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How Aromatic Are the Benzene Rings in Biphenylene? The Synthesis and NMR Properties of a Biphenyleno Fused Dihydropyrene

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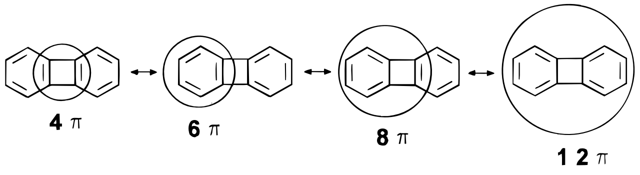
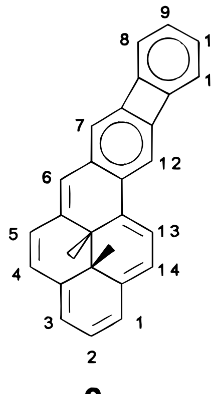
Abstract: The synthesis of the biphenylene fused dihydropyrene **2** is described by cycloaddition of dibromobenzocyclobutadiene with the oxa[17]annulene **3** and deoxygenation of the adduct with Ti(0). Analysis of the NMR data indicates that biphenylene has about 55% of the relative bond fixing ability of benzene, which is equated to relative aromaticity. The experimentally determined Dewar resonance energy is 1.59 times that of benzene, while Dewar calculates 1.55 times benzene.

Biphenylene (**1**) is one of the more interesting aromatic hydrocarbons because it contains the skeletons of the prototypes of both "aromatic" and "anti-aromatic" hydrocarbons, benzene and cyclobutadiene. Within biphenylene can be seen 4π, 6π, 8π, and 12π circuits:



1

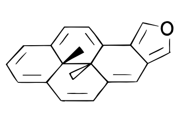
and thus the overall aromaticity is not obvious. Indeed, estimates of the resonance energy of biphenylene relative to that of benzene, range from 0.43 to 1.78 in the literature.[1] We were thus interested in applying our recently developed method[2] of estimating the resonance energies of "aromatics" from analysis of the NMR data of "aromatic"-fused dihydropyrenes, to obtain an experimental comparison of **1** with benzene. This would require the synthesis of the biphenylene fused dimethyldihydropyrene **2**. We present here the synthesis of **2** and a comparison of the relative aromaticity of **1** with benzene.



2

Syntheses

The most expedient synthesis of **2** appeared to be from the isofuran **3** via a Diels−Alder reaction with *in situ* generated benzocyclobutadiene by following the general procedure developed by Cava.[3] Indeed, reaction of **3**[2] with a large excess of 1,2-dibromobenzocyclobutene and zinc dust at 40 °C gave a 46% yield of the expected adduct **4** as a mixture of two isomers, **4a**,**b**. The gross structure of **4** followed from the mass spectrum molecular ion and elemental analysis, while the assignment of both isomers as *exo* followed from the lack of coupling between H-7 and H-8 (close to orthogonal), whereas the *endo* isomers would have shown a coupling of about 7 Hz. By integration of the methyl signals at δ −4.06, −4.11, and −4.08, −4.13, or the signals due to H-7 or H-14, the ratio of the two isomers was found to be 2:3, but assignment of which is not possible. The very similar values found for these methyl proton shifts also ruled out formation of *endo* isomers because, in these isomers, *one* of the internal methyl groups would have been strongly shielded by the ring current of the adjacent benzene ring. The dehydration of adduct **4** was then attempted under a



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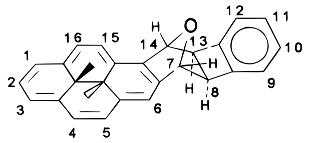
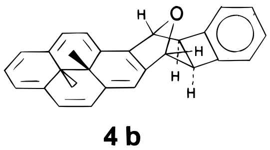


4 a



4 b

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.

[1] See, for example: (a) Dewar, M. J. S.; De Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789−795. (b) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305−310. (c) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750−2758. (d) Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692−1704. (e) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344−1348. (f) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371−7379. (g) Moyano, A.; Paniagua, J. C. *J. Org. Chem.* **1991**, *56*, 1858−1866. (h) Trinajstic, N.; Schmalz, T. G.; Zivkovic, T. P.; Nikolic, S.; Klein, D. J.; Seitz, W. A. *New J. Chem.* **1991**, *15*, 27−31. (i) Behrens, S.; Koster, A. M.; Jug, K. *J. Org. Chem.* **1994**, *59*, 2546−2551. (j) Maksic, Z. B.; Kovacek, D.; Eckert-Maksic, M.; Bockmann, M.; Klessinger, M. *J. Phys. Chem.* **1995**, *99*, 6410−6416.

[2] Mitchell, R. H.; Iyer, V. S.; Khalifa, N.; Mahadevan, R.; Venugopalan, S.; Weerawarna, S. A.; Zhou, P. *J. Am. Chem. Soc.* **1995**, *117*, 1514−1532.

[3] Cava, M. P.; Pohlke, R. *J. Am. Chem. Soc.* **1962**, *87*, 1564−1567. Cava, M. P.; Narasimhan, K. *J. Org. Chem.* **1971**, *36*, 1419−1423.

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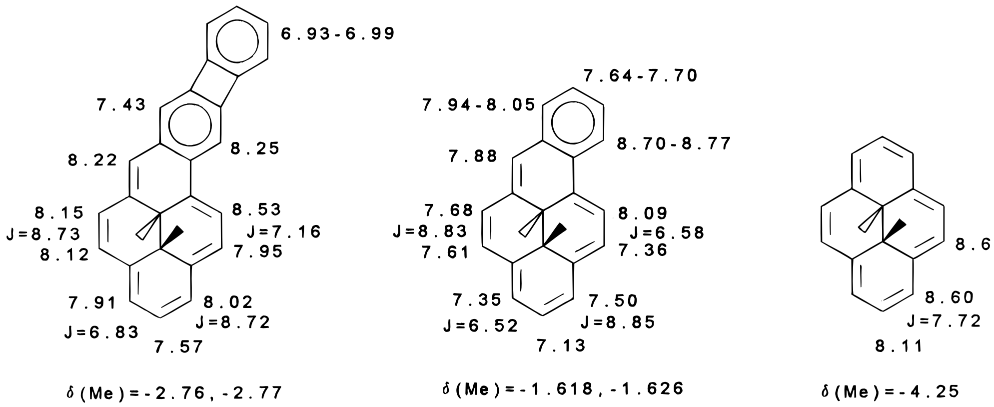
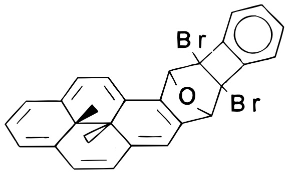


2 **6** **7**

Figure 1. Proton chemical shift (δ) and coupling constant (Hz) data for **2**, **6**, and **7**.

variety of conditions (HCl/AcOH; HCl/PhH; H_2F_2; HI/PhH; $TiCl_4$/THF; $SnCl_4$/THF; $BF_3 \cdot OEt_2$; Al_2O_3/PhH; Nafion-H), but <1% of the desired annulene **2** could be isolated in each case. An alternate strategy was tried. Reaction of **3** with 1,1,2,2-tetrabromobenzocyclobutene and zinc dust yielded 41% of the dibromoadduct **5**, again as a mixture of two isomers in a 2:3 ratio. The internal methyl protons appeared at δ −4.00 and −4.04, −4.01, and −4.03 in a 3:2 ratio, indicating only *exo*-isomer formation. The gross structure was confirmed by ms and elemental analysis. In this case, use of acid could be avoided by treatment of **5** with low-valent titanium generated from $TiCl_4$−Zn, and then 30% of the desired biphenylene-fused annulene **2** was obtained. It is interesting that titanium species generated by other methods failed. The biphenylene **2** was obtained as dark red needles, mp 190 °C, giving satisfactory elemental analysis and a strong molecular ion in its mass spectrum, with successive loss of the two internal methyl groups to give the pyrene, characteristic of most dimethyldihydropyrenes. The ^{13}C NMR spectrum gave the expected 24 aromatic carbon peaks and two internal bridge carbon, and two internal methyl carbon peaks. The ^1H NMR spectrum showed the internal methyl protons at δ −2.76 and −2.77. All the external dihydropyrene protons could be assigned using COSY and NOESY spectra.



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Discussion of the NMR Data

The relevant ^1H shift and coupling constant data for **2**, the benzannulene **6**, and the parent **7** are shown in Figure 1. Comparison of the vicinal coupling constants $^3J_{4,5}$ and $^3J_{13,14}$ or of $^3J_{1,2}$ and $^3J_{2,3}$ of **2** with the corresponding values for **6** immediately indicates that the macrocyclic ring of **2** is less bond alternating than that of **6**, and thus biphenylene is less able to bond fix the [14]annulene ring than is benzene, indicating it is less aromatic. A quantitative estimate of the relative bond fixing ability and hence relative aromaticity[2] (RA) can be obtained from the chemical shift data for the internal methyl protons and the most distant protons, H-2.

The change in ring current on going from **7** to **6** divided by the change in ring current on going from **7** to **2** gives the relative aromaticity (RA) of biphenylene to benzene:

$$\mathrm{RA} = \frac{-2.765 - (-4.25)}{-1.62 - (-4.25)} \quad \text{or} \quad \frac{7.57 - 8.11}{7.13 - 8.11}$$
$$= 56\% \qquad\qquad = 55\%$$

Thus biphenylene is about one-half as aromatic as benzene as judged by its relative ability to bond fix the dihydropyrene. Note that the two values are consistent, indicating that the ring current is the primary driver of chemical shift change and that the biphenylene does not affect the periphery protons in a way different from the internal methyl protons. The shifts found for the internal methyl protons and H-2 are thus consistent with the relationship equation derived in other benzenoid systems.[4] Even when the relative aromaticity comparison is carried out using the shift for H-6 instead of H-2, a relative aromaticity of 53% is obtained. This indicates that the through-space effect of the biphenylene annelating ring is rather small, which is also supported by comparison of H-3 with H-6, which would otherwise have the same chemical shift. The bay protons, H-12 and H-13, are deshielded because of steric compression. The reduction of aromaticity in the annelating biphenylene ring of **2** relative to the analogous benzene ring of **6** can also be readily seen. Despite the fact that the [14]annulene ring current in **2** is larger than in **6**, the benzene protons in **6** are all more deshielded than the biphenylene protons in **2**. The more shielded biphenylene protons reflect both the reduced aromaticity in the individual ring and any paratropic ring currents. Scott[5] has shown that fusion of a [4*n*]annulene and a [4*n*+2]annulene induces bond fixation in each, and that for benzannelation a [4*n*] and [4*n* + 2]annulene are affected similarly. Thus, the fact that we are attempting to measure a partially diatropic, partially paratropic system, i.e. **1**, will not invalidate the results, which will reflect the total effect of fusing **1** to **7**. Separation of the effects of the diatropic and paratropic parts of **1** is however not trivial.

The (Dewar) resonance energy of biphenylene can also be estimated by using the relationship[2] derived between the relative aromaticity determined above, RA, and the bond localization energy (BLE relative to benzene) of the annelating aromatic:

$$\mathrm{RA} = 0.978(\mathrm{BLE}) + 0.04$$

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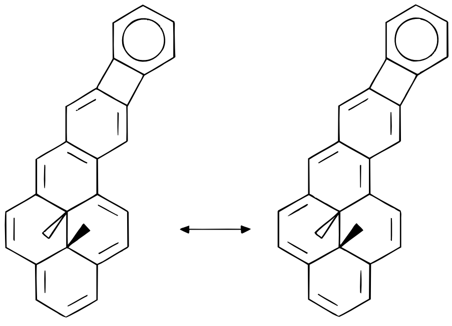
(4) δ(Me) = 17.515 − 2.685δ(H-2) (see ref 2). Insertion of δ 7.57 for δ(H-2) leads to a value of δ −2.81 expected for δ(Me), in excellent agreement with that found, δ −2.765.

(5) Scott, L. T.; Kirms, M. A.; Gunther, H.; von Puttkamer, H. *J. Am. Chem. Soc.* **1983**, *105*, 1372−1373.

from which BLE for biphenylene = 0.588(BLE for benzene). Consideration of the Kekulé structures **6A**,**B** indicates that the distant benzene ring can delocalize independently in both structures **6A** and **6B**, which together delocalize the [14]-annulene ring. Thus, to obtain the RE of biphenylene, one benzene unit must be added to the BLE determined above, and so the experimental RE of biphenylene is determined to be 1.588 benzene units (or 1.588 times the RE for benzene). Dewar[1a] gives the RE of benzene as 0.869 eV and of biphenylene as 1.346 eV, and thus, biphenylene is 1.55 benzene units, in amazingly good agreement with our experimental value. Moyano[1g] reports global REPE values of 0.064β for benzene and 0.035β for biphenylene, suggesting that on average the value for biphenylene is 55% of the value for benzene, again agreeing amazingly well with the experimental relative aromaticity of 55% determined above. Trinajstic's conjugated circuit model[1h] predicts 50%, while the Hess and Schaad approach[1b] predicts 41%. Parr's hardness approach[1f] predicts 45%, and Jug's bond-order approach[1e,i] predicts 67−76%. All in not bad agreement with our experimental approach.



6A **6B**

While ^{13}C shifts do not give data that can be used quite as reliably as protons, the same trends are evident. The bridge carbons for **7**, **2**, and **6** appear at δ 30.0, 33.6, and 33.9 and 35.5 and 36.0, respectively, while the internal methyl carbons appear at δ 14.0, 16.1, and 16.2 and 17.0 and 17.7, respectively, which using the RA equation derived above (for protons) yields about 65% as the relative aromaticity of biphenylene relative to benzene based on carbon shift data. This is fairly good agreement considering the ring current effect for carbon is the same magnitude as for protons, yet in general, shifts for carbon are of much wider range.

Conclusions

The aromaticity of biphenylene relative to benzene has been determined to be about 55% based on the relative bond fixing ability of the two aromatic systems. This agrees quite well with their relative global resonance energy per electron predictions. The Dewar resonance energy of biphenylene is estimated from chemical shift data to be 1.59 times the DRE of benzene, while Dewar's calculations predict 1.55. This suggests that this method of estimating Dewar resonance energies is valid even though biphenylene contains [4*n*] circuits.

Experimental Section

Melting points were determined on a Reichert 7905 melting point apparatus integrated to a chrome−alumel thermocouple. Infrared spectra, major peaks only, calibrated with polystyrene, were recorded on a Bruker IFS25 FT-IR or on a Perkin-Elmer 283 spectrometer as KBr disks unless otherwise stated. Ultraviolet−visible spectra were recorded on a Cary 5 or a Perkin-Elmer Lambda-4B spectrometer in cyclohexane. Proton NMR spectra were recorded at 250 MHz on a Bruker WM 250 or at 360 MHz on a Bruker AMX 360 using $CDCl_3$ as the solvent and either TMS as the internal standard or the $CHCl_3$ peak at 7.24 ppm. Carbon NMR spectra were recorded at 62.9 or 90.6 MHz in $CDCl_3$, using the solvent peak at 77.0 ppm for calibration. Mass spectra were recorded on a Finnigan 3300 gas chromatography−mass spectrometer using methane gas for chemical ionization (CI) or electron impact (EI) at 70 eV. Exact mass measurements used a Perkin-Elmer-Hitachi RMU-6E or a Kratos Concept-H instrument with perfluorokerosene as the calibrant. Elemental analyses were carried out by Canadian Microanalytical Services Ltd, Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, and all organic extracts were washed with water and dried over anhydrous $MgSO_4$, Na_2SO_4, or K_2CO_3 as appropriate. SiGel refers to Merck Silica Gel, 70-230 mesh. PE refers to distilled petroleum ether, bp 30−60 °C.

Benzocyclobutadiene Adducts of Furan 3: 4a,b. Zinc dust (1 g, large excess) was added in one portion to a solution of 1,2-dibromobenzocyclobutene[3] (0.600 g, 2.3 mmol) and the oxa[17]-annulene[2] **3** (0.200 g, 0.73 mmol) in dry THF (50 mL). The mixture was then heated to 40 °C with magnetic stirring under argon. After 12 h, the mixture was cooled to room temperature, and then inorganic solids were removed by filtration and the filtrate was concentrated. The crude product was chromatographed over SiGel and eluted with 9:1 pentane:ether to give a mixture of the olive green exoadducts **4a**,**b** (0.125 g, 46%). ^{1}H NMR (250 MHz): δ 8.65 and 8.64 (s, 1H total, H-6), 8.60−8.49 (m, 6H, H-1,3,4,5,15,16), 8.06−7.99 (m, 1H, H-2), 7.37−7.26 (m, 4H, H-9,10,11,12), 6.26 and 6.25 (s, 1H total 2:3 ratio, H-14), 5.88 and 5.82, (s, 1H total 3:2 ratio, H-7), 3.60 and 3.44 (d, 1H each, J = 3.7 Hz, H-8,13), −4.06, −4.11 and −4.08, −4.13 (s, 6H total 2:3 ratio, internal $-CH_3$) ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 141.6, 137.2, 136.8, 128.4, 127.3, 124.6, 124.5, 123.8, 123.3, 123.1, 122.5, 122.4, 119.6, 115.7, 80.5, 78.2, 52.6, 51.1, 31.9, 30.9, 14.5, 14.4. CI MS, *m/z* 375 (MH^+). Anal. Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.38; H, 5.88.

Attempted Dehydration of the *Exo* Adducts 4a,b. As detailed in the following table, an acid (0.1 mmol) in solvent (1 mL) was added to exo adducts **4a/4b** (10 mg) at the stated temperature. The runs were conducted until some change in the starting material occurred (monitored by TLC). All the attempted reactions led to extensive decomposition of the starting material and only trace formation of product **2**, which was identified from its internal methyl signals at δ −2.77.

Table 1

no.	temp, °C	solvent	acid
1	0−25	AcOH	36%HCl
2	0−25	benzene	HCl (gas)
3	−50−25	none	H_2F_2 (liquid)
4	−10−25	benzene	47% HI
5	−10−25	AcOH	HCl (gas)
6	−10−50	THF	$TiCl_4$
7	−10−50	THF	$SnCl_4$
8	0−25	Et_2O	$BF_3{\cdot}Et_2O$
9	80	benzene	Al_2O_3
10	25−55	CH_2Cl_2	Nafion-H
11	25	benzene	Nafion-H, light

1,1,2,2-Tetrabromobenzocyclobutene. The mixture of 1,2-dibromobenzocyclobutenes obtained by the procedure of Cava and co-workers[3] was purified (*this is essential*) according to the procedure of Barton and co-workers.[6] NBS (17.80 g, 0.1 mol) and propylene carbonate (10 mL) were added to the dibromide thus obtained (5.62 g, 20 mmol) in CCl_4 (100 mL), and then AIBN (∼10 mg, catalyst) was added to the mixture, which was then refluxed with good stirring and irradiation with two 250 W sunlamps for 12 h. The mixture was cooled to 25 °C and filtered under suction. The residue was washed with dichloromethane (50 mL), and the combined filtrates were washed well with water, 10% sodium bisulfite, then saturated aqueous NaCl, and then were dried and evaporated to leave an orange oil. Trituration of this oil with pentane gave white cubic crystals of product, 5.44 g (60%),

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[6] Barton, J. W.; Shepherd, M. K.; Willis, R. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 967−971.

mp 117−118 °C (lit.[3] mp 117−118 °C). ^{1}H NMR (250 MHz): δ 7.64−7.51 (m, 2H), 7.34−7.29 (m, 2H).

Dibromobenzocyclobutene Adduct 5. Zinc dust (1 g, large excess) was added to a solution of the oxa[17]annulene **3** (200 mg, 0.73 mmol) and the tetrabromide from above (600 mg, 1.4 mmol) in dry THF (50 mL). The mixture was stirred at 40 °C under argon. After 6 h, an additional amount of the tetrabromide (600 mg, 1.4 mmol) was added and the reaction continued for another 6 h. The reaction mixture was cooled to 25 °C and filtered. The solid residue was washed with diethyl ether (50 mL), and the combined filtrates were evaporated to give a green residue which was chromatographed on SiGel, with pentane: ether (9:1) as the eluant, and gave the green adduct **5**, 159 mg (41%) as two isomers in a 2:3 ratio. ^{1}H NMR (250 MHz): δ 8.77−8.54 (m, 7H, H-1,3,4,5,6,13,14), 8.07 and 8.06 (two t, 1H total, H-2), 7.55−7.36 (m, 4H, H-8,9,10,11), 6.34 and 6.32 (s, 1H total 2:3 ratio, H-7), 5.90 and 5.89 (s, 1H total 3:2 ratio, H-14), −4.00 and −4.04, −4.01 and −4.03, (s, 6H total 3:2 ratio, $-CH_3$). ^{13}C NMR (62.9 MHz): δ 142.6, 142.2, 137.9, 137.7, 137.6, 136.9, 136.8, 136.0, 134.4, 132.4, 131.4, 131.0, 130.7, 129.7, 129.4, 129.3, 128.6, 126.1, 125.5, 125.0, 124.8, 124.0, 123.9, 123.7, 123.5, 123.3, 122.7, 121.7, 121.6, 121.0, 120.6, 119.3, 118.2, 116.5, 91.5, 89.4, 84.7, 84.0, 82.2, 82.0, 71.4, 71.3, 71.1, 70.6, 66.4, 65.6, 33.6, 31.8, 31.6, 30.8, 29.7, 29.0, 28.7, 14.4 (broad). EI MS: *m/z* 534, 532, 530 (1:2:1, M$^+$). IR 927, 852, 751, 664, 613 cm^{-1}. UV λ_{max} nm (ϵ_{max}): 342 (84 000), 380 (39 000), 473 (9500). Anal. Calcd for $C_{28}H_{20}Br_2O$: C, 63.18; H, 3.79. Found: C, 62.98; H, 3.79. HRMS: calcd for $C_{28}H_{20}{}^{81}Br_2O$ 533.9842, found 533.9870.

***trans*-14b,14c-Dimethyl-14b,14,c-dihydrobenzo[1′,2′:3,4]cyclobuta[1,2-*b*]naphtho[2,1,8-*fgh*]anthracene (2).** $TiCl_4$ (0.5 mL, 4.5 mmol) was injected by syringe into a stirred suspension of zinc dust (2 g, large excess) in dry THF (20 mL) under argon at room temperature. After the mixture was stirred for 3 h at 25 °C (the suspension was dark green in color), the solid dibromide **5** (100 mg, 0.18 mmol) was added at once to the suspension and the stirring was continued for an additional 4 h. The reaction was then quenched with ice−water (10 mL). Diethyl ether (50 mL) was added and the organic layer separated off. The ether layer was washed with saturated $NaHCO_3$ and saturated NaCl and was then dried and evaporated to leave a dark red residue. This residue was taken up in pentane (50 mL) and filtered through SiGel (5 g). The pentane solution after evaporation and recrystallization from pentane gave dark-red (almost black) crystals of **2**, 20 mg (31%), mp 190 °C. ^{1}H NMR (360 MHz): δ 8.53 (d, 1H, J = 7.16 Hz, H-13), 8.25 (s, 1H, H-12), 8.22 (s, 1H, H-6), 8.15 and 8.12 (d, 1H each, J = 8.73 Hz, H-4, H-5), 8.02 (d, 1H, J = 8.72 Hz, H-1), 7.95 (d, 1H, J = 7.16 Hz, H-14), 7.91 (d, 1H, J = 6.83 Hz, H-3), 7.57 (dd, 1H, H-2), 7.43 (s, 1H, H-7), 6.99−6.93 (m, 4H, H-8,9,10,11), −2.76, −2.77 (s, 3H each, $-CH_3$) (the COSY spectrum indicated a small coupling between H-7 and H-6 and H-12). ^{13}C NMR (90.6 MHz): δ 151.7, 151.5, 149.0, 148.7 (quat. C in biph), 138.6, 138.5 (quat. C in biph-DHP junction), 136.5, 134.0, 131.0, 128.8 (quart. C in DHP), 129.8 and 129.7 (C-9,10), 125.9 (C-5), 125.6 (C-4), 125.3 (C-1), 124.8 (C-6), 123.9 (C-2), 122.9 (C-3), 122.3 (C-14), 119.4 and 119.2 (C-8,11), 117.9 (C-13), 117.7 (C-7), 111.9 (C-12), 34.0, 33.7 (bridge quat.), 16.3, 16.2 (internal $-CH_3$). EI MS: *m/z* 356 (M$^+$). UV [λ_{max} nm (ϵ)]: 526 (32 000), 435 sh (35 000), 394 (160 000), 370 sh (122 000), 342 (65 000), 327 sh (43 000), 272 (56 000). Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 93.93; H, 5.65. HRMS: calcd for $C_{28}H_{20}$ 356.1565, found: 356.1594.

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