348 *J. Org. Chem.* 1992, *57*, 348–352

Photoisomerization of 2,2″-Ethano-Bridged *m*-Terphenyl Derivatives: Ring Constraint Activates an Unreactive Chromophore

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Received July 15, 1991

The photochemistry of 2,2″-ethano-bridged *m*-terphenyl derivatives **4**, **8**, and **9** was investigated. These compounds are chiral and may be suitable photoresolvable additives to discotic liquid crystals. Unlike their unbridged analogues, **4**, **8**, and **9** rearrange rapidly when irradiated with UV light to the *o*-terphenyl compounds **10**, **11**, and **12**, respectively. This rearrangement is likely to proceed through an intermediate benzvalene valence-bond isomer. The high reactivity of the 2,2″-ethano-bridged compounds is attributed to distortion in their lowest excited singlet states and to the relief of strain when the ortho isomers are formed.

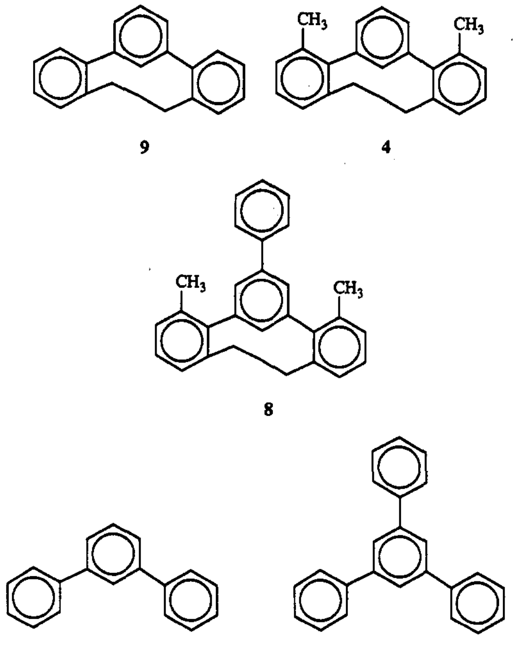
Introduction

Disk-shaped molecules substituted with several long alkyl "arms" (discogens) are known to form special liquid crystalline phases with nematic or columnar order.[1] In some cases, optically active additives will induce twisted phase (cholesteric) properties in these liquid crystals.[2] All such additives known to date intercalate in columns of the discogen and are chiral by virtue of substitution in the arms. We sought examples of disk-shaped compounds that are chiral because of nonplanar core structures that might be resolved photochemically by irradiation with circularly polarized light. In this quest we were led to consider 2,2″-ethano-bridged *m*-terphenyl (**9**). The synthesis of this compound was reported in 1969 by Vögtle who showed by NMR spectroscopy that it exists as thermally interconvertable diastereomers.[3] We reasoned that the tendency for *m*-terphenyl to adopt a planar structure in the triplet state[4] would provide pathways for photoracemization and photoresolution. We prepared ethano-bridged terphenyls **4** and **8** and studied their photochemistry to judge their suitability as additives for liquid crystals. Unlike *m*-terphenyl (**13**) itself, compounds **9**, **4**, and **8** rearrange rapidly when irradiated with ultraviolet light.

Results

1. Syntheses of 2,2″-Ethano-Bridged *m*-Terphenyls 4 and 8. The syntheses of *m*-terphenyls **4** and **8** (Chart I) were achieved following the general strategy developed by Vögtle for **9** with some significant modifications as shown in Scheme I. Preparation of substituted *m*-terphenyls **2** and **6** was based on the "one-pot" method perfected recently by Hart and co-workers.[5] Reaction of substituted iodobenzene **1** with trihaloarenes **15** and **5** according to this procedure gives *m*-terphenyls **2** and **6** in 66% and 52% isolated yields, respectively. In an attempt to prepare **9**, Vögtle and Schunder[6] tried unsuccessfully a direct cyclization of 2,2″-bis(bromomethyl)-*m*-terphenyl (**16**) by coupling with organometallic reagents. Similarly, we are unable to prepare **9** in meaningful yield by treatment of **16** with phenyllithium. However, both **3** and **7** cyclize smoothly to **4** and **8**, respectively, under these conditions.

Chart I



9 4 8

meta-Terphenyl (13) 1,3,5-Triphenylbenzene (17)

2. Spectroscopic Properties of *m*-Terphenyls 4, 8, and 9. The ^{1}H NMR spectrum of bridged terphenyl **9** exhibits temperature-dependent behavior attributed to rocking of the central phenyl group through the center of the 9-membered ring and, at higher temperature, rotations of the ethano bridge. Complete coalescence was observed by Vögtle at ca. 130 °C (60 MHz), which corresponds to $\Delta G^{\ddagger} = 20$ kcal/mol. Since one of the objectives of this research was the isolation of the enantiomers of these 2,2″-ethano-bridged terphenyls, we prepared **4** and **8** which have 6,6″-dimethyl substitution in an attempt to raise the barrier for racemization.[7] The ^{1}H NMR spectra of **4** and **8** do not show complete coalescence up to 145 °C (200 MHz).

The UV absorption spectra of 2,2″-ethano-bridged terphenyls **4**, **8**, and **9** are shown in Figure 1 along with those of *m*-terphenyl and 1,3,5-triphenylbenzene for comparison. These compounds show two bands in their absorption spectra: a lower energy ^1L_b transition ($\epsilon_{max} \approx 10^3$ cm^{-1} M^{-1}) and a more allowed ^1L_a transition ($\epsilon_{max} \approx 5 \times 10^4$ cm^{-1} M^{-1}). The observation of the low-energy ^1L_b band in the ab-

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[5] Vinod, T.; Hart, H. *J. Org. Chem.* 1990, *55*, 881.

[6] Vögtle, F.; Schunder, L. *Liebigs Ann. Chem.* 1969, *721*, 129.

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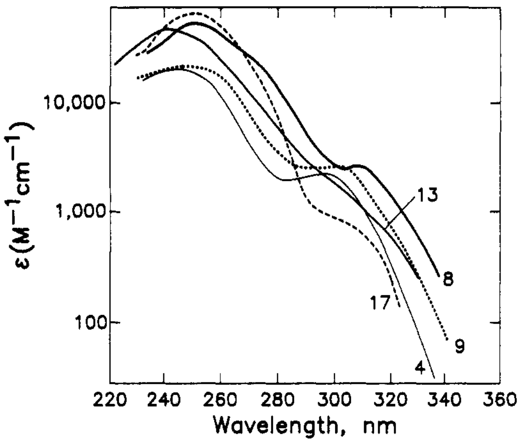
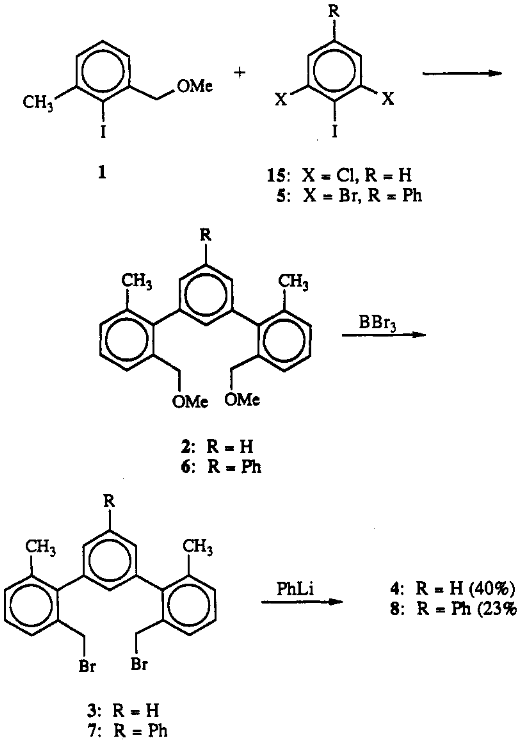


Figure 1. Absorption spectra of bridged *m*-terphenyls **4**, **8**, and **9** recorded in cyclohexane solution at room temperature and compared with the spectra of *m*-terphenyl (**13**) and 1,3,5-triphenylbenzene (**17**).

Scheme I



sorption spectra of **4** and **8** was encouraging since one objective of this work was to resolve their enantiomers photochemically. The enantiomeric excess that such a process will yield depends, in part, on the electronic nature of the lowest energy absorption band.[8a]

The fluorescence emission spectra of **4**, **8**, and **9** are shown in Figure 2 as well as those of *m*-terphenyl and 1,3,5-triphenylbenzene for comparison. The spectra of fresh samples of **4**, **8**, and **9** resemble closely those of their "unbridged" analogues. But after a few minutes of irradiation in the spectrometer, the intensity of the emissions decrease and shift slightly to shorter wavelength. Under these conditions there is no alteration in the emission spectrum of either *m*-terphenyl or 1,3,5-triphenylbenzene. These changes in the emission spectra of the meta-bridged terphenyls indicate a photochemical reaction that is undetected in the unbridged analogues.

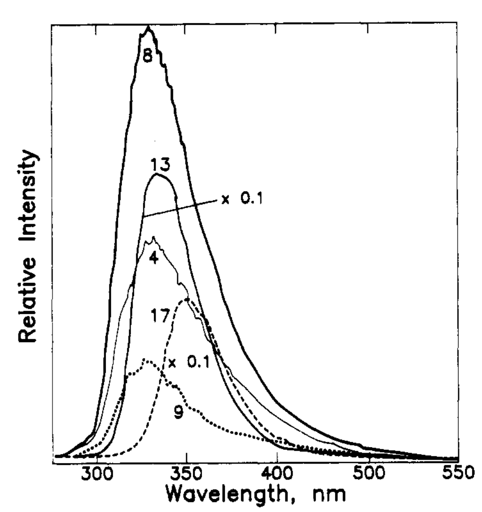
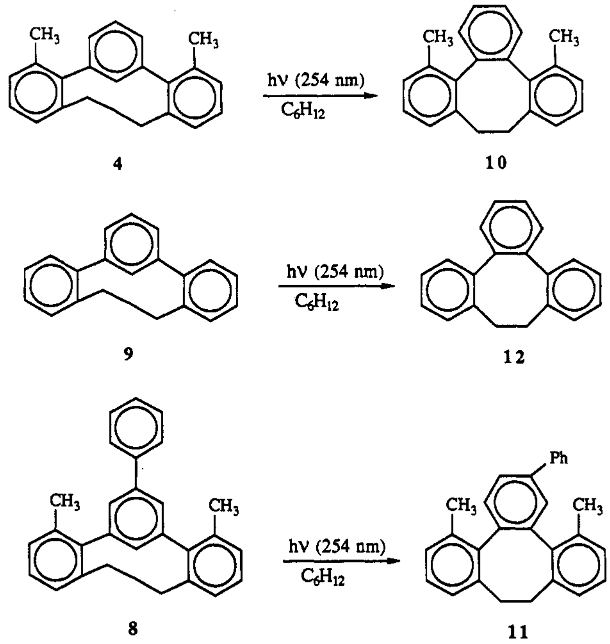


Figure 2. Fluorescence spectra of bridged *m*-terphenyls **4**, **8**, and **9** recorded in cyclohexane solution at room temperature and compared with the spectra of *m*-terphenyl (**13**) and 1,3,5-triphenylbenzene (**17**).

Scheme II



The triplet states of *m*-terphenyl and 1,3,5-triphenylbenzene exhibit characteristic ESR spectra at 77 K in frozen media.[8b] We sought to determine the conformation of bridged-terphenyl triplets **4**, **8**, and **9** by analysis of their zero field parameters. However, under conditions where the unbridged analogues give easily measured spectra, no signals could be detected from the bridged compounds. Evidently, even at low temperature some process results in the rapid consumption of the excited states.

3. Photochemistry of *m*-Terphenyls 4, 8, and 9. Irradiation of a cyclohexane solution of 2,2″-ethano-bridged terphenyl **4** at 254 nm leads to its rapid consumption with formation of a single isomeric product in 81% isolated yield. This photoproduct was purified by recrystallization from ethanol after evaporation of the reaction solvent. ^1H and ^{13}C NMR spectral analysis reveal it to be bridged *o*-terphenyl **10**. This assignment was confirmed by the comparable irradiation of **9** which yields bridged *o*-terphenyl **12**, a previously synthesized compound.[9] Similarly,

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(8) (a) Rau, H. *Chem. Rev.* **1983**, 535. (b) Tanigaki, K.; Taguchi, N.; Yagi, M.; Higuchi, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 668.

(9) Gugel, H.; Meier, H. *Chem. Ber.* **1980**, *113*, 1431.

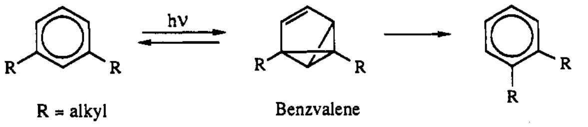
irradiation of **8** leads to the formation of two isomeric products in a ratio of 6:1. The major photoproduct was isolated by chromatography in 63% yield and was shown to be bridged ortho isomer **11**. The minor product was not identified. These results are summarized in Scheme II.

Triplet sensitization was employed to decide if the rearrangements of **4**, **8**, and **9** proceeds from their singlet or triplet states. Irradiation of oxygen-free benzene solutions of these compounds containing benzophenone as sensitizer with $\lambda > 345$ nm ($Ph_2CO - E_t = 69$ kcal/mol; *m*-terphenyl $- E_t = 64.9$ kcal/mol: triplet energies of the bridged terphenyls will certainly be below this value) does not give any photoisomerized products. Thus it appears that the rearrangement of the bridged *m*-terphenyls occurs from their singlet excited states.

For the purpose of comparison, *m*-terphenyl and 1,3,5-triphenylbenzene were irradiated under the conditions that lead to isomerization of **4**, **8**, and **9**. *m*-Terphenyl rearranges to *o*-terphenyl, but the rate of this rearrangement is at least 200 times slower than for the bridged compounds. No rearranged product could be detected from the irradiation of 1,3,5-triphenylbenzene. Evidently, the bridging ethano group found in **4**, **8**, and **9** enables a reaction of these chromophores that, at best, is very inefficient when the bridge is absent.

Discussion

The photochemical properties of aromatic hydrocarbons have been studied extensively. Of particular relevance to this work is the discovery by Wilzbach and Kaplan[10] that irradiation of dialkylbenzenes initiates a 1,2-alkyl group shift. Elegant isotope labeling experiments demonstrated that these shifts are the consequence of ring-carbon interchange.[11] This rearrangement was postulated to proceed through an intermediate benzvalene, and this compound was eventually isolated from the irradiation of benzene in the gas phase and solution, see eq 1.[12] Numerous studies have shown that this valence-bond isomerization reaction generally occurs for alkyl-substituted benzenes and for various single-ring aromatic heterocycles. However, it has been noted that the efficiency for formation of the benzvalenes is greatly reduced when the benzene ring is substituted with aryl groups.[13]



(1)

Griffin and co-workers irradiated a series of alkyl-substituted biphenyls.[14] They observed that rearrangement to (unisolated) benzvalenes occurs only when the biphenyl is substituted at the 2- and 2′-positions. Similarly, Abramovitch and Takaya report the rearrangement of substituted biphenyls through a presumed benzvalene intermediate.[15] Also, Zimmerman and Crumrine account for the photoracemization of optically active biphenyl derivatives, in part, by formation of a benzvalene valence-bond isomer.[16] In contrast, Masamune and coworkers report that *o*-, *p*-, or *m*-terphenyls are not isomerized when they are irradiated with UV light.[17] Similarly, Warrener and Bremner could detect no photoisomerization when alkyl-substituted terphenyls were irradiated.[18]

The rearrangement of benzene to benzvalene occurs in the excited singlet state. Bryce-Smith and Gilbert explain the mechanism of the rearrangement in the lowest excited singlet states (S_1, ^1L_b) in terms of state symmetry arguments.[13] The S_1 state of benzene is nonbonding between C_1 and C_3 in its equilibrium geometry of a regular hexagon. But these atoms tend to become bonding as a consequence of a distortion that brings them closer together. This conclusion appears to be of special significance in the comparison of the photochemical properties of terphenyls with the ethano-bridged compounds **4**, **8**, and **9**.

We are unable to detect any isomerization of 1,3,5-triphenylbenzene even after prolonged irradiation; and *m*-terphenyl rearranges very slowly to give *o*-terphenyl. In contrast, bridged *m*-terphenyls **4**, **8**, and **9** rearrange readily to their *o*-terphenyl isomers. It is clear that the bridging ethano groups of **4**, **8**, and **9** will distort the regular hexagon structure in their S_1 states. From the analysis of Bryce-Smith and Gilbert, we conclude that this distortion is the primary factor that simulates C_1–C_3 bonding and the eventual formation of the benzvalene for the 2,2″-ethano-bridged terphenyls.

A second factor that may contribute to the high efficiency observed for the rearrangements of *m*-terphenyls **4**, **8**, and **9** to *o*-terphenyls **10**, **11**, and **12**, respectively, is the relief of ring strain. Presumably the benzvalene formed from valence-bond isomerization could open to re-form starting material or isomerize to give the observed product. The results of PCMODEL calculations indicate that the standard free energies for formation of **4**, **10**, and the expected intermediate benzvalene isomer are 74, 52, and 150 kcal/mol, respectively. This finding suggests that the *o*-terphenyl isomer is much less strained than the *m*-terphenyl starting material. Thus it seems likely that the benzvalene intermediate will open to form **10** rather than **4**. We feel that this fact, too, accounts for the unexpectedly efficient photochemical reactions of the 2,2″-ethano-bridged terphenyls.

Conclusions

Unlike *m*-terphenyl and 1,3,5-triphenylbenzene, 2,2″-ethano-bridged terphenyls **4**, **8**, and **9** react rapidly from their excited single states when irradiated with UV light. Analysis of the products suggest the formation of an intermediate benzvalene derivative for each compound which isomerizes to form *o*-terphenyls **10**, **11**, and **12**. The high reactivity of the 2,2″-ethano-bridged compounds is attributed to a distortion from hexagonal symmetry in their S_1 states and to the relief of strain when the intermediate benzvalene isomerizes to the ortho isomer. The high photochemical reactivity of the 2,2″-ethano-bridged compounds makes them unsuitable for use as photochemically resolvable additives to discotic liquid crystals.

Experimental Section

General. A Hewlett-Packard 5890 GC and HP-5970 mass selective detector were used for GC–MS analyses which were performed at 70 eV with 0.25 mm × 12 m HP-1 capillary column programmed at 150 °C for 3 min and then 250 °C at the rate of 15 °C min^{-1}. A Hewlett-Packard 5890 GC equipped with a flame

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[18] Warrener, R. N.; Bremener, J. B. *Tetrahedron Lett.* **1966**, 5691.

ionization detector and an HP 3390A electronic integrating recorder was used for analytical separations. Helium was the carrier gas. GC analyses were performed with 0.53 mm × 10 m HP-1 column (column A). Melting points are uncorrected. Standard workup procedures for reactions typically involved dilution with ether (or CH_2Cl_2) and multiple extractions with water (occasionally with dilute acid or base as required), washing the organic layer with saturated NaCl solution to reduce its water content, drying over a solid desiccant (usually $MgSO_4$), and finally evaporation of the solvent. Elemental analyses were preformed by the Microanalytical laboratory of the University of Illinois.

General Procedure for Preparative Direct Irradiation. Direct preparative irradiations at 253.7 nm were conducted at 27 °C in a 20-mL quartz tube placed in a Rayonet photochemical reactor equipped with 12 lamps. Generally, 10^{-2}–10^{-3} M solutions of the 2,2″-ethano-*m*-terphenyls in cyclohexane (distilled from CaH_2) were purged with N_2 for 30 min prior to irradiation. The solutions were magnetically stirred throughout the irradiation.

Determination of Photochemical Product Yields of Photolyses Conducted in Cyclohexane. Direct photolyses of 0.01 M solutions of 2,2″-ethano-*m*-terphenyls containing octadecane as internal standard in 3 mL of cyclohexane (distilled from CaH_2) were conducted in a 3-mL quartz cell following the above procedure for direct photolyses. The light source consisted of five Rayonet photochemical lamps (253.7 nm) mounted symmetrically in the Rayonet photochemical reactor. Aliquots taken at time intervals were analyzed by GC on column A (programmed at 150 °C for 3 min, then to 250 °C at the rate of 15 °C/min) to quantify unreacted starting materials and the photoproducts.

2-(Methoxymethyl)-6-methyliodobenzene (1). A suspension of 22.4 g (0.40 mol) of powdered potassium hydroxide in 200 mL of dimethyl sulfoxide was stirred for 10 min under a nitrogen atmosphere. A solution of 24.8 g (0.20 mol) of 2-iodo-3-methylbenzyl alcohol[19] in 25 mL of DMSO was added, followed immediately by addition of 12.5 mL (28.4 g, 0.20 mol) of iodomethane. The reaction mixture was stirred for 1 h and then poured onto 250 g of crushed ice. The organic layer was worked up in the standard way to give 24.9 g (95%) of **1** as a lemon yellow oil that was purified by distillation: bp 63–64 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 2.46 (s, 3 H, methyl), 3.50 (s, 3 H, methoxy), 4.49 (s, 2 H, benzyl), 7.14–7.20 (m, 3 H, aromatic); GC–MS *m/z* (relative intensity) 262 (M^+, 31), 231 (19), 135 (100), 119 (11), 105 (41), 91 (42), 77 (30), 63 (21), 45 (10), 39 (25). Anal. Calcd for $C_9H_{11}IO$: C, 41.25; H, 4.23. Found: C, 41.27; H, 4.54.

1,3-Bis[2-(methoxymethyl)-6-methylphenyl]benzene (2). In a 500-mL, three-necked flask was prepared 57.0 mmol of [2-(methoxymethyl)-6-methylphenyl]magnesium iodide by adding dropwise 200 mL of a dry THF (distilled over sodium) solution of 2-(methoxymethyl)-6-methyliodobenzene (15.0 g, 58.0 mmol) to 1.42 g (58.0 mmol) of preheated magnesium under Ar while constant reflux was maintained.

In a separate 200-mL, three-necked flask was placed 7.78 g (28.6 mmol) of 2,6-dichloroiodobenzene[20] dissolved in 100 mL of dry THF. The solution was cooled to −18 °C and kept under an Ar atmosphere. A solution of vinylmagnesium bromide (29 mmol, 1 M solution in THF, Aldrich) was added dropwise to the 2,6-dichloroiodobenzene solution. The reaction mixture was stirred at −18 °C for 2 h after the addition was complete and then added dropwise to the [2-(methoxymethyl)-6-methylphenyl]magnesium bromide. Reflux was maintained overnight, the reaction mixture was cooled with an ice–water bath, and 50 mL of 10% HCl was added slowly. The product layer was worked up in the standard way. Column chromatography on silica gel using 1:4 ether–hexane gave 6.5 g (65.7% yield) of **2**: ^1H NMR ($CDCl_3$) δ 2.10 (s, 3 H, methyl), 2.13 (s, 3 H, methyl), 3.25 (s, 3 H, methoxy), 3.29 (s, 3 H, methoxy), 4.18–4.22 (m, 4 H, benzyl), 6.98 (s, 1 H, aromatic), 7.10–7.54 (m, 9 H, aromatic); GC–MS *m/z* (relative intensity) no parent, 314 (M − 32, 27), 283 (26), 282 (63), 267 (100), 253 (18), 252 (21), 239 (7), 165 (3), 157 (2), 141 (3), 133 (5), 127 (4), 126 (7), 113 (2), 91 (2). Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.24; H, 7.58.

1,3-Bis[2-(bromomethyl)-6-methylphenyl]benzene (3). To 9.40 g (27.1 mmol) of 1,3-bis[2-(methoxymethyl)-6-methylphenyl]benzene dissolved in 75 mL of methylene chloride at −65 °C under an Ar atmosphere was added dropwise with stirring 2.57 mL (6.80 g, 27.17 mmol) of boron tribromide. After 30 min at −65 °C, the reaction mixture was slowly warmed to room temperature and allowed to stand for 10 min. The reaction mixture was again cooled to −60 °C, followed by a standard workup. The crude product obtained after evaporating the solvent was purified by column chromatography on silica gel using 1:4 methylene chloride–hexane to give 11.45 g (95% yield) of white, powdery **3** that was recrystallized from hexane: mp 106–107 °C; ^1H NMR ($CDCl_3$) δ 2.06 (s, 3 H, methyl), 2.11 (s, 3 H, methyl), 4.28–4.33 (m, 4 H, methylene), 7.10 (s, 1 H, aromatic), 7.18–7.49 (m, 9 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.12, 20.24, 31.78, 32.06, 127.01, 127.15, 127.32, 127.34, 127.87, 127.91, 129.18, 129.29, 129.41, 129.50, 134.96, 135.13, 136.17, 136.50, 138.36, 138.41, 140.85, 140.88; GC–MS *m/z* (relative intensity) 444 (M^+, 3), 285 (3), 284 (24), 283 (100), 269 (9), 268 (34), 267 (12), 254 (8), 253 (26), 252 (15), 239 (5), 142 (10), 133 (8), 126 (17), 119 (5). Anal. Calcd for $C_{22}H_{20}Br_2$: C, 59.48; H, 4.54. Found: C, 59.85; H, 4.56.

2,2″-Ethano-6,6″-dimethyl-*m*-terphenyl (4). To a refluxing ether solution (50 mL) containing 20 mmol of phenyllithium (10 mL, 2 M solution from Fluka) was added dropwise 3 g (6.76 mmol) of 1,3-bis[2-(bromoethyl)-6-methylphenyl]benzene dissolved in 25 mL of ether. The reaction mixture was heated at reflux for 18 h and then cooled with an ice–water bath. The excess phenyllithium was destroyed by the slow addition of cold water, and the ether layer was worked up in the standard way. Column chromatography on neutral alumina (*n*-hexane as eluant) gave 0.775 g (40.4% yield) of pure **4**: mp 143–144 °C; ^1H NMR ($CDCl_3$)[21] δ 2.68 (s, 6 H, methyl), 7.02–7.43 (m, 9 H, aromatic), 7.79 (s, 1 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.86, 126.38, 127.30, 127.63, 128.27, 129.29, 133.22, 140.82; GC–MS *m/z* (relative intensity) 284 (M^+, 100), 283 (14), 270 (15), 269 (57), 226 (3), 189 (3), 179 (7), 155 (9), 152 (3), 142 (6), 132 (5), 127 (7), 126 (13), 119 (5), 77 (2); UV (cyclohexane solution) $\lambda_{\max}$ ($\epsilon_{\max}$) 247 (20 000), 296 nm (2000). Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.88; H, 7.06.

3,5-Dibromo-4-iodobiphenyl (5). A 3.30-g (10-mmol) portion of 4-amino-3,5-dibromobiphenyl[23] was dissolved in 20 mL of concd sulfuric acid at 50 °C. After the solution was cooled to 2 °C with an ice–water bath, 1.38 g (20 mmol) of sodium nitrite was added portionwise with continuous stirring, maintaining the temperature below 5 °C. Stirring was continued for an additional 2 h at 0 °C to complete the diazotization. The diazonium salt solution was poured onto 1000 g of crushed ice in a 2-L beaker, and then 5 g (30 mmol) of potassium iodide dissolved in 25 mL of water was added. The reaction mixture was then heated at to 80 °C for 15 min, and the solid product that formed was removed by filtration. The solid was washed several times with cold water and finally dried under vacuum at 100 °C to yield 3.30 g (75.3%) of **5**: mp 103–104 °C; ^1H NMR ($CDCl_3$) δ 7.54–7.75 (m, 5 H, aromatic), 7.75 (s, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 107.97, 127.47, 129.26, 129.72, 130.21, 132.13, 138.06, 144.37; GC–MS *m/z* (relative intensity) 438 (M^+, 100), 436 (51), 232 (30), 230 (36), 219 (6), 151 (46), 150 (39), 127 (4), 115 (8), 98 (7), 77 (7), 75 (20), 62 (5). Anal. Calcd for $C_{12}H_7Br_2I$: C, 32.91; H, 1.61; Br, 36.49. Found: C, 33.07; H, 1.57; Br, 36.45.

3,5-Bis[2-(methoxymethyl)-6-methylphenyl]biphenyl (6). A 79.4-mmol portion of [2-(methoxymethyl)-6-methylphenyl]magnesium iodide was prepared in a 1-L, three-necked flask by the dropwise addition of 20.8 g (79.4 mmol) of 2-(methoxymethyl)-6-methyliodobenzene (**2**, in 275 mL of dry THF) to 2.0

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(21) At room temperature the methylene protons of the enantiomers exchange rapidly, and hence no signal was observed. However, when the NMR spectrum was obtained in DMSO solution at 65 °C, the methylene proton peaks were observed as broad multiplets; ^1H NMR (DMSO, 65 °C) δ 1.91–2.26 (br m, 2 H, methylene), 2.68 (s, 6 H, methyl), 2.85–3.04 (br m, 2 H, methylene), 7.10–7.51 (m, 9 H, aromatic), 7.80 (s, 1 H, aromatic). The coalescence for the methylene peaks at 200 MHz was incomplete at the maximum temperature available (145 °C).

(22) When the spectrum of **10** was determined with acetone-d_6 as solvent, the methylene protons appeared as AA′BB′ pattern multiplets centered around δ 2.74.

(23) Scarborough, H. A.; Water, W. A. *J. Chem. Soc.* **1926**, 577.

g (82.3 mmol) of preheated magnesium under an Ar atmosphere. The addition rate was adjusted to maintain constant reflux, and the reaction mixture was heated at reflux for 2 h after the addition was complete. In a separate 300-mL, three-necked flask, 39.7 mL of vinylmagnesium bromide (39.7 mmol, 1 M, Aldrich) was added dropwise to 17.4 g (39.7 mmol) of 3,5-dibromo-4-iodobiphenyl dissolved in 150 mL of dry THF at −18 °C under an Ar atmosphere. After this mixture was stirred for 2 h it was added dropwise to a previously prepared [2-(methoxymethyl)-6-methylphenyl]magnesium iodide solution, and then the mixture was heated at reflux overnight. After the mixture was cooled with an ice–water bath, 50 mL of cold water was slowly added and the organic layer was worked up in the standard way. Column chromatography on silica gel (1:4 ether–hexane as eluent) gave 8.68 g (52% yield) of **6** as a yellow oil: ^{1}H NMR (CDCl$_3$) δ 2.15 (s, 3 H, methyl), 2.16 (s, 3 H, methyl), 3.28 (s, 3 H, methoxy), 3.29 (s, 3 H, methoxy), 4.23–4.25 (m, 4 H, methylene), 6.97 (s, 1 H, aromatic), 7.23–7.69 (m, 13 H, aromatic); GC–MS *m/z* (relative intensity) 422 (M$^+$, 0.23), 391 (5), 390 (22), 375 (11), 359 (27), 358 (63), 346 (100), 343 (43), 331 (39), 315 (19), 253 (18), 252 (20), 239 (18), 163 (12), 157 (13), 150 (9), 91 (6); high-resolution MS-EI calcd for $C_{30}H_{30}O_2$ (M$^+$) 422.2245, found 422.2235.

3,5-Bis[2-(bromomethyl)-6-methylphenyl]biphenyl (7). To 3.29 g (7.79 mmol) of 3,5-bis[2-(methoxymethyl)-6-methylphenyl]biphenyl (**6**) in 75 mL of methylene chloride under an Ar atmosphere at −65 °C was added dropwise 7.82 g (2.95 mL, 31.2 mmol) of boron tribromide. The reaction mixture was stirred at that temperature for an additional 1 h and then warmed to room temperature for 5 min. After the mixture was cooled to −20 °C, it was worked up by slowly adding a saturated sodium bicarbonate solution. The organic layer was worked up in the standard way. Column chromatography on silica gel (3:2 CH_2Cl_2–hexane) gave 3.87 g (96% yield) of pure **7**: mp 44–45 °C; ^{1}H NMR (CDCl$_3$) δ 2.12 (s, 3 H, methyl), 2.16 (s, 3 H, methyl), 4.32–4.37 (m, 4 H, methylene), 7.09–7.72 (m, 14 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 20.85, 20.94, 32.53, 32.78, 126.58, 127.13, 127.57, 127.70, 127.81, 127.87, 128.24, 128.80, 130.11, 130.21, 135.66, 135.81, 136.82, 127.13, 139.47, 141.14, 141.40, 141.45; GC–MS *m/z* (relative intensity) 520 (M + 2, 10), 518 (6), 360 (33), 267 (9), 253 (8), 252 (9), 239 (5), 180 (8), 163 (5), 151 (3); high-resolution MS-EI calcd for $C_{28}H_{24}Br_2$ (M$^+$) 518.0244, found 518.0246. Anal. Calcd: C, 64.64; H, 4.65. Found: C, 64.53; H, 4.67.

2,2″-Ethano-6,6″-dimethyl-5′-phenyl-*m*-terphenyl (8). To a refluxing solution of phenyllithium (10.8 mmol, 5.41 mL, 2 M solution from Fluka) in 300 mL of dry ether under an Ar atmosphere was added dropwise 2.19 g (4.22 mmol) of 3,5-bis[2-(bromomethyl)-6-methylphenyl]biphenyl dissolved in 100 mL of ether. The mixture was heated at reflux for 18 h, cooled with an ice–water bath, and subjected to standard aqueous workup. Chromatography on silica gel (8% benzene in hexane as eluent) gave 441 mg (22.6% yield) of **8**: mp 202–203 °C; ^{1}H NMR (CDCl$_3$)[24] δ 2.75 (s, 6 H, methyl), 7.05–7.68 (m, 13 H, aromatic), 7.79 (s, 1 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 34.61, 35.42, 127.28, 127.34, 127.44, 128.72, 139.98, 140.88, 140.99; GC–MS *m/z* (relative intensity) 360 (M$^+$, 100), 345 (39), 329 (15), 283 (9), 269 (9), 267 (13), 253 (19), 252 (15), 239 (11), 215 (7), 163 (11), 157 (7), 126 (7), 77 (4). UV (cyclohexane solvent) λ_{max} (ϵ_{max}) 252 (52 000); 310 nm (2500). Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.22; H, 6.78.

Photoproduct from Direct Irradiation of 2,2″-Ethano-6,6″-dimethyl-*m*-terphenyl (4). A 0.018 M solution (102 mg, 0.36 mmol) of **4** in 20 mL of dry cyclohexane was irradiated at 253.7 nm for 3 h following the general procedure. GC analysis showed only one product peak (retention time 10.6 min) in addition to 5% of residual starting material. The reaction mixture was concentrated, and 82.5 mg (81% yield) of the pure photoproduct was isolated by column chromatography on neutral alumina (10% CH_2Cl_2 in hexane was the eluent). The product was recrystallized from ethanol to give colorless crystals of 9,10-dihydro-5,14-dimethyltribenzo[*a*,*c*,*e*]cyclooctene (**10**): mp 153 °C; ^{1}H NMR (CDCl$_3$)[22] δ 2.02 (s, 6 H, methyl), 2.77 (s, 4 H, methylene), 6.81–7.64 (m, 10 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 20.47, 33.51, 123.11, 126.75, 126.88, 127.00, 127.67, 129.29, 134.94, 139.60, 141.03; GC–MS *m/z* (relative intensity) 284 (100), 269 (10), 254 (20), 253 (30), 239 (20), 202 (10), 179 (20), 126 (20), 113 (10), 77 (10); high-resolution MS-EI calcd for $C_{22}H_{20}$ M$^+$ 284.1565, found 284.1567.

Photoproduct from the Direct Irradiation of 2,2″-Ethano-6,6″-dimethyl-5′-phenyl-*m*-terphenyl (8). A 9.38 × 10^{-3} M solution (101 mg, 0.281 mmol) of **8** in 20 mL of dry cyclohexane was irradiated at 253.7 nm following the general procedure. After 2.5 h of irradiation, GC analysis on column A showed two product peaks in ratios of 6:1 in addition to 2% of unreacted **8**. The major product had a retention time 9.55 min and the minor product 10.34 min. GC–MS analysis showed that the products are isomers of **8**. The reaction mixture was concentrated, and the major product was isolated by chromatography on neutral alumina with 5% benzene in hexane as eluent to give 63.5 mg (63% yield) of 9,10-dihydro-5,14-dimethyl-2-phenyltribenzo[*a*,*c*,*e*]cyclooctene (**11**): ^{1}H NMR (CDCl$_3$) δ 2.07 (s, 6 H, methyl), 2.82 (m, 4 H, methylene), 6.84–6.97 (m, 6 H, aromatic), 7.36–7.71 (m, 8 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 20.74, 20.79, 33.75, 33.78, 125.82, 127.00, 127.17, 127.48, 127.89, 127.93, 127.99, 128.99, 129.97, 135.16, 135.21, 139.80, 139.86, 140.40, 140.86, 140.90, 141.16, 141.71; GC–MS *m/z* (relative intensity) 360 (M$^+$, 100), 345 (21), 330 (7), 329 (6), 315 (5), 267 (4), 255 (9), 252 (7), 239 (4), 215 (2), 165 (3), 157 (3), 151 (2); high-resolution MS-EI calcd for $C_{28}H_{24}$ M$^+$ 360.1878, found 360.1872.

Identification of the Photoproduct in the Direct Photolysis of 2,2″-Ethano-*m*-terphenyl (9). A 0.046 M (6 mg, 0.023 mmol) solution of **9** in 0.5 mL of cyclohexane-d_{12} was irradiated at 253.7 nm in a quartz NMR tube following the general procedure. After 20 min of irradiation, the ^{1}H NMR spectrum of the reaction mixture showed an AA′BB′ pattern in the aliphatic region (δ 2.72–3.07, 4 H, methylene) and aromatic multiplets (δ 6.90–7.32, 12 H), which are identical with the previously reported spectrum of 9,10-dihydrotribenzo[*a*,*c*,*e*]cyclooctene (**12**):[9] GC–MS *m/z* (relative intensity) 256 (M$^+$, 100), 255 (34), 252 (12), 241 (37), 239 (22), 228 (10), 215 (8), 178 (7), 165 (9), 141 (3), 126 (9), 120 (10), 113 (8), 101 (4), 100 (2).

Acknowledgment. This work was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, for which we are grateful. Mr. Sean Murphy of this department performed the PCMODEL calculations.

Registry No. **1**, 137300-31-3; **2**, 137300-32-4; **3**, 137300-33-5; **4**, 137300-34-6; **5**, 135990-00-0; **6**, 137300-35-7; **7**, 137300-36-8; **8**, 137300-37-9; **9**, 24400-28-0; **10**, 137300-38-0; **11**, 137300-39-1; **12**, 71493-82-8; **15**, 19230-28-5; 2-iodo-3-methylbenzyl alcohol, 100959-88-4; 4-amino-3,5-dibromobiphenyl, 3366-59-4.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of compounds **6**, **7**, **10**, and **11** (9 pages). Ordering information is given on any current masthead page.

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(24) Here, too,[21] the methylene protons are not observed because of broadening.