

Crystal data

[B(C₆H₅)₃(H₂O)]·C₄H₈O₂·
CH₂Cl₂*M_r* = 703.04

Monoclinic

*C*2/*c**a* = 17.036 (6) Å*b* = 16.501 (4) Å*c* = 19.517 (5) Å

β = 104.62 (2)°

V = 5309 (3) Å³*Z* = 8*D_x* = 1.759 Mg m⁻³*D_m* not measured

Data collection

Enraf–Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction: none

12 129 measured reflections

6077 independent reflections

3197 reflections with

I > 2σ(*I*)

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25
reflections

θ = 9.9–11.9°

μ = 0.377 mm⁻¹*T* = 160 (2) K

Irregular platelet

0.33 × 0.30 × 0.21 mm

Colourless

*R*_{int} = 0.069θ_{max} = 27.47°*h* = -22 → 22*k* = 0 → 21*l* = -25 → 25

3 standard reflections

every 200 reflections

intensity decay: none

Refinement

Refinement on *F*²*R* [*F*² > 2σ(*F*²)] = 0.046*wR* (*F*²) = 0.124*S* = 1.003

6077 reflections

431 parameters

H atoms: see below

w = 1/[σ²(*F*_o²) + (0.0466*P*)²
+ 3.0089*P*]where *P* = (*F*_o² + 2*F*_c²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 0.421 e Å⁻³Δρ_{min} = -0.306 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

B1—O1	1.565 (3)	O1—H12	0.96 (4)
B1—C11	1.633 (4)	C11—C1	1.763 (4)
B1—C31	1.633 (4)	C12—C1	1.729 (4)
B1—C21	1.635 (4)	O5—H11	1.72 (4)
O1—H11	0.86 (4)	O4—H12	1.64 (4)
O1—B1—C11	107.8 (2)	C31—B1—C21	114.2 (2)
O1—B1—C31	105.8 (2)	B1—O1—H11	119 (3)
C11—B1—C31	115.5 (2)	B1—O1—H12	118 (2)
O1—B1—C21	104.4 (2)	H11—O1—H12	114 (4)
C11—B1—C21	108.3 (2)		

H atoms were refined with fixed displacement parameters. The H atoms on the disordered dioxane molecule were calculated.

Data collection: *CAD-4/PC* (Kretschmar, 1994). Cell refinement: *CAD-4/PC*. Data reduction: *XCAD4* (Harms, 1996). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1004). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1724–1727

1,5-Diphenylbicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic Anhydride and 1,5-Diphenylbicyclo[2.2.1]hept-5-ene-*exo*-2,*exo*-3-dicarboxylic Anhydride

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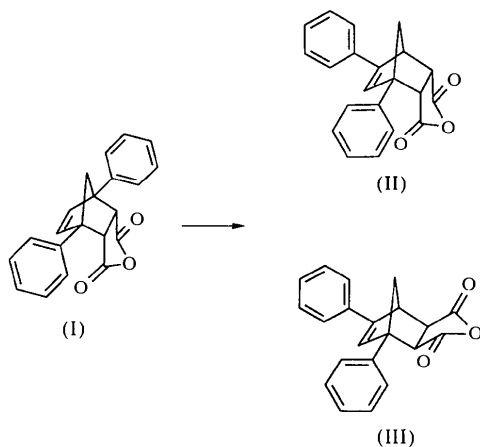
Abstract

The change of the anhydride group with respect to the cyclopentene ring in the *endo* and *exo* isomers of C₂₁H₁₆O₃ is reflected in the conformation of the phenyl

rings and in the torsion angles around the C1—C10 bond.

Comment

The primary Diels–Alder adduct of 1,4-diphenyl-1,3-cyclopentadiene and maleic anhydride is 1,4-diphenylbicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic anhydride, (I), when the reaction is carried out in benzene or in toluene using a reaction time of less than 1 h. This primary addition product isomerizes at a higher temperature or after a longer reaction time in toluene to the title compounds (II) and (III).



There are many structural investigations of substituted norbornenes but only a few articles concerning the aryl-substituted norbornenes (Beugelmans-Verrier *et al.*, 1976; Leppänen, 1965; Prinzbach & Thyges, 1971; Wilt & Ahmed, 1979). The low-field (60 MHz) spectra of diaryl-substituted bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides clearly show the different influences of the *endo* or *exo* anhydride ring on the chemical shifts of the aromatic protons (Kokko, 1980). In the aromatic region, the *endo* anhydrides display a complex multiplet while the *exo* anhydride shows a strong accumulation of signals along with a multiplet from aromatic protons. Complete assignment of the aromatic protons was not successful at the low applied fields (60 and 100 MHz). Using a high-field spectrometer (400 MHz) and the *PERCH* simulation program (Laatikainen, 1991), complete analysis of the ^1H spectra of the diphenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides was achieved. Also, the ^{13}C spectra of these compounds were measured and analysed for the first time (Kokko *et al.*, 1998). The crystal structure determinations of (II) and (III) were undertaken in order to explain the differences in the aromatic resonances of their ^1H NMR spectra.

On the whole, the bond lengths and angles of (II) and (III) compare well with the values reported for the corresponding unsubstituted compounds, bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic anhydride

(Destro *et al.*, 1969) and bicyclo[2.2.1]hept-5-ene-*exo*-2,*exo*-3-dicarboxylic anhydride (Filippini *et al.*, 1972). The bond lengths are very similar to each other in both isomers, the difference in most cases not being significant. The two C—C single bonds which connect the anhydride ring with the cyclopentene ring are significantly longer [1.590(2) and 1.575(2) Å in the *endo* isomer, and 1.590(3) and 1.560(3) Å in the *exo* isomer] than the other C—C single bonds.

The change of the anhydride group with respect to the cyclopentene ring is reflected in the bond angles and torsion angles of the two isomers. Slight differences are found for some angles, such as C2—C1—C7 and C3—C4—C7 which are both larger [100.02(18) and 100.54(19)°] in the *exo* isomer than in the *endo* isomer [98.98(13) and 98.40(13)°]. Also, the angles C2—C1—C6 and C3—C4—C5 [103.50(18) and 105.91(18)°] in the *exo* isomer are smaller than in the *endo* isomer [104.92(14) and 108.10(14)°]. Major differences in the structure of the two isomers were found in the conformation of the phenyl rings and in the torsion angles around the C1—C10 bond. The torsion angle C7—C1—C10—C11 of $-5.2(3)^\circ$ in the *exo* isomer changes to $-17.4(2)^\circ$ in the *endo* isomer. The geometry around the C5=C6 double bond is not planar, as found in a neutron diffraction study of bicyclo[2.2.1]hept-5-ene-*exo*-2,*exo*-3-dicarboxylic anhydride (Ermer *et al.*,

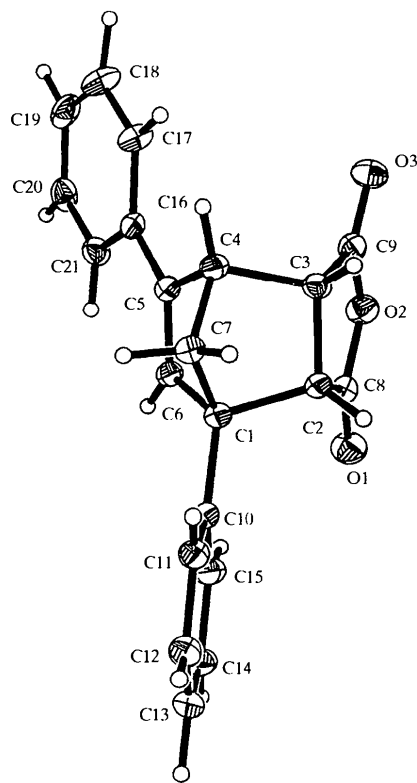


Fig. 1. The structure of (II) showing the displacement ellipsoids at 30% probability.

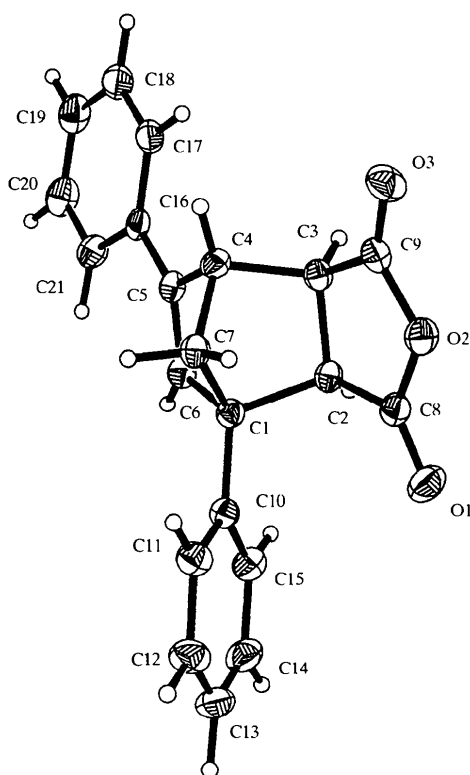


Fig. 2. The structure of (III) showing the displacement ellipsoids at 30% probability.

1989). Atom H6 does not lie in the plane of the C atoms C1, C6, C5 and C4. The deviation is seen in the torsion angle C4—C5—C6—H6, which is -174.3 (17) $^\circ$ in the *exo* isomer and -178.7 (15) $^\circ$ in the *endo* isomer.

In both structures, no intermolecular contacts are shorter than normal van der Waals separations.

Experimental

The title compounds were synthesized and separated from each other according to the methods described by Leppänen (1965) and Kokko (1980). Crystals were obtained by recrystallization from chloroform.

Compound (II)

Crystal data

$C_{21}H_{16}O_3$
 $M_r = 316.34$
 Monoclinic
 $P2_1/n$
 $a = 10.881$ (5) \AA
 $b = 10.878$ (5) \AA
 $c = 13.794$ (4) \AA
 $\beta = 109.77$ (3) $^\circ$
 $V = 1536.5$ (11) \AA^3
 $Z = 4$
 $D_x = 1.368$ Mg m^{-3}
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ \AA
 Cell parameters from 26 reflections
 $\theta = 5.84$ – 10.21 $^\circ$
 $\mu = 0.091$ mm^{-1}
 $T = 193$ (2) K
 Prismatic
 $0.45 \times 0.45 \times 0.40$ mm
 Colourless

Data collection

Rigaku AFC-7S diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 3189 measured reflections
 3032 independent reflections
 2728 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$
 $\theta_{\text{max}} = 26.52$ $^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 13$
 $l = -17 \rightarrow 16$
 3 standard reflections every 200 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.132$
 $S = 1.078$
 3032 reflections
 282 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.9025P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.037$
 $\Delta\rho_{\text{max}} = 0.259$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.225$ e \AA^{-3}
 Extinction correction: SHELXL97
 Extinction coefficient: 0.024 (3)
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (II)

O2—C9	1.380 (2)	C2—C3	1.538 (2)
O2—C8	1.402 (2)	C3—C9	1.495 (3)
C1—C6	1.522 (2)	C3—C4	1.575 (2)
C1—C7	1.543 (2)	C4—C5	1.527 (2)
C1—C2	1.590 (2)	C4—C7	1.533 (2)
C2—C8	1.504 (3)	C5—C6	1.342 (2)
C2—C1—C10	114.32 (14)	C4—C3—C9	114.79 (14)
C2—C1—C6	104.92 (14)	C3—C4—C5	108.10 (14)
C2—C1—C7	98.98 (13)	C3—C4—C7	98.40 (13)
C1—C2—C8	113.19 (15)	C1—C7—C4	94.92 (14)
C1—C2—C3—C4	-4.52 (16)	C4—C5—C16—C17	-2.1 (3)
C7—C1—C10—C11	-17.4 (2)	C4—C5—C6—H6	-178.7 (15)

Compound (III)

Crystal data

$C_{21}H_{16}O_3$
 $M_r = 316.34$
 Monoclinic
 $P2_1/c$
 $a = 6.455$ (1) \AA
 $b = 24.917$ (5) \AA
 $c = 10.016$ (2) \AA
 $\beta = 103.11$ (3) $^\circ$
 $V = 1569.0$ (5) \AA^3
 $Z = 4$
 $D_x = 1.339$ Mg m^{-3}
 D_m not measured

Data collection

Rigaku AFC-7S diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 2718 measured reflections
 2496 independent reflections
 2001 reflections with $I > 2\sigma(I)$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ \AA
 Cell parameters from 25 reflections
 $\theta = 5.31$ – 10.69 $^\circ$
 $\mu = 0.089$ mm^{-1}
 $T = 193$ (2) K
 Prismatic
 $0.40 \times 0.35 \times 0.25$ mm
 Pale yellow

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25$ $^\circ$
 $h = 0 \rightarrow 7$
 $k = 0 \rightarrow 29$
 $l = -11 \rightarrow 11$
 3 standard reflections every 200 reflections
 intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.000$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{\max} = 0.167 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.113$	$\Delta\rho_{\min} = -0.155 \text{ e } \text{\AA}^{-3}$
$S = 1.061$	Extinction correction:
2496 reflections	<i>SHELXL97</i>
266 parameters	Extinction coefficient:
H atoms: see below	0.0030 (10)
$w = 1/[\sigma^2(F_o^2) + (0.038P)^2$	Scattering factors from
$+ 0.5973P]$	<i>International Tables for</i>
where $P = (F_o^2 + 2F_c^2)/3$	<i>Crystallography</i> (Vol. C)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (III)

O2—C9	1.385 (3)	C2—C3	1.534 (3)
O2—C8	1.401 (3)	C3—C9	1.505 (3)
C1—C6	1.527 (3)	C3—C4	1.560 (3)
C1—C7	1.539 (3)	C4—C5	1.520 (3)
C1—C2	1.590 (3)	C4—C7	1.533 (3)
C2—C8	1.499 (3)	C5—C6	1.339 (3)
C2—C1—C10	114.62 (19)	C4—C3—C9	110.88 (19)
C2—C1—C6	103.50 (18)	C3—C4—C5	105.91 (18)
C2—C1—C7	100.02 (18)	C3—C4—C7	100.54 (19)
C1—C2—C8	112.49 (19)	C1—C7—C4	94.72 (18)
C1—C2—C3—C4	-1.5 (2)	C4—C5—C16—C17	8.6 (3)
C7—C1—C10—C11	-5.2 (3)	C4—C5—C6—H6	-174.3 (17)

The data for (III) were collected to somewhat smaller θ than for (II), resulting in a reflection-to-parameter ratio of 9.4. H atoms were located from difference maps. For (II), the H atoms were refined isotropically. For (III), only the positional coordinates of the H atoms were refined. Their isotropic displacement parameters were set equal to 1.2 times the equivalent value for the bonded C atom.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a); cell refinement: *MSC/AFC Diffractometer Control*

Software; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993b); program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1031). Services for accessing these data are described at the back of the journal.

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