenyl group at C(6), proximal to the ester function (structure **2**), while **B**, the higher melting isomer showing lower population disparity, bears the group at C(5), distal to the ester function (structure **3**), just as conjectured. There was neither evidence of positional disorder of atoms nor of orientational disorder of groups. It appeared from the crystal-packing diagrams (Figs. 2a, 2b, and 2c) that all three structures are stabilized chiefly by van der Waals forces. While the molecules are stacked linearly in structure **2** (of **A**), with the methoxyphenyl groups on adjacent molecules facing each other in parallel fashion, the aromatic rings are clustered centrosymmetrically, enclosing large spaces, in both structures **1** and **3** (of **B**).

Maintenance of a high torsion angle (43.2°) by the phenyl rings with respect to the central double bond in the gaseous phase of *cis*-stilbene has been attributed to minimization of the steric interaction between *ortho* hydrogens.[22] The two (chemically equivalent) phenyl rings exhibit different torsional angles (43.8 and 47.5°) in the crystalline phase of 1,2-diphenylcyclopentene.[23] The observed rotational orientations of the aryl rings of the *cis*-stilbene moiety, part of a cyclopentene restricted to an envelope conformation in all three cases of present interest (**1**—**3**), could well be the resultants of additional intramolecular steric forces from the bridgehead methyls in the norbornenes and, when bearing an *o*-methoxy substituent, from electrostatic influences of the C(2) *endo*-ester function as well. The aromatic rings are rotated about the C(5)–C(13) and C(6)–C(19) axes to high and different extents with respect to the C(5)–C(6) line in all cases (Table 2. 1a) and the extents of rotation of the *o*-methoxyphenyls are generally higher than of the phenyls in all three cases. The *o*-methoxyphenyl group is 'outward' rotated in **2**, whereas it is 'inward' rotated, but obliquely, in **3**. Interestingly, the situation in **1** can be regarded as representing a 'sum' of those in **2** and **3** (Figs. 1a, 1b, and 1c).

While the C(4)–C(5)–C(6)–C(1) torsion angles are small, showing the atoms constituting the norbornene side of the double bond maintain near planarity, the C(13)–C(5)–C(6)–C(19) torsion angles depart significantly from zero in all three cases, indicating an apparent tendency on the part of the aryl substituents to move away from a fully eclipsing interaction (Table 2. 1b).

There are some C–C single bonds within the norbornenone moiety that are shorter or longer than average in the series considered (Table 2.2a):

i) C(4)–C(7) longer in **1** and shorter in **4**;

ii) C(4)–C(3) longer in **2**;

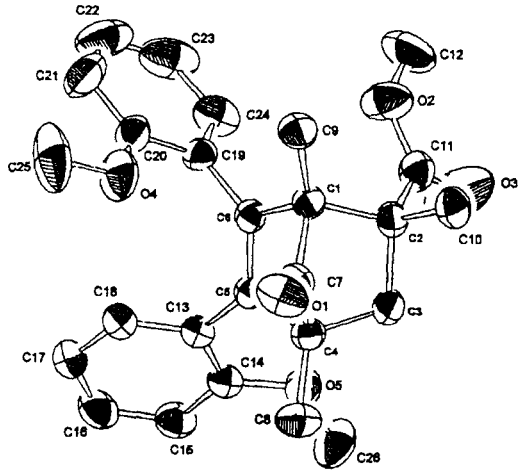
iii) C(1)–C(2) shorter in **2**; longer than 1.58 Å, bonds of this class in the other systems fall among the longest C–C single bonds;

iv) C(1)–C(7) shorter in **3**.

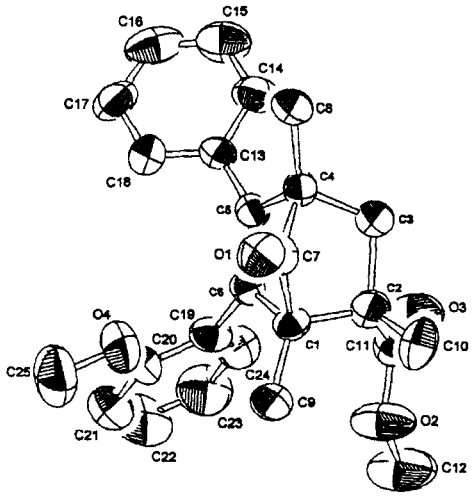
These differences do not appear to correlate with any specific structural feature but, together, could contribute to differences in the distortion of the norbornenone framework (see below).

The C(5)–C(6) double bonds remain more or less closely comparable in length (Table 2.2b) with the central double bond in *cis*-stilbene (1.338 Å)[23] and the C(4)–C(1) and C(13)–C(19) non-bonded distances (calculated from atom

a)



b)



c)

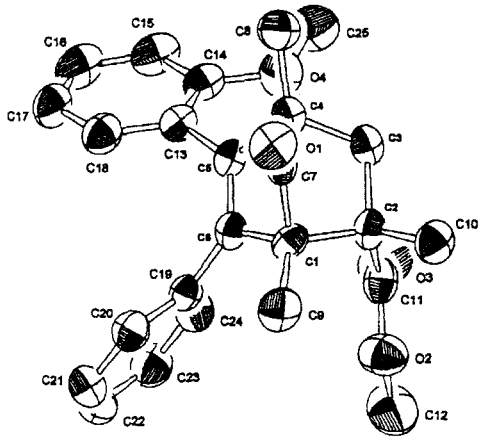
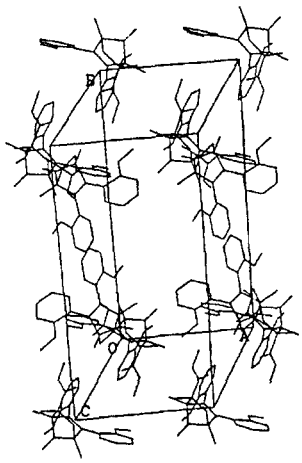
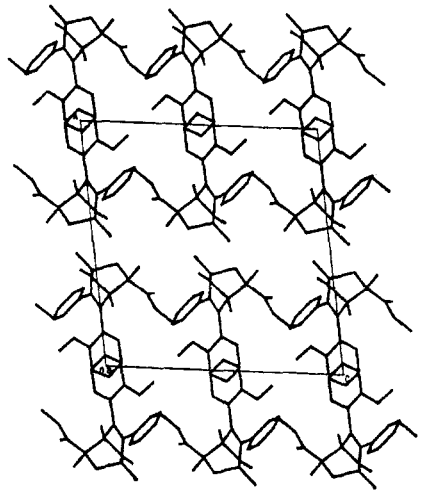


Fig. 1. ORTEP diagrams: a) Compound **1**, b) Compound **A**, and c) Compound **B**.

a)



b)



c)

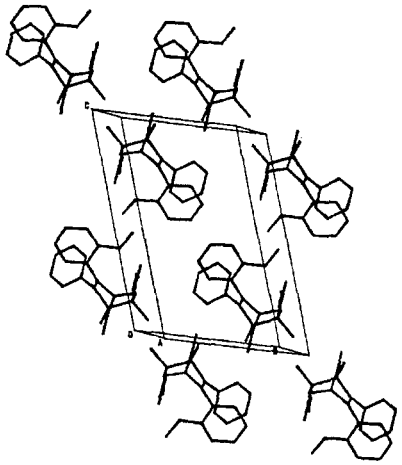


Fig. 2. Molecular packing in unit cells: a) **1**, b) **A**, and c) **B**.

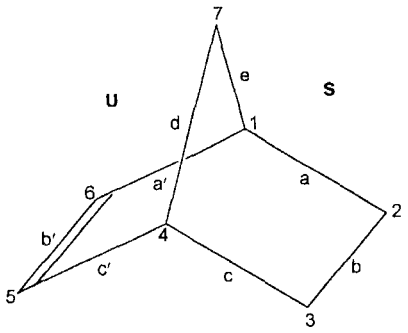


Fig. 3. Twist designations:
Synchro
S(+,+) when a > c & a′ < c′
S(−,−) when a < c & a′ > c′
Contra
C(+,−) when a > c & a′ > c′
C(−,+) when a < c & a′ < c′

coordinates) do not differ significantly in any of the systems (Table 2.2c).

Both structures show angle strain associated with a cyclohexene constrained in a boat form by the 1,4-bridging (i.e. 3,6-bridging in a cyclohexene). With the exception of C(5)–C(4)–C(3) and C(6)–C(1)–C(2), all angles at the saturated centers internal to the norbornene are closed-in and range in value between 95.2 and 99.5°, significantly less than the 'tetrahedral value' of ca. 109.5° (Table 2.3a). More interestingly, both the carbonyl and C–C=C bond angles are narrowed to extents considerably less than the sp^2 trigonal value of ca. 120°. At the same time, the external angles C(6)–C(5)–C(13) and C(5)–C(6)–C(19) open out to large extents (Table 2.3b).

Magnitudes of torsion angles pertinent to the twist of the norbornene framework have been gathered in Table 2.4. While dihedral angles **a′** and **c′** are equal or do not differ significantly on the unsaturated side **U** (Fig. 3), the relationship **a** > **c** is maintained on the saturated side **S** in all cases. There is a clear distinction in twist between the systems bearing one monosubstituted aryl ring and those with either disubstitution or no substitution: adopting a standard designation,[24] it is seen that, while **1**, **4**, and **5** show *contra* (+,−) twist, the twists are (+,0) in **2** and *synchro* (+,+) in **3**. The first sign in the twist codes ('pseudorotations')[24] is, however, positive in all cases (**a** > **c**), signifying that torsional angle C(3)–C(2)–C(1)–C(7) is greater than torsional angle C(2)–C(3)–C(4)–C(7) without exception. A study of molecular models has shown that this feature moves the *endo* ester group at C(2) as a whole somewhat away from the aryl group at C(6), probably optimizing any interaction between the two (cf. the effect of an 'inward' oriented methyl hydrogen in an *endo*-methylnorbornane),[24] especially in the circumstance that the aryl group prefers a non-coplanar arrangement of high angle in relation to the C(5)–C(6) double bond.

Taking the signs and magnitudes of the differences between the angles M(5,6)–M(4,1)–C(7) [θ_1] and M(2,3)–M(4,1)–C(7) [θ_2] (where M signifies the midpoints of the lines joining the numbered centers) as measures of the tilt of the C(4)–C(7)–C(1) plane within the norbornene moiety, it is found that θ_1 is greater than θ_2 ($\theta_1 - \theta_2$ positive) in the series, without exception (Table 2.5), the tilt being away from the double bond. It appears as though the presence of a positive tilt here and in most C(7)–oxo or C(7)–methylene norbornenes arises from a repulsive interaction between the C(5)–C(6) and the C(7)–*exo* atom π-orbitals.[25] However, it can also be seen as arising from a tendency of the C(4)–C(7) and C(1)–C(7) bonds to come into eclipsing conformation with the C(5)–C(6) double bond (cf. eclipsing of C=C by a C–H in propene).[26] Though the magnitude of the positive tilt is small (maximum found, so far, is 6° in dimethyl 7-oxonorbornene-5-*endo*-6-*endo*-dicarboxylate),[27] the possible *increase* in steric hindrance to approach *anti* to the double bond has been seen as overcome by electronic interactions between a nucleophilic reagent and the substrate norbornenone having electron-withdrawing *endo,endo*-disubstitution.[27,28]

A number of studies have shown that alkyl ester groups unbranched at C(α') have a high preference for the *s-cis* periplanar conformation about the O=C–O–C(α') bond.[29] The ester groups maintain this preference (Figs. 1a, 1b, and 1c) and behave virtually as planar units. Ester groups are also known to prefer a rotational conformation in which the carbonyl eclipses a C(α)–C(β) bond;[30] this preference is maintained in cases **1**—**4** in that the departure of the ester carbonyl from *syn*-periplanarity with the C(2)–C(3) bond is by low dihedral angles (Table 2.6). The choice falling on the C(2)–C(3) bond may optimise interactions with *both* of the aryl groups, at C(5) and C(6). The C(2) *exo*-methylated norbornene *ethyl* ester **5** is exceptional in that the ester group has the opposite orientation, with O(2)=C(11)–C(2)–C(3) nearly *anti*-periplanar, and the ester methylene carbon showing positional disorder.[21]

Conclusion

X-Ray crystallographic determinations have shown DNMR-based assignments of locations to the *o*-methoxyphenyl group in **A** and **B** to be correct, even while confirming the *endo* configuration of the ester group in all three systems studied: **1**, **A** and **B**.

This research was partly supported by an Emeritus Scientists' project awarded to SNB by the Council of Scientific and Industrial Research, India. SNB thanks Prof. C. N. R. Rao, President, Jawaharlal Nehru Centre for Advanced Scientific Research, for the award of an Honorary Fellowship. MMB and SPR thank the Director, Indian Institute of Science, for the award of fellowships. Invaluable assistance was very kindly provided by Prof. C. Ramakrishnan.

References

1 Studies of possibility of atropisomerism in the corresponding norbornanone esters, C(5)–C(6) saturated derivatives with both substituted phenyls in *endo*-configuration [S. N. Balasubrahmanyam and V. B. Reddy, *Tetrahedron Lett.*, **1976**, 2915]. While the C(5)–C(6) double bond in the *o,o′*-methoxylated system **1** could not be

saturated under any of the conditions tried (see Ref. 9, below), the *m,m'*-methoxylated, C(5)–C(6) saturated analogue shows neither atropisomerism nor even VT behavior.

2 a) Partial overlap and complexity of changes, possibly arising from differences in the rates of change of line-width of the different signals, effectively prevented keeping track of line associations in high-to-low-to-high variable-temperature NMR experiments; b) Sample spectra (Figs. 4a—4f) form part of the supplementary material deposited as Document No. 73001 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

3 K. N. Houk and L. J. Luskus, *J. Am. Chem. Soc.*, **93**, 4606 (1971): See Ref. 16.

4 Coplanar arrangements of the aryl groups can be expected to be more *endo*-energetic in a system like **1** than in a *cis*-stilbene in view of the additional steric demand placed by the methyl groups at C(4) and C(1). The situation may be qualitatively compared with *cis*-3,4-diphenyl-3-hexene ("1,2-diethyl-*cis*-stilbene") with the ethyl groups rotated into *syn* conformation with respect to the phenyl groups.

5 Those with the methoxyphenyls rotated the same way would be destabilized by large contributions from dipolar factors, the one with both rotated 'inward' suffering additional destabilization from a large steric factor.

6 Forms described in this general way can attain further stabilisation by the three substituent groups (two methoxyphenyls and the ester group, the last considered as a planar unit stabilized with a low O=C–C–O torsion angle) assuming specific 'attitudes' of minimal mutual interaction through rotation about the bonds of their attachment to the bicycloheptene framework, as has been confirmed by molecular mechanics calculations on structures **1**—**3** (Dr. A. Sampath Kumar; results to be published). Attendant changes in chemical shifts and line-separations of the doubled resonances of the NMR-active groups (C-*Me* and O-*Me*) can be attributed mainly to the differences in shielding when the highly magnetically anisotropic aryl groups come into specific stabilized orientations.

7 An *endo*-methyl at C(2) in the norbornenone ester of the alternative configuration appeared less likely to exert the required polar and steric influence.

8 S. Prahlada Rao, Ph. D. Thesis, Indian Institute of Science, Bangalore (1980).

9 In the cases of a number of norbornenone esters, cognate in structure with systems **1**—**3** but without an *o*-substituent on either phenyl, a method different from that described in the reference in Ref. 3, was adopted to confirm the *endo*-configuration of the ester function. Catalytic hydrogenation (5% Pd–C) yielded C(5)–C(6) saturated products in which the $-CO_2Me$ singlet was shifted upfield by ca. 0.6 ppm on the average with respect to its position in their unsaturated precursors (Ref. in Ref. 1). This result proved at once that hydrogenation of the C(5)–C(6) double bond is favored from the *zu*-face, that the ester function was, originally, *endo*-oriented and that the aryl groups become *endo*-oriented on hydrogenation of the C(5)–C(6) double bond. The assumption here is that the aryl groups preferentially adopt rotational conformations conductive to the shielding of the $-CO_2Me$ group. This strategy could not be adopted with systems **1**—**3** since the C(5)–C(6) double bond in them totally resisted saturation under conditions that had succeeded in other cases (Ref. 8).

10 A matter of some additional interest was to see if any of these systems would show positional disorder of atoms of the groups pendant on the bicyclohepetene. Presence of positional disorder could be indicatory that combinations of rotamerically different conformational states of the substituent groups remain preserved in the crystalline phase.

11 C. H. F. Allen and J. A. van Allan, *J. Am. Chem. Soc.*, **64**, 1260 (1942).

12 "Method A" in N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Am. Chem. Soc.*, **71**, 2997 (1949).

13 Y. Asahina and M. Ishidate, *J. Pharm. Soc.*, **521**, 624 (1925).

14 The deep colour was presumed to indicate that, unlike the monomethoxylated dienone described later, this dienone is not a dimer. Compare this, and the monomethoxylated cases, with the unsubstituted case described in Ref. 11.

15 L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy," "Vol. 10 in International Series on Organic Chemistry," 2nd ed, ed by D. H. R. Barton and W. Doering, Pergamon, Oxford (1969); see also, M. Oki, "Applications of Dynamic NMR in Organic Chemistry," "Vol. 4 in Methods in Stereochemical Analysis," ed by A. P. Marchand, VCH, Deerfield Beach (1985).

16 In later work, Dr. I. N. N. Namboothiri has isolated in low yield (ca. 9%) the *endo*-methyl, *exo*-ester isomer of **1** from the product mixture obtained in a similar experiment.

17 a) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, "MULTAN-78, A System of Computer Programs for the Automatic Solution of Crystal Structures," University of York, York, and University of Louvian, Belgium (1978). b) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **A27**, 368 (1971). c) G. M. Sheldrick, "SHELXL Program for Crystal Structure Determination," Göttingen University, Germany (1993).

18 a) Mohan M. Bhadbhade, Ph.D. Thesis, Indian Institute of Science, Bangalore (1982). b) R. Shiono, SFLS program (1968) by personal communication to the author.

19 These data form part of the supplementary material deposited as Document No. 73001 at the Office of the Editor of the Bull. Chem. Soc. Jpn. They have also been deposited with the Cambridge Crystallographic Data Centre (139645 for **1**, 139646 for **A**, and 139647 for **B**).

20 S. Motherwell, J. L Sussman, and N. H. F. Beebf, "PLUTO 82, Programme for Plotting Molecular and Crystal Structures," University of Cambridge, England (1982).

21 S. N. Balasubrahmanyam, R. Usha, and K. Venkatesan, *Acta Crystallogr., Sect. B*, **B37**, 629 (1981).

22 Microwave study by M. Traetteberg and E. B. Frantsen, *J. Mol. Struct.*, **26**, 69 (1975).

23 J. Bernstein, *Acta Crystallogr., Sect. B*, **B31**, 418 (1975).

24 C. Altona and M. Sundaralingam, *J. Am. Chem. Soc.*, **92**, 1995 (1970).

25 R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

26 G. J. Karabatsos and D. J. Fenoglio, "Rotational Isomerism about sp^2–sp^3 Carbon–Carbon Single Bonds in Topics in Stereochemistry," ed by N. L. Allinger, E. L. Eliel, Wiley Interscience, New York (1970), Vol. 5, pp. 167—204.

27 G. Mehta and F. A. Khan, *Tetrahedron Lett.*, **33**, 3065 (1992); V. A. Kumar, K. Venkatesan, B. Ganguly, J. Chandrasekhar, F. A. Khan, and G. Mehta, *Tetrahedron Lett.*, **33**, 3069 (1992).

28 H. Li and W. J. le Noble,. *Recl. Trav. Pays-Bas*, **111**, 199 (1992).

29 L. Leiserowitz and G. M. J. Schmidt, *Acta. Crystallogr.*, **18**, 1058 (1965); A. McL. Mathieson and H. K. Welsh, *Acta Crystallogr.*, **18**, 953 (1965); J. M. R. Riveros and E. B. Wilson, *J. Chem. Phys.*, **46**, 4605 (1967); J. D. Dunitz and P. Strickler, "Preferred Conformation of the Carboxyl Group in Structural Chemistry and Molecular Biology," ed by A. Rich and N. Davidson, W. H.

Freeman, San Francisco (1968), pp. 595—602; G. I. L. Jones and N. L. Owen, *J. Mol. Struct.*, **18**, 1 (1973); P. W. Borthwick, *Acta Crystallogr., Sect. B*, **B36**, 628 (1980); T. B. Grindley, *Tetrahedron Lett.*, **23**, 1757 (1982).

30 ^{13}C NMR: G. J. Karabatsos, N. Hsi, and C. E. Orzech, Jr., *Tetrahedron Lett.*, **1966**, 4639; N. V. Riggs and S. M. Verma, *Tetrahedron Lett.*, **1968**, 3767; R. L. Vold and R. R. Vold, *J. Mag. Reson.*, **13**, 38 (1974); Semi-Empirical Calculations: G. Usha, Ph. D. Thesis, Indian Institute of Science, Bangalore (1984); also, S. N. Balasubrahmanyam, S. Narasimha Bharati, and G. Usha, *Org. Magn. Reson.*, **21**, 474 (1983).