Crystal data

$C_{17}H_{20}N_2S$
$M_r = 284.41$
Trigonal
$P3_1$
$a = 10.3144\ (12)$ Å
$c = 13.177\ (2)$ Å
$V = 1214.1\ (3)$ Å^3
$Z = 3$
$D_x = 1.167$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 56
reflections
$\theta = 12.5–14.0°$
$\mu = 0.193$ mm^{-1}
$T = 296\ (2)$ K
Needle
$1.08 \times 0.16 \times 0.16$ mm
Colourless

Data collection

Stoe Stadi-4 four-circle
diffractometer
ω–θ scans with width
$(1.32 + 0.35\tan\theta)°$
Absorption correction: none
1890 measured reflections
1053 independent reflections
719 reflections with
$I > 2\sigma(I)$

$R_{int} = 0.0451$
$\theta_{max} = 22.51°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F > 4\sigma(F)] = 0.0456$
$wR(F^2) = 0.0788$
$S = 1.018$
1053 reflections
192 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.044$
$\Delta\rho_{max} = 0.136$ e Å^{-3}
$\Delta\rho_{min} = -0.154$ e Å^{-3}

Extinction correction:
SHELXTL (Sheldrick,
1995)
Extinction coefficient:
0.008 (2)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)
Absolute configuration:
Flack (1983)
Flack parameter = 0.18 (17)

Table 1. *Selected geometric parameters (Å, °)*

| S—C	1.710 (7)	N1A—C2A	1.444 (8)
C—N1A	1.318 (8)	N1B—C2B	1.446 (8)
C—N1B	1.324 (7)		
N1A—C—N1B	115.5 (6)	C—N1A—C2A	127.3 (6)
N1A—C—S	121.4 (5)	C—N1B—C2B	128.7 (7)
N1B—C—S	123.1 (6)		

The crystal diffracted only weakly at high angle, so data were not collected beyond $\theta = 22.5°$. H atoms attached to C atoms were placed in calculated positions and subsequently allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Methyl groups were treated as rotating rigid groups with $U_{iso}(H) = 1.5U_{eq}(C)$. H atoms attached to N atoms were located in a difference synthesis; the positional parameters were refined subject to similarity restraints on the N—H distances and the isotropic displacement parameters refined freely.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1995). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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2',3'-Diphenyl-Substituted p-Terphenyls

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Abstract

The crystal structure analyses of the title substituted p-terphenyls, 2'-(p-methoxyphenyl)-3'-phenyl-p-terphenyl, $C_{31}H_{24}O$, and 2',3'-bis(p-methoxyphenyl)-p-

terphenyl, $C_{32}H_{26}O_2$, show that the pendant phenyl rings greatly affect the conformation. Different conformations result from rotation of the terminal rings about the long molecular axis of the *p*-terphenyl part of the molecule.

Comment

In an attempt to increase the rigidity of various aromatic polymers by the introduction of terphenyl (Kallitsis & Naarmann, 1991; Kallitsis, Wegner & Pakula, 1992; Kallitsis, Kakali & Gravalos, 1994) or pentaphenyl (Kallitsis, Kakali & Gravalos, 1994) moieties into the main chain, it is essential to know the conformation of these rigid parts. In addition, recent publications (Herrema *et al.*, 1995; Oberski *et al.*, 1995) have noted that the presence of small conjugated sequences in a polymer confer photonic properties. As the size of the substituents used to enhance the solubility increases, this greatly affects the conformation of the substituted oligophenyls. We have therefore studied the crystal structures of model terphenyl molecules bearing phenyl and *p*-methoxyphenyl, (I), and two *p*-methoxyphenyl, (II), substituents.
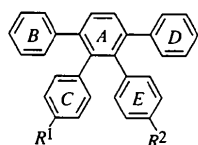
(I) R^1=OMe; R^2=H
(II) R^1=R^2=OMe

The asymmetric compound, (I), containing the electron-withdrawing methoxy group, is regarded as a potential non-linear optical material. The 2′,3′-di-phenyl-*p*-terphenyl skeletons of compounds (I) and (II) adopt propeller conformations, as was also observed for 2′,3′-diphenyl-*p*-terphenyl (Irngartinger & Kallfass, 1987). The *p*-terphenyl parts of (I) and (II) are approximately linear; the atoms constituting the molecular axis (C4B, C1B, C2A, C5A, C1D and C4D) in each case lie in a plane [maximum deviation from the mean plane: 0.017 (1) for (I) and 0.064 (2) Å for (II)] and the angles between those atoms are close to 180° (Table 1). The interplanar angles between the central ring A and the two terminal rings B and D are 44.30 (10) and 57.13 (9)°, respectively, for compound (I) and 48.77 (12) and 48.13 (9)° for compound (II). The corresponding value obtained for 2′,3′-diphenyl-*p*-terphenyl at 213 K was 49.8° (Irngartinger & Kallfass, 1987) and we found a similar value of 50.30 (6)° for the same molecule in a recent room-temperature redetermination (Nastopoulos, Kallitsis, Naarmann, Dideberg & Dupont, 1996). In addition, the interplanar angles obtained here are significantly different from those reported for unsubstituted *p*-terphenyl. At room temperature, it is nearly planar and the angle between the central and terminal rings is about

1° (Delugeard, Desuche & Baudour, 1976). At low temperature (113 K), as a result of a structural transition, the molecule conserves its centre of symmetry, is stabilized in one of the two minima of a double-well potential and so the angles can take either of two values of about 16 or 25° (Baudour, Delugeard & Cailleau, 1976). The presence of the substituents thus influences the planarity of the *p*-terphenyl part of the molecule.
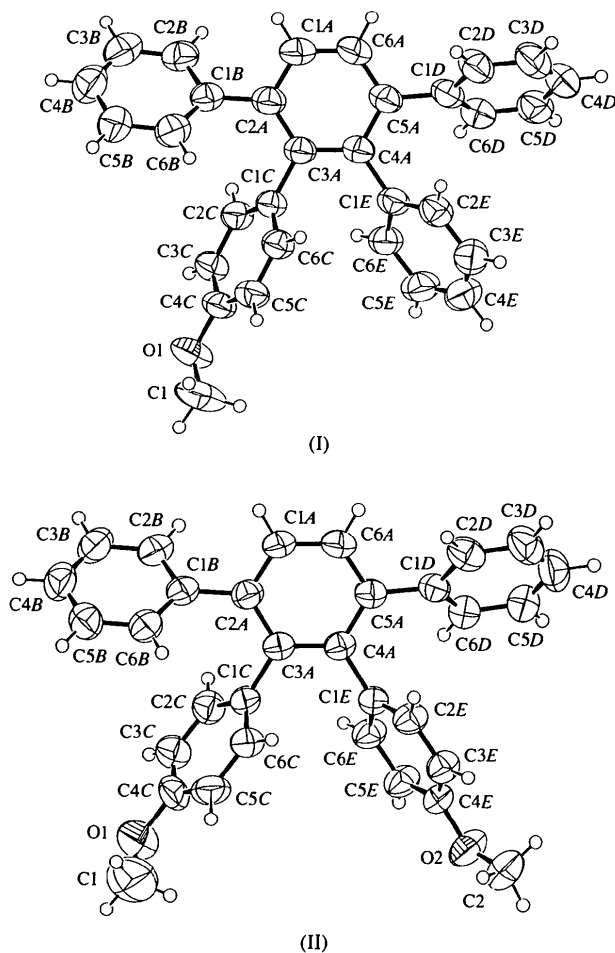

(I)

(II)

Fig. 1. The molecular structures of compounds (I) and (II) with the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary size.

Experimental

Compounds (I) and (II) were prepared according to literature procedures (Wolfe & Arnold, 1981; Kallitsis & Naarmann, 1991).

Compound (I)

Crystal data

$C_{31}H_{24}O$	Cu $K\alpha$ radiation
$M_r = 412.50$	$\lambda = 1.5418$ Å

Monoclinic
$P2_1/c$
$a = 6.284\,(3)$ Å
$b = 14.415\,(7)$ Å
$c = 25.633\,(13)$ Å
$\beta = 96.42\,(3)°$
$V = 2307\,(2)$ Å^3
$Z = 4$
$D_x = 1.187$ Mg m^{-3}
D_m not measured

Data collection

Stoe Siemens AED four-
circle diffractometer
ω scans
Absorption correction:
empirical *via* ψ scans
(Stoe & Cie, 1988b)
$T_{min} = 0.888$, $T_{max} = 0.922$
3153 measured reflections
2855 independent reflections

Refinement

Refinement on F^2
$R(F) = 0.0416$
$wR(F^2) = 0.1230$
$S = 1.007$
2855 reflections
290 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0833P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Cell parameters from 30
reflections
$\theta = 29.5{-}36.0°$
$\mu = 0.539$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.49 \times 0.16 \times 0.15$ mm
Colourless

1912 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.0194$
$\theta_{max} = 57.52°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 15$
$l = -27 \rightarrow 27$
2 standard reflections
frequency: 60 min
intensity decay: 4.8%

$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction:
SHELXL93
Extinction coefficient:
0.0041 (5)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, $°$) for (I)*

C2A—C1B	1.487 (3)	C5A—C1D	1.483 (3)
C3A—C1C	1.496 (3)	C4C—O1	1.366 (3)
C4A—C1E	1.504 (3)	O1—C1	1.426 (4)
C4C—O1—C1	117.7 (2)		
C1B—C2A—C3A—C1C	1.1 (3)	C2A—C3A—C1C—C2C	−62.9 (3)
C1C—C3A—C4A—C1E	0.7 (3)	C3C—C4C—O1—C1	−177.2 (3)
C1E—C4A—C5A—C1D	−3.1 (3)	C6A—C5A—C1D—C2D	−56.4 (3)
C1A—C2A—C1B—C2B	−43.5 (3)	C3A—C4A—C1E—C2E	129.1 (2)

Compound (II)

Crystal data

$C_{32}H_{26}O_2$
$M_r = 442.53$
Monoclinic
$P2_1/n$
$a = 10.2274\,(6)$ Å
$b = 10.6632\,(9)$ Å
$c = 22.7258\,(13)$ Å
$\beta = 102.799\,(10)°$
$V = 2416.8\,(3)$ Å^3
$Z = 4$
$D_x = 1.216$ Mg m^{-3}
D_m not measured

Data collection

Stoe Siemens AED four-
circle diffractometer

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 30
reflections
$\theta = 30.4{-}38.6°$
$\mu = 0.580$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.48 \times 0.27 \times 0.23$ mm
Colourless

2130 reflections with
$I > 2\sigma(I)$

ω scans
Absorption correction:
empirical *via* ψ scans
(Stoe & Cie, 1988b)
$T_{min} = 0.849$, $T_{max} = 0.875$
3255 measured reflections
3062 independent reflections

Refinement

Refinement on F^2
$R(F) = 0.0523$
$wR(F^2) = 0.1637$
$S = 1.101$
3062 reflections
308 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.101P)^2 + 0.2377P]$
where $P = (F_o^2 + 2F_c^2)/3$

$R_{int} = 0.0435$
$\theta_{max} = 59.02°$
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 11$
$l = -24 \rightarrow 24$
2 standard reflections
frequency: 60 min
intensity decay: 3.9%

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction:
SHELXL93
Extinction coefficient:
0.0040 (6)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, $°$) for (II)*

C2A—C1B	1.479 (4)	C4C—O1	1.401 (4)
C3A—C1C	1.497 (4)	O1—C1	1.330 (5)
C4A—C1E	1.503 (4)	C4E—O2	1.368 (3)
C5A—C1D	1.485 (4)	O2—C2	1.398 (4)
C1—O1—C4C	117.5 (4)	C4E—O2—C2	118.9 (2)
C1B—C2A—C3A—C1C	1.9 (4)	C3C—C4C—O1—C1	172.3 (4)
C1C—C3A—C4A—C1E	1.8 (4)	C6A—C5A—C1D—C2D	−46.8 (4)
C1E—C4A—C5A—C1D	−6.0 (4)	C3A—C4A—C1E—C2E	118.1 (3)
C1A—C2A—C1B—C2B	−48.0 (4)	C3E—C4E—O2—C2	−1.7 (5)
C2A—C3A—C1C—C2C	−61.8 (4)		

H atoms were fixed with a riding model for the positional parameters and $U(\text{H}) = 1.2U_{eq}(\text{C})$.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1988a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1988c); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL93*.

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A Functionalized Dimethyl 1,3-Butadiene-2,3-dicarboxylate

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Abstract

The crystal structure of dimethyl *syn*-(Z)-2-(4-methyl-phenylmethylene)-3-(1,5,5-trimethylpyrrolidin-2-ylidene)-butanedioate, $C_{21}H_{27}NO_4$, has been determined in order to establish its constitution and configuration, and to characterize the preferred conformation in the solid state. There are notable differences in the conformations of the functional groups; the essential structural features are discussed and compared.

Comment

The experimental investigations have been carried out as part of reactivity studies with specifically substituted 1-methyl-3,4-dihydro-2*H*-pyrrolium salts and dimethyl acetylenedicarboxylate under basic conditions. The formation of dimethyl *syn*-(Z)-2-(4-methylphenyl-methylene)-3-(1,5,5-trimethyl-1,3,4,5-tetrahydro-2*H*-pyrrolidene)butanedioate, (4), can be explained as a result of consecutive transformations. Deprotonation of 5-(4-methylphenylmethyl)-1,2,2-trimethyl-3,4-dihydro-2*H*-pyrrolium trifluoromethane sulfonate, (1), by ethyldi-isopropylamine generates 2-(4-methylphenylmethylene)-1,5,5-trimethylpyrrolidine, (2). The reactive enamine, (2), undergoes a [2+2] cycloaddition with dimethyl

acetylenedicarboxylate to afford the spiro-annulated intermediate, (3), followed by a cycloreversion to yield the title compound, (4). These consecutive reactions are of particular interest with respect to the reactivity of the semicyclic 1-azaallyl system and the spiro-annulated cyclobutenyl ring system (*cf.* reviews concerning enamines: Chinchilla & Bäckvall, 1994; Hickmott, 1994; Hubschwerlen, Fleury & Fritz, 1976; Jung 1991).

Ar: 4-CH3-C6H4
E: CO-OCH3
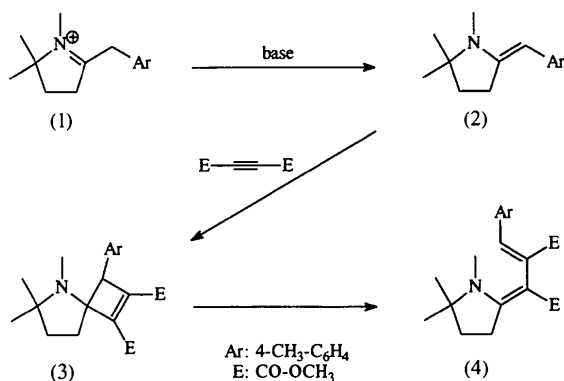
The constitution of the reaction product, (4), can be deduced by 1D and 2D ^1H and ^{13}C NMR experiments (COSY and COLOC). A signal degeneration and spreading for the cyclic methylene groups is observed in ^1H NMR spectra (CDCl3, 400 MHz) measured at 296 K; this phenomenon disappears when the temperature is increased to 330 K. In ^{13}C NMR spectra (CDCl3, 100.6 MHz) analogous behaviour is observed for the methyl groups at position 5 of the heterocyclic ring. Obviously, the ring inversion is sterically hindered by the methyl groups; in accordance with this assumption the spectroscopic phenomenon does not occur if the 5-position is unsubstituted (Zellmer, Preut & Kreher, 1997). X-ray diffraction was carried out in order to confirm the NMR results and to determine the configuration and characterize the conformation in the solid state.

The C=C double bond connected to the phenyl ring has the Z configuration and the C=C double bond linked to the heterocyclic ring has the E configuration. The butadienyl C11=C3—C4=C21 segment, with a non-planar sequence of alternating single and double bonds, prefers a *syn*-(Z) conformation in the solid state. Structural evidence that π-delocalization appears to be restricted comes from the typical values of single and double bonds (*cf.* Table 1).

The angles around the N atom [C21—N1—C27 123.9 (2) and C27—N1—C24 120.0 (2)°, and the somewhat compressed C24—N1—C21 angle of 114.3 (2)° inside the five-membered heterocycle] are indications of the planarity of the nitrogen environment. The short N1—C21 distance of 1.355 (3) Å, in contrast to the bond lengths N1—C24 of 1.480 (3) and N1—C27 of 1.454 (3) Å, demonstrates the double-bond character of N1—C21 and the conjugation of the lone pair at the