Experimental

The title compound was prepared using a method described by Viñas *et al.* (1997).

Crystal data

$C_{19}H_{18}P^+ \cdot C_6H_{20}B_9^-$
$M_r = 466.81$
Monoclinic
$P2_1/c$
$a = 11.6141\ (15)$ Å
$b = 15.9238\ (14)$ Å
$c = 15.115\ (2)$ Å
$\beta = 100.31\ (1)°$
$V = 2750.3\ (6)$ Å^3
$Z = 4$
$D_x = 1.127$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 6.6–9.2°$
$\mu = 0.114$ mm^{-1}
$T = 294\ (2)$ K
Prism
0.38 × 0.36 × 0.26 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: none
5449 measured reflections
4836 independent reflections
2427 reflections with $I > 2\sigma(I)$

$R_{int} = 0.139$
$\theta_{max} = 25.09°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -18 \rightarrow 18$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.149$
$S = 1.006$
4836 reflections
356 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.9040P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.231$ e Å^{-3}
$\Delta\rho_{min} = -0.274$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

P—C19	1.780 (3)	B2—B6	1.734 (7)
P—C25	1.782 (3)	B2—B3	1.744 (7)
P—C12	1.787 (3)	B3—B4	1.730 (7)
P—C13	1.795 (3)	B4—B5	1.745 (6)
C7—C8	1.567 (4)	B5—B6	1.807 (7)
C7—B11	1.610 (5)	B9—B10	1.843 (7)
C8—B9	1.620 (5)	B10—B11	1.784 (6)
C1—C7—C8	119.1 (3)	B3—B4—B5	109.8 (3)
C8—C7—B11	114.5 (3)	B4—B5—B6	106.0 (3)
C3—C8—C7	118.3 (3)	B2—B6—B5	107.3 (3)
C7—C8—B9	110.6 (3)	C8—B9—B10	106.7 (3)
B6—B2—B3	109.1 (4)	C7—B11—B10	106.5 (3)
B4—B3—B2	107.7 (3)		

H atoms bonded to C were fixed and the H atoms bonded to B were refined with isotropic displacement parameters.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995). Cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1036). Services for accessing these data are described at the back of the journal.

References

Buchanan, J., Hamilton, E. J. M., Reed, D. & Welch, A. J. (1990). *J. Chem. Soc. Dalton Trans.* pp. 677–680.

Cowie, J., Donohoe, D. J., Douek, N. L. & Welch, A. J. (1993). *Acta Cryst.* C**49**, 710–714.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sillanpää, R., Kivekäs, R., Teixidor, F., Viñas, C. & Nuñez, R. (1996). *Acta Cryst.* C**52**, 2223–2225.

Viñas, C., Pedrajas, J., Bertran, J., Teixidor, F., Kivekäs, R. & Sillanpää, R. (1997). *Inorg. Chem.* **36**, 2482–2486.

Acta Cryst. (1999). C**55**, 1009–1012

(1*R*,2*R*,3*S*,4*S*,5*S*,6*S*)-*exo*-2-Cyano-*exo*-3-[(*S*)-1,2-dibenzyloxyethyl]-*exo*-5-iodobicyclo[2.2.1]heptane-*endo*-2,6-carbolactone

MIRIAM ALÍAS, ELENA BUÑUEL, CARLOS CATIVIELA, MARÍA D. DÍAZ-DE-VILLEGAS AND JOSÉ A. GÁLVEZ

Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza–CSIC, 50009 Zaragoza, Spain. E-mail: jagl@posta.unizar.es

(Received 8 July 1998; accepted 3 February 1999)

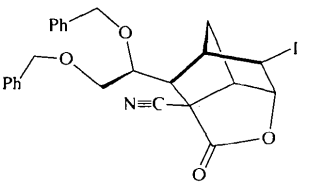
Abstract

In the title compound ($C_{25}H_{24}INO_4$), an enantiomerically pure iodolactone, the absolute configurations at the chiral C1, C2, C3, C4, C5 and C6 centres have been unambiguously assigned as 1*R*, 2*R*, 3*S*, 4*S*, 5*S* and 6*S*, respectively. In the bicyclo[2.2.1]heptane (norbornane) unit, the six-membered ring presents a boat conformation, and is fused with a five-membered lactone ring which adopts an envelope conformation.

Comment

There is an ever-growing interest in the synthesis, pharmacology and conformational properties of non-proteinogenic amino acids. In particular, cyclic non-metabolizable α-amino acids have useful biological properties, for example, 2-aminobicyclo[2.2.1]heptane-2-carboxylic acid has proved to be a substrate for transport into *Escherichia coli* (Christensen *et al.*, 1969), and a stimulator of insulin release from the rat pancreas (Christensen & Cullen, 1969). In addition, their incorporation into peptides is often a powerful approach for generating analogues of bioactive peptides with enhanced biological activities (Malin *et al.*, 1993; Arttamangkul *et al.*, 1995; Tóth *et al.*, 1997).

During the last few years we have been interested in the asymmetric synthesis of amino acids with a norbornane skeleton (Buñuel, Cativiela & Díaz-de-Villegas, 1996). In this context we have developed a synthetic methodology for 2-amino-3-phenyl-2- norbornanecarboxylic acids based on the reaction of methyl (*E*)-2-cyanocinnamates and cyclopentadiene and subsequent rearrangement and hydrolysis of the cyano and carboxylate groups (Avenoza *et al.*, 1989) which, recently, has prompted us to use chiral cyano-ester as a synthetic precursor of those cyclic amino acids in enantiomerically pure form. With this aim, we have tested the reaction of cyclopentadiene with methyl (*E*)-2-cyano-3-[(*S*)-1,2-dibenzyloxyethyl]acrylate. When this starting material was treated with an excess of cyclopentadiene in dichloromethane at room temperature, a mixture of the four possible Diels–Alder adducts was obtained. A mixture of the two major *exo*/*endo* diastereoisomers could be easily separated from the reaction mixture by flash chromatography and, after a typical iodolactonization procedure, enantiomerically pure *endo* iodolactone (I) was isolated. X-ray analysis of this compound was carried out in order to determine unambiguously the absolute configuration at the new chiral C atoms formed in the Diels–Alder reaction.



(I)

The molecular structure of (I) is shown in Fig. 1. The X-ray analysis established the stereochemistry at the chiral C1, C2, C3, C4, C5 and C6 atoms as 1*R*, 2*R*, 3*S*, 4*S*, 5*S* and 6*S*, respectively. The absolute configuration is unambiguously deduced from the known stereochemistry of the chiral centre at C10 which originated from (*R*)-2,3-di-*O*-benzylglyceraldehyde. Moreover, the Flack parameter confirms the assigned configuration. This result indicates that the addition of cyclopentadiene occurred preferably to the (2*Si*,3*Re*) diastereotopic face of the dienophile.

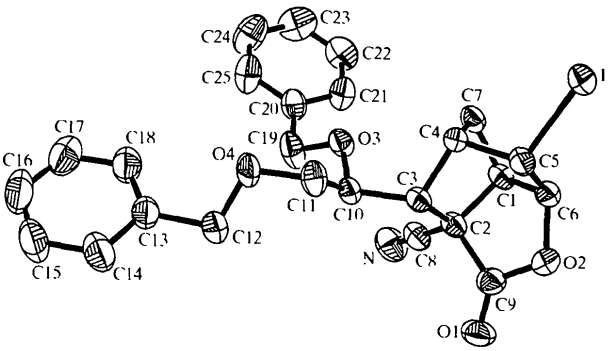


Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

The norbornane six-membered ring adopts a distorted boat conformation which is evidenced by the puckering parameters (Cremer & Pople, 1975) q_2 = 1.054 (5), q_3 = −0.064 (5) Å, φ_2 = 177.3 (3), θ_2 = 93.5 (3)° and Q_T = 1.056 (5) Å. In the norbornane system, the bond lengths and angles show small variations from reported values (Buñuel *et al.*, 1997; Back *et al.*, 1998). The mean value of the bond length is 1.545 (7) Å. The C4—C7—C1 angle is contracted to 95.8 (4)° with respect to the regular tetrahedral value, while the endocyclic angles of the five-membered norbornane rings are in the range 100.7 (4)–104.2 (4)°. The asymmetric substitution of the norbornane nucleus produces a twist *S*-(+,+) (Altona & Sundaralingam, 1970) about the C1···C4 vector.

The (1,2-dibenzyloxyethyl) moiety adopts a conformation that avoids eclipsing of the C2—C3 and C3—C4 bonds of the norbornane ring [C2—C3—C10—O3 and C4—C3—C10—O3 torsion angles are −69.3 (5) and 49.0 (6)°, respectively]. The two phenyl rings are nearly coplanar, with an interplanar angle of 13.3 (2)°.

The five-membered lactone ring adopts an almost envelope conformation [puckering parameters, q_2 = 0.394 (5) Å and φ_2 = 6.1 (8)°] with atom C1 deviating by 0.611 (5) Å from the plane formed by the remaining four ring atoms. The exocyclic bond angles about the carbonyl group C9—O1 differ by 5.7°, with the larger value for the O1—C9—C2 angle [129.3 (6)°]. This is in agreement with published data on other lactones (Buñuel, Cativiela, Díaz-de-Villegas & Gálvez, 1996; Soriano-García *et al.*, 1994; Rychlewska *et al.*, 1992).

Experimental

The title compound was obtained *via* the diastereoselective Diels–Alder reaction of methyl (*E*)-2-cyano-3-[(*S*)-1,2-dibenzyloxyethyl]acrylate (1 mmol) with dicyclopentadiene

(5 mmol) in dichloromethane (20 mml) carried out under an atmosphere of argon at room temperature for 2 h. A mixture of the two major *exo/endo* adducts was separated from the crude reaction mixture by flash chromatography (eluant: ethyl acetate/hexane 1/4) and saponified with 10% KOH/EtOH (20 ml) at reflux for 4 h. Finally, the enantiomerically pure iodolactone (I) was isolated after a typical iodolactonization procedure (Cativiela *et al.*, 1992). Crystals were obtained by slow evaporation of a water–ethanol solution.

Crystal data

$C_{25}H_{24}INO_4$
M_r = 529.35
Monoclinic
$P2_1$
a = 6.425 (1) Å
b = 7.895 (1) Å
c = 21.883 (2) Å
β = 95.50 (1)°
V = 1104.9 (2) Å^3
Z = 2
D_x = 1.591 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 49 reflections
θ = 6.00–16.92°
μ = 1.481 mm^{-1}
T = 293 (2) K
Prism
0.44 × 0.38 × 0.1 mm
Colourless

Data collection

Siemens $P4$ diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.562, T_{max} = 0.866
5013 measured reflections
2332 independent reflections (plus 1983 Friedel-related reflections)

3886 reflections with $F > 4\sigma(F)$
R_{int} = 0.040
θ_{max} = 26°
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -26 \rightarrow 26$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.097
S = 1.017
4315 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.1130P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.651 e Å^{-3}
$\Delta\rho_{min}$ = −0.652 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.04 (3)

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

I—C5	2.159 (5)	C2—C8	1.470 (9)
O1—C9	1.180 (6)	C2—C9	1.530 (8)
O2—C9	1.367 (7)	C2—C3	1.590 (8)
O2—C6	1.461 (6)	C3—C4	1.548 (7)
N—C8	1.135 (8)	C4—C7	1.539 (7)
C1—C7	1.512 (7)	C4—C5	1.544 (7)
C1—C6	1.545 (7)	C5—C6	1.536 (8)
C1—C2	1.549 (6)		
C9—O2—C6	110.0 (4)	C5—C4—C3	105.9 (4)
C7—C1—C6	104.2 (4)	C6—C5—C4	102.8 (4)
C7—C1—C2	104.0 (4)	C6—C5—I	112.2 (3)
C6—C1—C2	97.1 (4)	C4—C5—I	110.9 (3)
C8—C2—C9	111.6 (5)	O2—C6—C5	110.8 (4)
C8—C2—C1	114.2 (5)	O2—C6—C1	106.3 (4)
C9—C2—C1	103.9 (4)	C5—C6—C1	103.9 (4)
C8—C2—C3	115.0 (4)	C1—C7—C4	95.8 (4)
C9—C2—C3	108.0 (5)	N—C8—C2	178.4 (6)
C1—C2—C3	103.3 (4)	O1—C9—O2	123.6 (5)
C4—C3—C2	101.8 (4)	O1—C9—C2	129.3 (6)
C7—C4—C5	100.7 (4)	O2—C9—C2	107.1 (4)
C7—C4—C3	103.3 (4)		

The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all non-H atoms. H atoms were fixed at idealised positions and, during the refinement, allowed to ride on the carrier atoms with individual isotropic displacement parameters constrained to $1.2U_{eq}$ of the carrier atom.

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989). Software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1983).

This work was supported by the Dirección General de Investigación Científica y Técnica (project number PB97-0998-C02-01).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1323). Services for accessing these data are described at the back of the journal.

References

Altona, C. & Sundaralingam, M. (1970). *J. Am. Chem. Soc.* **92**, 1995–1998.

Arttamangkul, S., Murray, T. F., DeLander, G. E. & Aldrich, J. V. (1995). *J. Med. Chem.* **38**, 2410–2417.

Avenoza, A., Cativiela, C., Mayoral, J. A. & Roy, M. A. (1989). *Tetrahedron*, **45**, 3923–3934.

Back, T. G., Dyck, B. P., Nan, S. & Parvez, M. (1998). *Acta Cryst.* C**54**, 425–427.

Buñuel, E., Cativiela, C. & Díaz-de-Villegas, M. D. (1996). *Tetrahedron Asymmetry*, **7**, 1521–1528.

Buñuel, E., Cativiela, C., Díaz-de-Villegas, M. D. & Gálvez, J. A. (1996). *Acta Cryst.* C**52**, 1456–1458.

Buñuel, E., Cativiela, C., Díaz-de-Villegas, M. D. & Gálvez, J. A. (1997). *Acta Cryst.* C**53**, 626–628.

Cativiela, C., Mayoral, J. A., Avenoza, A., Peregrina, J. M., Lahoz, F. J. & Gimeno, S. (1992). *J. Org. Chem.* **57**, 4664–4669.

Christensen, H. N. & Cullen, A. M. (1969). *J. Biol. Chem.* **244**, 1521–1526.

Christensen, H. N., Handlogten, M. E., Lum, I., Tager, H. S. & Zand, R. (1969). *J. Biol. Chem.* **244**, 1505–1509.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Malin, D. H., Lake, J. R., Payza, K., Corriere, L. S., Benson, T. M., Garber, T. L., Waller, M. L., Luu, T. A., Kelley, R. S., Smith, D. A., Ho, K. K. & Burgess, K. (1993). *Peptides*, **14**, 731–734.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Rychlewska, U., Szczepańska, B. & Serkerov, S. V. (1992). *Acta Cryst.* C**48**, 1543–1547.

Sheldrick, G. M. (1989). *SHELXTL-Plus*. Release 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1993). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Soriano-García, M., Rodríguez-Romeros, A., Villena, R. & Yuste, F. (1994). *Acta Cryst.* C**50**, 2093–2094.
Tóth, G., Darula, Z., Péter, A., Fülöp, F., Tourwé, D., Jaspers, H., Verheyden, P., Böcskey, Z., Tóth, Z. & Borsodi, A. (1997). *J. Med. Chem.* **40**, 990–995.

Acta Cryst. (1999). C**55**, 1012–1014

An investigation of 2,4′-dihydroxy-3,3′-dimethoxy-5′-methylstilbene using X-ray crystallography and NMR spectroscopy

SHIMING LI,[a] KNUT LUNDQUIST[a] AND ROLF STOMBERG[b]

[a]*Department of Organic Chemistry, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden, and* [b]*Department of Inorganic Chemistry, University of Gothenburg, SE-412 96 Gothenburg, Sweden. E-mail: rolf@inoc.chalmers.se*

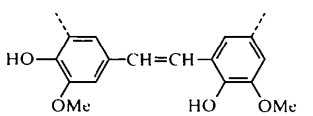
(*Received 21 October 1998; accepted 6 January 1999*)

Abstract

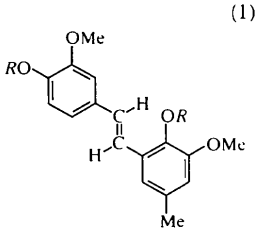
The *E* and *Z* forms of the title compound, $C_{17}H_{18}O_4$, were examined by ^{13}C NMR and ^1H NMR spectroscopy, and the crystal structure of the *E* form (m.p. 397–398 K) was determined by X-ray crystallography. Earlier reported spectral data for these two isomeric stilbenes are complemented or revised on the basis of these results.

Comment

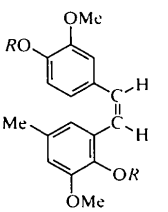
It is known from experiments with lignins and model compounds that stilbenes of type (1) are produced from lignin structures of the phenylcoumaran type by the action of various treatments such as alkaline pulping (Adler *et al.*, 1964; Yoon *et al.*, 1981), acidolysis (Li & Lundquist, 1999) and mechanical pulping (Lee *et al.*, 1990). Several stilbenes of type (1) have been reported to be present in spent liquors from alkaline pulping (Gierer & Lindeberg, 1980; Niemelä, 1990). One of these compounds is 2,4′-dihydroxy-3,3′-dimethoxy-5′-methylstilbene, (2). This stilbene has also been obtained through alkaline (Yoon *et al.*, 1981) and acid (Yasuda, 1988, and references therein) treatment of the phenylcoumaran model, *trans*-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzo[*b*]furan. In this study, a mixture of the stereoisomeric forms, (2*a*) and (2*b*), was prepared by a synthetic method involving a Wittig reaction; the method has been applied earlier to the synthesis of 8-(3,5-di-*tert*-butylstyryl)fluoranthene (Brink *et al.*, 1998). NMR examinations of the *E* form, (2*a*), and the *Z* form, (2*b*), and their acetate derivatives, (3*a*) and (3*b*), are reported in this paper. A crystal structure determination of (2*a*) provided evidence of the molecular structure of the compounds. The compounds were prone to photochemical isomerization on exposure to daylight in chloroform solution: after one week, about 10% of the *E* form, (2*a*), had been converted to the *Z* form, (2*b*). The acetate of the *E* form, (3*a*), also gave a mixture of the two possible stereoisomeric forms on exposure to daylight in chloroform solution; the *Z* form, (3*b*), dominated (*ca* 90%).



(1)



(2*a*) *R* = H
(3*a*) *R* = COMe



(2*b*) *R* = H
(3*b*) *R* = COMe

Gierer & Nilvebrandt (1991) reported the synthesis of (2) *via* a 1,1-diaryl-2-chloroethane intermediate. However, the ^1H NMR spectral data given in their paper for the acetylated product are not in accordance with the spectral data for (3*a*) or (3*b*) obtained in this study. It was noted in previous ^1H NMR spectral studies of stilbenes of type (1) (Stomberg *et al.*, 1998) that the signal from one of the methoxy groups in the *Z* forms is located at a comparatively high field (*ca* δ 3.5). The present study shows that this is also true for (2*b*) (δ 3.62) and (3*b*) (δ 3.54). Gierer & Lindeberg (1980) reported the isolation of the *Z* isomer, (2*b*), as the acetate derivative, (3*b*), from a Kraft pulping liquor. However, the NMR spectral data reported for the product isolated by Gierer & Lindeberg (1980) deviate considerably from those of (3*b*) [or (3*a*)]. Mörck & Kringstad (1985) report ^{13}C NMR spectral data for (3*a*) and (3*b*). Their data do not agree completely with the data obtained in this study.

Awareness of the photochemical instability of (2) and (3) is of importance in connection with examination of these compounds. A partial explanation of the discrepancies between the NMR spectral data for (2) and (3) given in this paper and those given in the literature (see the papers referred to above) may be that the photochemical reactions have been overlooked in previous work.

The *E* stilbene, (2*a*), adopts a conformation that deviates only slightly from planarity [angle between the ring