$V = 663.3\ (3)\ \text{Å}^3$
$Z = 2$
0.7 × 0.4 × 0.2 mm
Colourless

Data collection

Siemens *R*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\text{min}} = 0.91$, $T_{\text{max}} = 1.11$
3067 measured reflections
1538 independent reflections
1416 observed reflections $[F > 4\sigma(F)]$
$R_{\text{int}} = 0.018$
$\theta_{\text{max}} = 27.5°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 147 reflections intensity variation: <1.5%

Refinement

Refinement on *F*
Final $R = 0.027$
$wR = 0.038$
$S = 2.0$
1416 reflections
84 parameters
$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.4\ \text{e Å}^{-3}$
$\Delta\rho_{\text{min}} = -0.4\ \text{e Å}^{-3}$
Extinction correction: $F_{\text{corr}} = F/(1 + 0.002xF^2/\sin 2\theta)^{-0.25}$
Extinction coefficient: $x = 0.0017\ (5)$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The structure was solved by direct methods and refined by full-matrix techniques with all atoms anisotropic. The program system *SHELXTL-Plus* (Sheldrick, 1990) was employed.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
P(1)	0.26261 (5)	0.41095 (6)	0.13623 (3)	0.0222 (1)
P(2)	0.42706 (5)	0.06743 (6)	0.29648 (3)	0.0228 (1)
S(1)	0.26484 (6)	0.59362 (7)	0.02213 (4)	0.0353 (2)
S(2)	0.60060 (6)	−0.11384 (8)	0.34939 (4)	0.0372 (2)
O(1)	0.25000	0.51488 (24)	0.25000	0.0246 (5)
O(2)	0.25000	−0.03744 (24)	0.25000	0.0241 (5)
O(3)	0.38255 (14)	0.23951 (17)	0.37926 (8)	0.0241 (3)
C(1)	0.44559 (19)	0.23870 (25)	0.18067 (12)	0.0245 (4)
F(1)	0.46540 (14)	0.11746 (17)	0.09698 (8)	0.0349 (3)
F(2)	0.58028 (12)	0.36018 (18)	0.20892 (9)	0.0353 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

P(1)—S(1)	1.869 (1)	P(1)—O(1)	1.615 (1)
P(1)—C(1)	1.872 (2)	P(2)—S(2)	1.869 (1)
P(2)—O(2)	1.616 (1)	P(2)—O(3)	1.618 (1)
P(2)—C(1)	1.868 (2)	O(3)—P(1$^{\text{i}}$)	1.614 (1)
C(1)—F(1)	1.354 (2)	C(1)—F(2)	1.351 (2)
S(1)—P(1)—O(1)	116.6 (1)	S(1)—P(1)—C(1)	118.3 (1)
O(1)—P(1)—C(1)	99.6 (1)	S(1)—P(1)—O(3$^{\text{i}}$)	117.1 (1)
O(1)—P(1)—O(3$^{\text{i}}$)	102.3 (1)	C(1)—P(1)—O(3$^{\text{i}}$)	99.9 (1)
S(2)—P(2)—O(2)	116.7 (1)	S(2)—P(2)—O(3)	116.7 (1)
O(2)—P(2)—C(1)	99.7 (1)	S(2)—P(2)—C(1)	118.3 (1)
P(1)—O(1)—P(1$^{\text{i}}$)	131.1 (1)	O(3)—P(2)—C(1)	100.0 (1)
P(2)—O(3)—P(1$^{\text{i}}$)	130.3 (1)	P(2)—O(2)—P(2$^{\text{i}}$)	130.7 (1)
P(1)—C(1)—F(1)	108.7 (1)	P(1)—C(1)—P(2)	113.5 (1)
P(1)—C(1)—F(2)	108.4 (1)	P(2)—C(1)—F(1)	108.7 (1)
F(1)—C(1)—F(2)	108.6 (1)	P(2)—C(1)—F(2)	108.9 (1)

Symmetry code: (i) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

We thank the Fonds der Chemischen Industrie for financial support. Crystals of the title compound were provided by Dr A. Groddeck and Professor M. Fild.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71200 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1040]

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Acta Cryst. (1993). C**49**, 1811–1813

Structure of 2,3-Diphenyl-2-norbornene: Comparison with Data for a *cis*-Stilbene

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(*Received* 11 *November* 1992; *accepted* 19 *March* 1993)

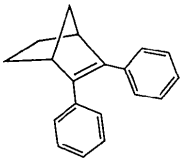
Abstract

The molecule 2,3-diphenyl-2-norbornene (2,3-diphenylbicyclo[2.2.1]hept-2-ene) (1) has been prepared as a model for *cis*-stilbene (2) in which single-bond but not double-bond torsion (within the π system) is sterically possible on both the ground-state and lowest triplet-state surfaces. A comparison of the crystal structure of (1) with previously published data for a derivative of (2) shows that the non-planar π-system geometries of (1) and (2) are indeed similar. This has allowed definitive conclusions to be

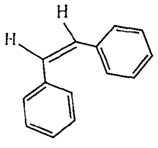
drawn concerning the phenomenon of 'nonvertical' triplet-energy transfer.

Comment

It has been proposed (Gorman, Hamblett, Irvine, Raby, Standen & Yeates, 1985) that the phenomenon of 'nonvertical' triplet-excitation transfer is dependent on non-planarity within the π system of the acceptor molecule and that the key to such behaviour lies in single-bond as opposed to double-bond torsional modes (Gorman, 1990). Since the archetypal 'nonvertical' acceptor is *cis*-stilbene (2) (Saltiel, Marchand, Kirkor-Kiminska, Smothers, Mueller & Charlton, 1984) the above proposal was tested by synthesis of a *cis*-stilbene analogue (1) in which double-bond torsion on both the ground-state and triplet-state surfaces would be severely restricted by constriction within a rigid σ framework. Photochemical comparison of (1) and (2) was only sensible given similar geometries of their individual non-planar π systems. This has been established by X-ray crystallographic determination of the structure of (1) and comparison with published data for a derivative of (2) as described herein. As anticipated the 'nonvertical' behaviour of (1) and (2) were extremely similar (Gorman, Beddoes, Hamblett, McNeeney, Prescott & Unett, 1991).



(1)



(2)

Compound (1) was synthesized *via* a seven-stage synthesis commencing with 2-norbornanone (McNeeney, 1989). The π system of (1) is clearly grossly non-planar with the acute angles between the best least-squares planes of the phenyl groups and the vinyl group being 35.9 (2) and 45.4 (2)°. The corresponding averaged torsional angles are 35.6 (4) and 45.7 (4)° which can be compared with values of 35.4 and 37.1° for a crystalline derivative of *cis*-stilbene (2) (Durant, Lefleure, Norberg & Evrard, 1982).

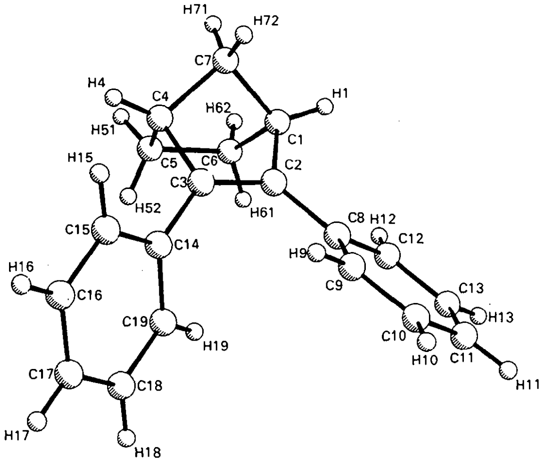


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of 2,3-diphenyl-2-norbornene (1) showing the numbering scheme.

Experimental

Crystal data

$C_{19}H_{18}$
$M_r = 246.35$
Orthorhombic
$P2_12_12_1$
$a = 6.103\ (1)$ Å
$b = 12.040\ (1)$ Å
$c = 18.997\ (2)$ Å
$V = 1395.9$ Å^3
$Z = 4$
$D_x = 1.172$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 72 reflections
$\theta = 12.25$-$14.03°$
$\mu = 0.076$ mm^{-1}
$T = 294$ K
Elongated tabular
0.33 × 0.17 × 0.05 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.80$, $T_{\max} = 1.04$
2383 measured reflections
2383 independent reflections

952 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 26$
2 standard reflections
frequency: 240 min
intensity variation: −9.2%

Refinement

Refinement on F
Final $R = 0.050$
$wR = 0.051$
$S = 0.83$
952 reflections
172 parameters
H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jB_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C1	0.535 (1)	0.3454 (5)	0.1676 (3)	3.9 (3)
C2	0.439 (1)	0.4280 (4)	0.1155 (3)	3.0 (2)
C3	0.364 (1)	0.5153 (5)	0.1524 (3)	3.5 (3)
C4	0.404 (1)	0.4885 (6)	0.2296 (3)	4.6 (3)
C5	0.648 (1)	0.5016 (7)	0.2416 (3)	5.6 (4)
C6	0.744 (1)	0.4020 (6)	0.1984 (3)	5.3 (4)
C7	0.378 (1)	0.3601 (6)	0.2297 (3)	4.8 (3)
C8	0.449 (1)	0.4127 (4)	0.0391 (3)	3.1 (2)
C9	0.282 (1)	0.4522 (5)	−0.0041 (3)	3.8 (3)
C10	0.284 (1)	0.4365 (5)	−0.0757 (3)	4.2 (3)
C11	0.452 (1)	0.3800 (5)	−0.1065 (3)	4.4 (3)
C12	0.617 (1)	0.3545 (5)	0.0066 (3)	4.2 (3)
C13	0.618 (1)	0.3394 (5)	−0.0657 (3)	4.5 (3)

C14	0.313 (1)	0.6266 (5)	0.1280 (2)	3.3 (2)
C15	0.124 (1)	0.6832 (5)	0.1482 (3)	4.7 (3)
C16	0.082 (1)	0.7903 (5)	0.1249 (4)	5.1 (4)
C17	0.227 (1)	0.8429 (5)	0.0818 (3)	5.1 (3)
C18	0.414 (1)	0.7905 (5)	0.0613 (3)	4.9 (3)
C19	0.457 (1)	0.6835 (5)	0.0848 (3)	4.1 (3)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C1—C2	1.521 (7)	C8—C12	1.382 (8)
C1—C6	1.559 (9)	C9—C10	1.373 (8)
C1—C7	1.529 (8)	C10—C11	1.364 (8)
C2—C3	1.344 (7)	C11—C13	1.369 (9)
C2—C8	1.465 (7)	C12—C13	1.386 (8)
C3—C4	1.521 (7)	C14—C15	1.395 (9)
C3—C14	1.451 (7)	C14—C19	1.381 (8)
C4—C5	1.520 (9)	C15—C16	1.388 (9)
C4—C7	1.554 (9)	C16—C17	1.360 (9)
C5—C6	1.57 (1)	C17—C18	1.363 (9)
C8—C9	1.395 (7)	C18—C19	1.388 (8)
C2—C1—C6	105.8 (5)	C2—C8—C12	122.4 (5)
C2—C1—C7	100.8 (5)	C9—C8—C12	116.9 (5)
C6—C1—C7	99.9 (5)	C8—C9—C10	121.9 (6)
C1—C2—C3	107.6 (4)	C9—C10—C11	120.0 (6)
C1—C2—C8	123.2 (5)	C10—C11—C13	119.6 (5)
C3—C2—C8	129.0 (5)	C8—C12—C13	120.9 (6)
C2—C3—C4	106.5 (5)	C11—C13—C12	120.6 (6)
C2—C3—C14	128.9 (4)	C3—C14—C15	122.7 (6)
C4—C3—C14	122.5 (5)	C3—C14—C19	120.8 (5)
C3—C4—C5	106.1 (6)	C15—C14—C19	116.4 (5)
C3—C4—C7	101.4 (5)	C14—C15—C16	121.3 (7)
C5—C4—C7	101.6 (6)	C15—C16—C17	120.3 (7)
C4—C5—C6	102.0 (6)	C16—C17—C18	120.1 (6)
C1—C6—C5	103.1 (5)	C17—C18—C19	119.6 (7)
C1—C7—C4	93.0 (5)	C14—C19—C18	122.3 (6)
C2—C8—C9	120.6 (5)		

We thank the SERC, UK, for the award of a Research Studentship to SPM.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry including angles involving H atoms, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71183 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1041]

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Acta Cryst. (1993). C49, 1813–1818

Structures of 1,1-Diphenyl-2-aza-1,3-butadienes. I. 3-Cyano-4-(*n*-methoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadienes (n = 2, 3, 4)

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(*Received* 25 *January* 1993; *accepted* 13 *April* 1993)

Abstract

The different position of the methoxy substituent in the three title 2-azabutadienes, 2MOPD, 3MOPD and 4MOPD [3-(2-methoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile, 3-(3-methoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile and 3-(4-methoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile], has a small influence on their geometry and conformation. The average bond lengths along the C=N—C=C fragment [1.286 (3), 1.405 (3) and 1.346 (3) Å] indicate a high degree of localization of the double and single bonds. The average torsion angle along the central N—C bond is 138°. The phenyl rings are tilted from the N=C(C_{Ph})—C_{Ph} plane by 4.5 (1)-65.0 (1)°. The substituents around the C=C bond are arranged in a *Z* configuration. The molecules are packed by van der Waals forces.

Comment

The 2-azadienes are attractive starting compounds for the preparation of a variety of heterocyclic systems because of their ability to react as heterodienes in Diels–Alder reactions (Boger, 1983; Boger & Weinreb, 1987; Barluenda, Joglar, Gonzales & Fustero, 1990; Barluenda, Aznar, Fustero & Tomas, 1990). A convenient procedure for the synthesis of functionalized 2-azadienes has been reported (Dryanska, 1990) and applied (Dryanska, 1992) for

Acta Crystallographica Section C
ISSN 0108-2701 ©1993