Forfeiture of the Aromaticity of a Bridged [10]Annulene by Benzannelation

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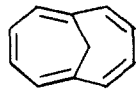
Abstract: This paper addresses the question of whether hydrocarbon **10**, a dibenzo derivative of 1,6-methano[10]annulene, retains the [10]annulene ring in **10a** or exists as the valence tautomer **10b**, a double norcaradiene. A rational synthesis of **10b** has been achieved in eight steps from *trans*-1,2-diphenyl-1,2-cyclopropanedicarboxylic acid. The spectroscopic properties, particularly the ^{13}C NMR spectrum, show that the stable form of **10** is the norcaradiene **10b**.

A landmark in the history of nonbenzenoid aromatic compounds[1] was 1,6-methano[10]annulene (**1**), the first stable, aromatic cyclodecapentaene. While the peripheral conjugated system



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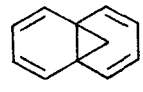
satisfies the Hückel $4n + 2$ requirement, attempts to prepare a stable cyclodecapentaene had been thwarted until Vogel's imaginative solution of removing the troublesome 1,6-hydrogen interactions by incorporating a methylene bridge in their place.[2] Although the bridge slightly distorts the skeleton from planarity, sufficient π overlap remains to provide an aromatic 10-membered ring that shows clear evidence of delocalization in the NMR spectrum, where the diamagnetic ring current is revealed by deshielding of the peripheral hydrogens and strong shielding of the bridge hydrogens, as well as in classical electrophilic substitution reactions. Theoretical calculations[3-5] estimate the resonance energy of **1** as 50–90% that of benzene, and an experimental value of 17.2 kcal/mol has been calculated on the basis of heats of hydrogenation.[6]

It will be recalled that the immediate product of Vogel's logical synthesis[2] was the norcaradiene tautomer **2**, which underwent spontaneous valence tautomerization to **1**. Tautomer **1** is only



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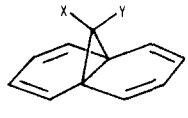
slightly more stable than **2**, however; ab initio calculations[7,8] estimate the enthalpy difference as 4.5–6.3 kcal/mol, and an experimental value of 5.7 kcal/mol, based on heats of combustion, has been published.[9] The barrier for conversion of **2** to **1** has been calculated[7,8] to be only 1.2–2.3 kcal/mol.

Given the delicate balance of the equilibrium **1** $\rightleftharpoons$ **2**, it is not surprising that substituents may reverse the stability order, similar to the parent norcaradiene $\rightleftharpoons$ cycloheptatriene equilibrium.[10] Single-crystal X-ray studies[11-13] show that the ground states of the bridge-substituted molecules **3–5** are double norcaradienes. Compounds **4** and **5** exhibit temperature-dependent ^{13}C NMR spectra, showing that the valence tautomers rapidly equilibrate in solution.[14]



3 X = Y = CH_3
4 X = Y = CN
5 X = CN, Y = CH_3

Our interest was aroused in the effect of fusing benzene rings onto the bridged annulene **1**. The consequences of benzannelation on a variety of aromatic annulenes have been investigated.[15,16] In nearly every system studied, annelation of benzene rings *reduces* the aromaticity of the parent ring, as measured by the loss of diatropicity in the NMR spectrum. Especially relevant are a series of papers by Mitchell et al.[16] that reported the effect of benzannelation at different positions of the [14]annulene, *trans*-15,16-dimethyl-15,16-dihydropyrene (**6**). Compared with the parent annulene, the derivatives with a single benzene ring fused at bonds a or b, as well as the *syn*-dibenzo derivative **7**, showed a marked reduction of diamagnetic ring current due to the bond-localization effect of the fused benzene ring. Remarkably, the *anti*-dibenzo derivative **8** showed little reduction in diatropicity and had almost the full ring current of **6**. It was argued that because **8** has two equivalent Kekulé structures, bond localization

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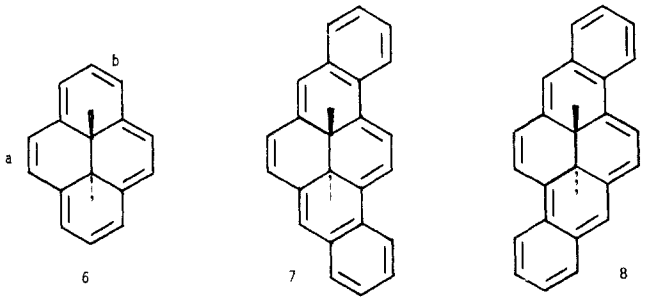
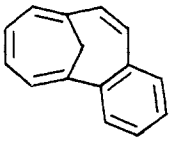


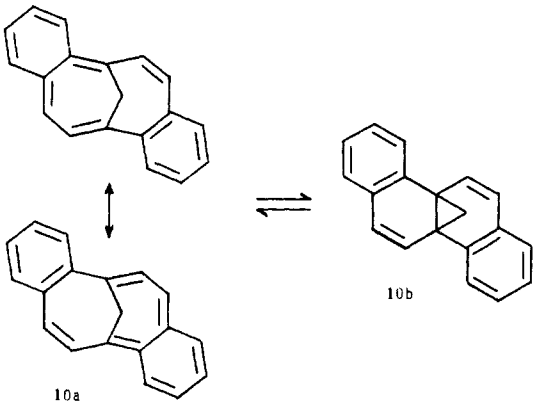
is minimized, and **8** might better be considered as a [22]annulene.

Scott et al. have shown that benzannelation reduces the paramagnetic ring current of a $4n$ annulene to about the same extent that it reduces the diamagnetic ring current of $4n + 2$ annulenes.[17]

Only one benzo derivative of **1** has been reported;[18] on the basis of its NMR spectrum hydrocarbon **9** retains an aromatic 10-membered ring, although the double bonds appear to be more localized than in **1** and the aromatic character is diminished.



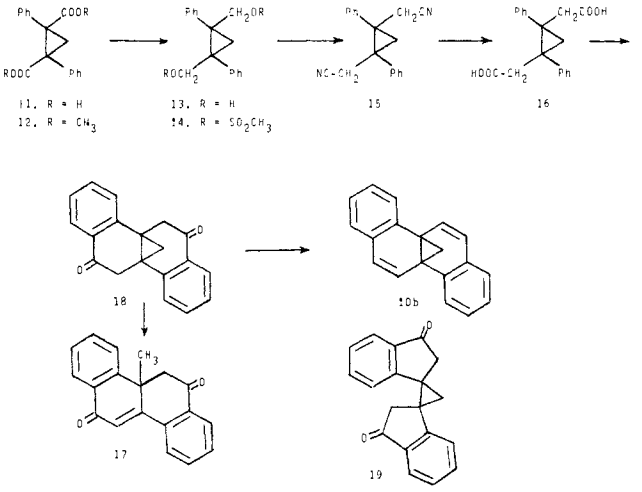
A critical case of the effect of benzannelation appeared to be the *anti*-dibenzo[10]annulene **10**. Structure **10a** contains a delocalized π system; it shares with anthracene the property of having three aromatic rings fused in such a fashion that Kekulé structures can be drawn in which *either*, but not *both*, of the terminal rings is benzenoid. Anthracene is a stable aromatic molecule despite



the limitation that all three rings cannot simultaneously be benzenoid, but compound **10a** has an option unavailable to anthracene: it can undergo valence tautomerization to **10b**. The question then arises as to which of the valence tautomers **10a** and **10b** should predominate. Structure **10a** retains the [10]annulene aromatic ring at the expense of losing the aromaticity of one of the benzene rings, while tautomer **10b** keeps the two benzene rings intact by sacrificing the aromaticity of the 10-membered ring. Intuitively, one might expect **10b** to be more stable, since the delocalization energy of **1** is less than that of benzene. However, like Mitchell's dibenzodihydropyrene **8**, tautomer **10a** has two equivalent Kekulé structures, reducing the localization effect of benzannelation, and might similarly retain most of the aromaticity of the large ring. This intriguing situation persuaded us to prepare compound **10** and determine the equilibrium structure.

Synthesis. We chose to attempt the preparation of **10** by a route that begins with an intact cyclopropane ring (Scheme I). The

Scheme I



starting material was the known *trans*-1,2-diphenylcyclopropane-1,2-dicarboxylic acid (**11**), prepared by the base-catalyzed condensation of ethyl atropate with ethyl α-chlorophenylacetate, followed by hydrolysis.[19] The cis and trans isomers produced in this synthesis can be separated by conversion of the *cis*-diacid to the soluble anhydride and filtration of the insoluble *trans*-diacid. The NMR spectra of the acids are diagnostic: the methylene hydrogens of the cis isomer are nonequivalent and appear as an AB quartet, while the corresponding protons of the trans isomer are magnetically equivalent and appear as a singlet.

Homologation of the trans diacid was achieved by hydride reduction of the dimethyl ester **12** to diol **13**, conversion to the bis(methanesulfonate) **14**, and displacement with cyanide ion to afford dinitrile **15**. The nitrile was recalcitrant to hydrolysis under usual conditions but could be converted with alkaline hydrogen peroxide, as recommended by Corey,[20] to *trans*-1,2-diphenylcyclopropane-1,2-diacetic acid (**16**).

Attempts to effect double intramolecular acylation with hot polyphosphoric acid (PPA) gave an unexpected product, a crystalline unsaturated diketone **17**, $C_{19}H_{14}O_2$. Two carbonyl bands were evident in the IR spectrum at 1720 and 1690 cm^{-1}, along with a conjugated alkene double bond at 1650 cm^{-1}. The NMR spectrum showed a methyl singlet at δ 1.5, a singlet for one vinyl proton at δ 6.95, and a doublet of doublets (δ 2.80 and 3.30) due to nonequivalent protons of a methylene group adjacent to a carbonyl. These data led to the assignment of structure **17**. A plausible mechanism for its formation is initial cyclization of **16** to the bis(tetralone) **18**, followed by ring opening in hot acid. The opening of the cyclopropane ring in acid solution to afford a new methyl group has close analogy in the work of Sims[21] and Mander.[22]

Repetition of the PPA ring closure of **16** *at room temperature* furnished a saturated diketone isomeric with **17**. Heating the new ketone (**18**) in PPA caused isomerization to **17**. The best conditions found for preparation of **18** involved cyclization of the bis(acid chloride) with $AlCl_3$, affording **18** in 45–67% yield.

It was, of course, conceivable that the intramolecular Friedel–Crafts acylation might have formed indanone rather than tetralone rings, leading to diketone **19** rather than **18**, though normally six-membered rings predominate in Friedel–Crafts acylations of this type.[23] Proton or carbon NMR spectroscopy cannot easily distinguish between these alternative structures, although the carbonyl infrared absorption band at 1670 cm^{-1} is in better accord with **18** (ν(tetralone) = 1680) rather than **19**

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(ν(indanone) = 1709). To settle this crucial question unambiguously, a single-crystal X-ray analysis was carried out. The structure, refined to an R factor of 0.044, confirmed the tetralone structure **18**. The central bond of the cyclopropane ring is somewhat longer (1.533 Å) than the other two bonds (1.509, 1.512 Å), and the mean planes of the two central rings are inclined at an angle of 15° to each other, relieving the crowding of the methano bridge.

Diketone **18** shows none of the character of an enol tautomer, which would be a dihydroxy derivative of **10**.

To complete the synthesis, **18** was reduced with sodium borohydride, and the mixture of diols was dehydrated with thionyl chloride. Alternatively, though in lower yield, the bis(tosylhydrazone) of **19** was subjected to Bamford–Stevens elimination with methyllithium.[24] The same crystalline hydrocarbon **10** was obtained by both routes.

Structure of 10. Compound **10** is a colorless hydrocarbon: mp 146.5–148 °C; m/z 242. The strong molecular ion and the absence of appreciable fragmentation in the mass spectrum are characteristic of aromatic compounds. The ultraviolet spectrum shows maxima at 280, 268, and 226 nm (ϵ 8700, 10 200, and 26 200, respectively). This spectrum bears little resemblance to that of **1**, chrysene, or any other polycyclic aromatic hydrocarbon and instead is more akin to the spectra of molecules with styrene chromophores, such as *o*-methylstyrene[25] and 1,2-dihydronaphthalene.[26]

In the ^{1}H NMR spectrum, the methylene protons appear as a singlet at δ 1.00. The bridging methylene protons of the [10]annulene **1** are shielded by the diamagnetic ring current and appear at δ −0.5; in the benzannulene **9** they appear at δ −0.06 and +1.38. Moreover, the vinyl protons of **10** appear as an AB quartet centered at δ 6.80, distinct from the benzene protons at δ 7.20–8.05. Consequently, the NMR spectrum is in better agreement with structure **10b**.

The most conclusive evidence for structure **10b** comes from the ^{13}C off-resonance decoupled NMR spectrum. Delocalized structure **10a** should show *nine* signals in the aromatic region and only *one* signal for saturated carbons. In annulene **1**, e.g., the bridgehead carbons appear at δ 114.6 and the bridging methylene at δ 34.8. Tautomer **10b**, on the other hand, would show *eight* signals for sp^2-hybridized carbons and *two* signals due to sp^3-hydridized carbons. The tricyclic tetraenes **3–5**, reasonably close models for **10b**, show ^{13}C signals[12,14] for the bridging carbon at δ 13.6–16.9 and for the bridgehead carbons at δ 54.5–81.7.

The ^{13}C NMR spectrum of **10** is unambiguous: it shows a total of *eight* signals in the region δ 122–136, only two of which are due to quaternary carbons, and *two* upfield signals at δ 20.1 (t, CH_2) and 34.3 (s, bridgehead). Only structure **10b** is consistent with these spectroscopic data. A variable-temperature NMR study was carried out to see whether any evidence of an equilibrium between tautomers **10a** and **10b** might be observed at higher temperature. In the temperature range 30–120 °C, however, no significant change in either the proton or ^{13}C spectrum was detected.

Discussion. This investigation has demonstrated that the 10-membered ring of 1,6-methano[10]annulene is forced to relinquish its aromaticity when fused to two benzene rings at positions such that both benzene rings cannot simultaneously be aromatic. While there are numerous previous examples in which benzannelation localizes bonds and reduces the diatropicity, this is the first instance in which an aromatic annulene loses its aromaticity completely upon benzannelation. In contrast to Mitchell's *anti*-dibenzoannulene **8**, the *anti*-dibenzoannulene **10a** does not retain the aromatic stability of the parent. The critical difference between these two cases is the ability of **10a** to form the more stable tautomer **10b**, with a new σ bond and two intact benzene rings.[27] The fragile aromaticity of 1,6-methano[10]annulene does not survive competition with that of a benzene ring.

Experimental Section

General Procedures. Melting points were taken on a Thomas oil immersion apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 257 and 297 instruments, using the 1601-cm^{-1} peak of polystyrene for calibration. Ultraviolet spectra were recorded by Dr. Charles Kutal on a Cary 14 spectrophotometer. Mass spectra were obtained by Courtney Pape on a Finnigan 4023 GC/MS instrument. Proton NMR spectra were run on Varian EM-190 and JEOL-FX 270 spectrometers, while the ^{13}C NMR spectra were obtained by Courtney Pape on a JEOL PFT-100 spectrometer. The variable-temperature NMR study was carried out on a Bruker WH-400 spectrometer at the NSF Regional NMR Center at the University of South Carolina. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

***trans*-1,2-Diphenylcyclopropane-1,2-dicarboxylic Acid (11).** A mixture of the cis and trans diethyl esters were prepared from the reaction of ethyl α-chlorophenylacetate and ethyl atropate as described by Bonavent et al.;[19] in 10 runs the average yield was 48%, the high yield 64%. After saponification, the crude acid was stirred with acetyl chloride for 3 days, cooled, filtered, and washed with cold $CHCl_3$ to give the crude trans acid, mp 245 °C (lit.[19] mp 270 °C). The average yield was 26%, the high yield, 36%.

Dimethyl Ester 12 was prepared by refluxing a solution of 10 g of the acid in 110 mL of CH_3OH and 5.8 mL of concentrated HCl for 2 days. The ester crystallized on cooling: 10.0 g (91%); mp 141–143 °C (lit.[19] mp 141 °C); NMR ($CDCl_3$) δ 2.55 (2 H, s), 3.35 (6 H, s), 7.5 (1 H, m).

***trans*-1,2-Diphenyl-1,2-bis(hydromethyl)cyclopropane (13).** A suspension of 3.3 g of $LiAlH_4$ in 300 mL of anhydrous ether was heated to gentle reflux in a Sohxlet apparatus containing 10.0 g of diester **12** in the thimble. After refluxing overnight, the solution was treated dropwise with saturated aqueous Na_2SO_4, followed by 2 g of solid $MgSO_4$, and then filtered. The solid salts were extracted overnight with ether in a Sohxlet apparatus, and the combined filtrate and extracts were concentrated, leaving diol **13** as colorless crystals: 8.14 g (99%); mp 141–143 °C; IR (KBr) 3560, 3480, 3030, 3010, 2980, 2940, 2890, 1600, 1500, 1020, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (2 H, br s), 1.45 (2 H, s), 3.15 (2 H, d, J = 11 Hz), 3.60 (2 H, d, J = 11 Hz), 7.45 (10 H, m); mass spectrum, m/z 252 (2), 237 (4), 219 (15), 205 (21), 137 (100), 119 (55), 105 (73), 92 (58), 77 (48). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.09. Found: C, 80.26; H, 7.17.

***trans*-1,2-Diphenyl-1,2-dicyanocyclopropane (15).** A mixture of 5.27 g of diol **13** and 7.64 g of methanesulfonyl chloride in 40 mL of dry acetone was cooled at 0 °C while 17.6 mL of dry pyridine was added slowly. The mixture was stirred 3 h at 0 °C and then overnight at room temperature. Cold water (25 mL) was added, and the mixture was extracted with $CHCl_3$. The extracts were washed with water, cold 2 N H_2SO_4, water, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated to a yellow only bis(mesylate) **14**.

Because of its limited stability, the bis(mesylate) was immediately mixed with 7.2 g of KCN, 0.1 g of KI, and 85 mL of DMF and stirred at 60–70 °C for 14 days. After cooling, 100 mL of water was added and the mixture was extracted with 1:1 ether/benzene. The extracts were washed with water, cold 2 N H_2SO_4, water, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated to leave an orange-yellow solid. Recrystallization from ethanol gave 2.11 g (37.4%) of the colorless dinitrile, mp 168–169.5 °C. The yield ranged from 30 to 49% over six runs: IR (KBr) 3060, 3030, 2930, 2240, 1600, 1560, 1500, 1450, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.6 (2 H, s), 2.05 (2 H, d, J = 16 Hz), 2.55 (2 H, d, J = 16 Hz), 7.4 (10 H, m); mass spectrum, m/z 272 (3), 245 (18), 231 (30), 205 (72), 191 (100), 154 (68), 115 (32), 103 (58), 77 (93), 63 (26), 51 (65), 39 (38).

***trans*-1,2-Diphenylcyclopropane-1,2-diacetic Acid (16).** A mixture of 1.96 g of dinitrile **15**, 27 mL of 30% aqueous KOH, 10 mL of 30% H_2O_2, and 37 mL of ethanol was stirred at reflux for 4 days, while a slow stream of N_2 was bubbled through the solution. After cooling, the mixture was washed with ether, acidified to pH 1 with concentrated HCl, and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated to leave a light yellow solid. Recrystallization from 5:1 benzene/$CHCl_3$ containing a little ethanol gave 0.92 g (41%) of colorless diacid, mp >240 °C. The average yield in six runs was 34%,

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(27) Calculations of resonance energies by the method of Herndon and Parkanyi[5] lead to values of 47 kcal/mol for **10a** and 40 kcal/mol for its valence tautomer **10b**. The difference of 7 kcal/mol is insufficient to compensate for the extra σ bond in **10b**, however, and the equilibrium is predicted to lie completely on the side of **10b**; Prof. W. C. Herndon, private communication.

with a high yield of 51%: IR (KBr) 3500–2500 (br), 1700, 1600, 1550, 1220, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.65 (2 H, s), 1.35 (2 H, d, J = 16 Hz), 2.60 (2 H, d, J = 16 Hz), 7.35 (10 H, m); mass spectrum, m/z 310 (1), 292 (14), 264 (21), 250 (27), 218 (12), 205 (100), 191 (64), 165 (8), 141 (12), 115 (23), 103 (30), 91 (34), 77 (44), 40 (82). Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.55; H, 5.81. Found: C, 73.50; H, 5.86.

2,3:7,8-Dibenzotricyclo[4.4.1.0^{1,6}]undecane-4,9-dione (18). (a) PPA Method. Diacid **16** (0.48 g) was thoroughly mixed with 31 g of PPA and kept at room temperature overnight protected from moisture. Crushed ice (70 g) was added, and the mixture was stirred until the pink color disappeared and then extracted with ether. The extracts were washed with water, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated to leave a yellow solid. Recrystallization from ether or ethanol gave the colorless diketone: mp 215–218 °C dec; 0.12 g (28.5%); IR (KBr) 3050, 3020, 2920, 2880, 1660, 1600, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (2 H, s), 3.15 (2 H, d, J = 18 Hz), 3.80 (2 H, d, J = 18 Hz), 7.30–8.15 (8 H, m); mass spectrum, m/z 274 (100), 259 (23), 246 (28), 231 (43), 215 (38) 202 (57), 189 (18), 144 (52), 131 (64), 115 (80), 102 (74), 89 (46), 76 (67), 63 (55), 51 (63), 39 (72). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.21; H, 5.11. Found: C, 82.48; H, 5.20.

(b) $AlCl_3$ Method. A mixture of 0.22 g of diacid **16** and 2.5 mL of $SOCl_2$ (purified by successive distillation from quinoline and linseed oil) was heated with stirring to about 60 °C, stirred overnight at 25 °C, and concentrated at aspirator vacuum. The residual acid chloride was taken up in 11 mL of CH_2Cl_2 and added to a suspension of 0.25 g of $AlCl_3$ in 8 mL of CH_2Cl_2, cooled in an ice bath. After being stirred for 1 h at 0 °C, the mixture was poured into 40 mL of ice–water and extracted with ether. The extracts were washed with water, 10% Na_2CO_3, and brine, dried over $MgSO_4$, and concentrated. The crude yellow solid was recrystallized from ethanol (1 mL/mg), giving 0.13 g (67%) of colorless diketone, mp 213–215 °C dec.

1-Methyl-2,3:1,8-Dibenzobicyclo[4.4.0^{1,6}]dec-5-ene-4,9-dione (17). Diacid **16** (0.40 g) was thoroughly mixed with 54.5 g of PPA and heated slowly to 105–110 °C with stirring. After 30 min at this temperature, 50 g of crushed ice was added and the mixture was stirred until homogeneous, neutralized to pH 8 with solid $NaHCO_3$ and 30% KOH, and extracted with ether. The extracts were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The oily residue was recrystallized from ether to afford 0.07 g (20%) of colorless solid: mp 146–147 °C; IR (KBr) 3030, 2950, 2920, 2850, 1720, 1690, 1650, 1600, 1450, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.5 (3 H, s), 2.80 (1 H, d, J = 15 Hz), 3.30 (1 H, d, J = 15 Hz), 6.95 (1 H, s), 7.2–8.3 (8 H, m); mass spectrum, m/z 274 (54), 259 (54), 245 (10), 231 (63), 215 (25), 202 (100), 115 (45), 101 (87), 88 (25), 75 (42), 63 (28), 51 (44), 39 (40). Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.21; H, 5.11. Found: C, 83.16; H, 5.16.

2,3:7,8-Dibenzotricyclo[4.4.1.0^{1,6}]undecane-4,9-diene (10b). (a) Via Diol. Sodium borohydride (0.4 g) was added in four portions over 2 days to a refluxing solution of 0.25 g of diketone **18** in 100 mL of ethanol. Methanol (25 mL) was added and reflux continued 1 h. The mixture was brought to pH 7 with concentrated HCl and concentrated, and the residue was taken up in 75 mL of water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The crude diol, which showed no carbonyl absorption at 1670 cm^{-1}, was dried under vacuum, taken up in 9 mL of pyridine, and cooled in ice, while 2.3 mL of $SOCl_2$ was slowly added. The mixture was stirred at 0 °C for 4 h, poured onto 50 g of crushed ice, and extracted with ether. The extracts were washed with water, cold 2 N H_2SO_4, water, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated to leave a yellow solid. This was chromatographed in hexane, first over silica gel, then alumina, to give a colorless solid contaminated by a small amount of yellow oil. The solid was sublimed at 120–135 °C (0.905 mm) and then recrystallized twice from ethanol to give 50 mg of colorless solid: mp 146.5–148 °C; IR (KBr) 3020, 2970, 2910, 1470, 1450, 750 cm^{-1}; UV (cyclohexane) 226 nm (ϵ 26 200), 268 (10 200), 280 (8 700); ^1H NMR ($CDCl_3$) δ 1.00 (2 H, s), 6.45 (2 H, d, J = 9 Hz), 7.10 (2 H, d, J = 9 Hz), 7.20–8.05 (8 H, m); ^{13}C NMR ($CDCl_3$) δ 20.1 (t), 34.3 (s), 122.3 (d), 124.2 (d), 124.9 (d), 126.5 (d), 127.6 (d) (double intensity), 128.9 (s), 135.9 (s); mass spectrum, m/z 242 (100), 228 (7), 226 (19), 215 (23), 200 (5), 189 (6), 163 (6), 139 (5), 119.4 (47), 106.4 (19), 94.4 (16), 87 (9), 74 (10), 63 (18) 39 (27). Anal. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 93.97; H, 5.95.

(b) Via Tosylhydrazone. A mixture of 0.12 g of diketone **18** and 0.17 g of (*p*-tolylsulfonyl)hydrazine in 35 mL of 7:3 CH_3OH/H_2O was heated under reflux for 4 days, cooled, and filtered. The yellow precipitate showed carbonyl absorption at 1670 cm^{-1} and was heated with 0.3 g of (*p*-tolylsulfonyl)hydrazine in 11 mL of 90% aqueous methanol at reflux for 3 days more. The fine yellow solid that precipitated on cooling was washed with cold 60% aqueous methanol: 0.08 g (30%); IR (KBr) 3180, 3060–3020, 2950–2900, 1600, 1310, 1150, 850, 740 cm^{-1}.

A solution of the crude bis(tosylhydrazone) in 5 mL of ether was treated with 4.5 mL of a 1.75 M solution of methyllithium in ether and stirred at 25 °C for 2 days. After 20 mL of water was added dropwise, the mixture was extracted with ether. The extracts were washed with 2 N H_2SO_4, water, and saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The solid residue was recrystallized from hexane to give 15 mg of **10b**, with an IR spectrum identical with that of the product from part (a).

X-ray Crystallography. Colorless prisms of **18** were grown by slow recrystallization from ethanol. Diffraction measurements were made with a Nonius CAD-4 diffractometer. The best E map gave a fragment that appeared consistent with the predicted molecular structure, but the model did not refine. The problem was solved by the usual technique of treating the space group as $P1$, whereupon a second image was generated that defined the position of the center of symmetry. The true molecular position was only about 0.6 Å from that given by the first E map. Standard sequences of least-squares refinement and difference maps allowed the positioning of all atoms including H. The structure refined to an R factor of 4.4%. Atomic parameters are given in Tables II and III, a stereoscopic drawing is shown in Figure 1, and the final crystal conformation and bond lengths are given in Figure 2 (supplementary material).

Principal computer programs employed are listed in ref 28.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic bond distances, bond angles, and crystal and refinement data, a stereoscopic drawing (Figure 1), and crystal conformation and bond lengths (Figure 2) (6 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

(28) (a) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, Universities of York and Louvain, 1978. (b) Scattering factors, Stewart, J. M.; Kruger, G. J.; Ammon, H. L.; Dickinson, C.; Hall, S. R. *XRAY system*, version of June 1972, Technical Report TR-192, University of Maryland. (c) Weights, Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70.