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Bis(heterocumulenes) Derived from the 1,4-Diphenyl-1,3-butadiyne Framework. Synthesis of Three New Classes of Axially Chiral Biheteroaryls

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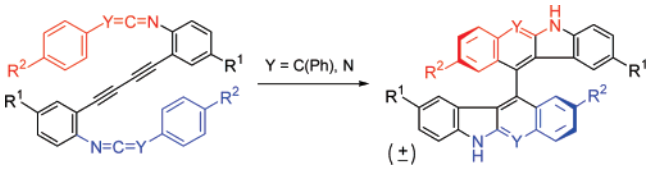

Bis(ketenimines) and bis(carbodiimides) derived from 1,4-bis(2-aminophenyl)-1,3-butadiynes via two independent biradical cyclizations provided, respectively, axially chiral bis(benzocarbazoles) and bis(quinindolines). Mixed biheteroaryls, consisting of benzocarbazole and quinindoline units, have been also prepared by a slightly modified strategy.

Compounds containing conjugated 1,3-butadiyne structures are somewhat amazingly found in nature.[1] This structural motif is also frequently encountered in acetylenic oligomers and polymers,[2] macrocycles,[3] and supramolecular structures,[4] some of them with applications in the area of new molecular materials. Moreover, butadiynes are of great interest in organic synthesis as carbon-rich building blocks and also as key structural moieties in the preparation of either intermediate in natural product synthesis, in which the 1,3-butadiyne functional group undergoes a transformation to another function[5] or remains as such,[6] or complex cyclic frameworks.[7]

Functionalized 2-alkynylanilines are accessible compounds which have found recent applications in heterocyclic chemistry, mainly as precursors of indoles. Thus, the metal-catalyzed intramolecular hydroamination of 2-alkynylanilines represents a useful synthesis of this class of heterocycles.[8] 2-Alkynylanilines have been also converted by standard chemistry into *N*-[2-(1-alkynyl)phenyl]ketenimines **1** [Y = C(R)] and *N*-[2-(1-alkynyl)phenyl]-*N*′-arylcarbodiimides **1** (Y = N) which proceed via thermal and photochemical biradical cyclization to produce, respectively, benzocarbazoles **3** and quinindolines **4** (Scheme 1).[9]

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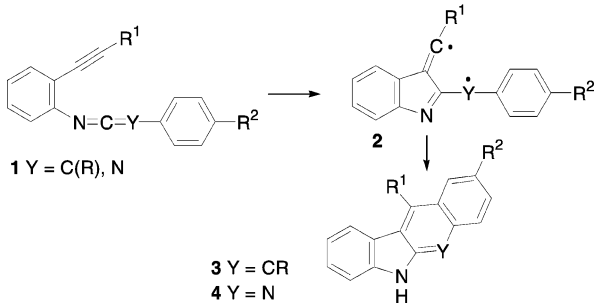
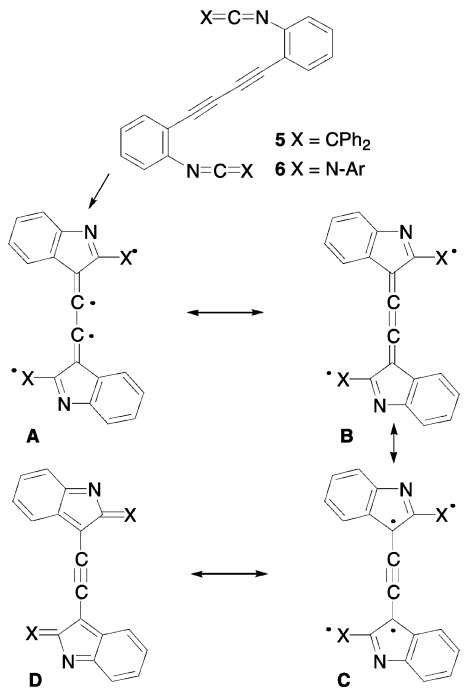
SCHEME 1. Biradical Cyclization of Alkynylketenimines and Alkynylcarbodiimides



SCHEME 2. Presumed Cyclization Mode of Bis(ketenimines) 5 and Bis(carbodiimides) 6



The attractiveness of combining two 2-alkynylaniline units in a conjugated diyne, that is, the use of 1,4-bis(2-aminophenyl)-1,3-butadiynes as reagents, has been implemented in a reduced number of investigations, directed either to polymerization studies[10] or to the synthesis of 2,2′-bisindoles.[8b,11]

For years, one of our research topics has been the study of the reactivity of ketenimines.[12] The rich and fascinating chemistry of this type of heterocumulenes led us now to focus our attention on the preparation of bis(ketenimines) and the study of their chemical behavior.[13] Thus, we envisaged the application of the thermal biradical cyclization shown in Scheme 1 to bis(ketenimines) built on a conjugated 1,3-butadiyne unit, such as compounds **5** (Scheme 2), derived from 1,4-bis(2-aminophenyl)-1,3-butadiynes.[14] For this particular skeleton we also considered of interest the extension of this investigation to bis(carbodiimides) **6**.

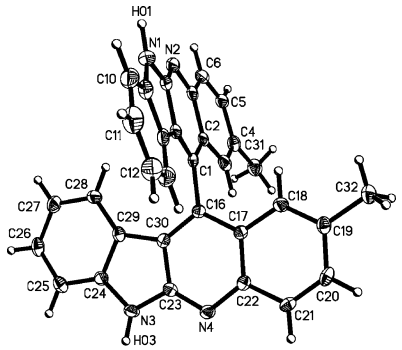


FIGURE 1. X-ray structure of compound **11a**.

We were intrigued by the nature of the reaction products that could result from the cyclization of these bis(heterocumulenes) **5** and **6**. It was conceivable that they could experiment a simultaneous biradical cyclization of the two enyne−ketenimine or enyne−carbodiimide fragments leading to the putative tetraradicaloid intermediate **A** (Scheme 2), which could drive the reaction course either to the initially predictable bis(benzocarbazoles) and bis(quinindolines), via double-radical coupling of **A**, or to other products of different nature. As shown in Scheme 2, the resonance hybrid of **A** may be contributed also by other canonical forms, such as a second tetraradicaloid **C,** the butatriene diradical **B**,[15] and even a neutral bis(3,3′-indolyl)alkyne **D**. Whereas the predictable biheteroaryls could form via tetraradical **A**, the contribution of forms **B**−**D** perhaps allows the formation of additional products, for instance those in which the two indolyl moieties of these structures become linked by additional new bonds between atoms of their X fragments, others resulting from intermolecular couplings, or even the proper 1,2-bis(3,3′-indolyl)acetylene **D**.

The new symmetrical diaminodiyne **8b** ($R^1 = CH_3$) was prepared via dimerization of 2-ethynyl-4-methylaniline (**7b)** in the presence of Cu(II) acetate. Treatment of compounds **8a** ($R^1 = H$)[8b] and **8b** with triphenylphosphine, carbon tetrachloride, and triethylamine, in acetonitrile solution, provided bis(iminophosphoranes) **9**. The classical aza-Wittig reaction of **9** with 2 equiv of diphenylketene, in toluene solution at 50 °C, was used for the synthesis of bis(ketenimines) **5**. Cyclization reaction of bis(ketenimines) **5** took place under the above reaction conditions resulting in the exclusive formation of the respective bis(benzocarbazoles) **10**, which were obtained in high yields (90−96%) (Scheme 3). We could not detect traces of any other additional product in the reaction crudes. When bis(iminophosphoranes) **9** were submitted to reaction with various arylisothiocyanates, in refluxing toluene, the bis(carbodiimides) **6** were formed and further converted in situ into the corresponding bis(quinindolines) **11** (65−98%) (Scheme 3).

The structural determination of the bis(benzocarbazoles) **10** and bis(quinindolines) **11** was accomplished following their analytical and spectral data. Moreover, the structure of **11a** ($R^1 = H$; $R^2 = CH_3$) was determined by an X-ray crystal diffraction study. The main feature of its structure is that its two quinindoline moieties adopt a nearly perpendicular orientation, the angle between their mean planes being 86.1° (see Figure 1).

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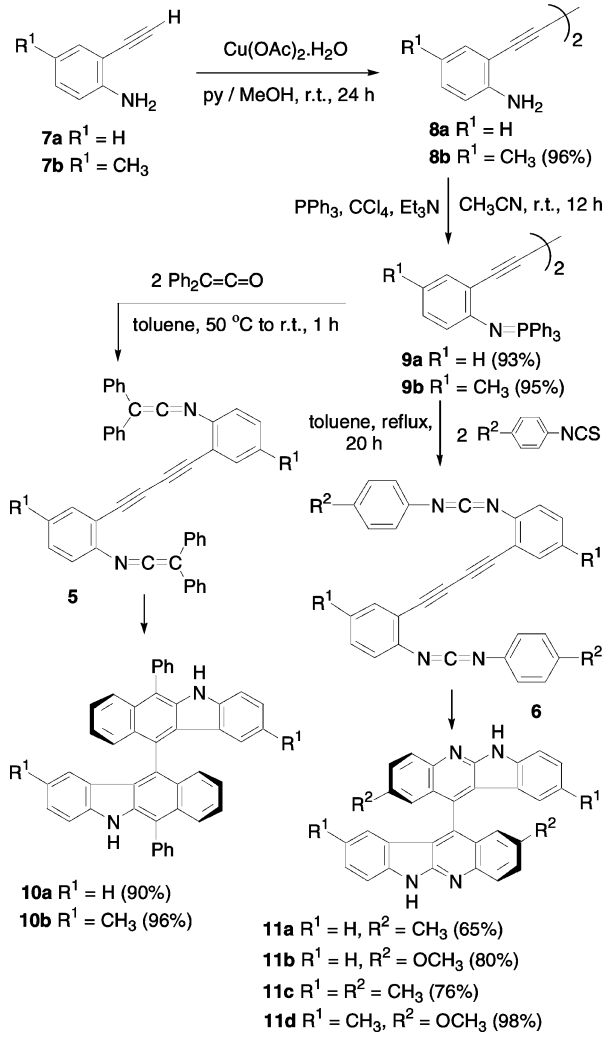
(14) The configuration along the 1,3-diyne axis of bis(ketenimines) **5** and bis(carbodiimides) **6** is drawn *anti*, as it has been shown that, at least in the solid state, 1,3-butadiynes adopt a centrosymmetric *anti* configuration. See: (a) Rodríguez, J. G.; Tejedor, J. L. *Tetrahedron* **2005**, *61*, 3033−3043. (b) Rodríguez, J. G.; Lafuente, A.; Martín-Villamil, R.; Martínez-Alcázar, M. P. *J. Phys. Org. Chem.* **2001**, *14*, 859−868.

(15) Planar butatrienes are know to *cis-trans* isomerize through orthogonal 2-butyne-1,4-diyl biradicals of structure similar to that of the central part of **C**. See: (a) Jarowski, P. D.; Diederich, F.; Houk, K. N. *J. Phys. Chem.* **2006**, *110*, 7237−7246. (b) Auffrant, A.; Jaun, B.; Jarowski, P. D.; Houk, K. N.; Diederich, F. *Chem. Eur. J.* **2004**, *10*, 2906−2911.

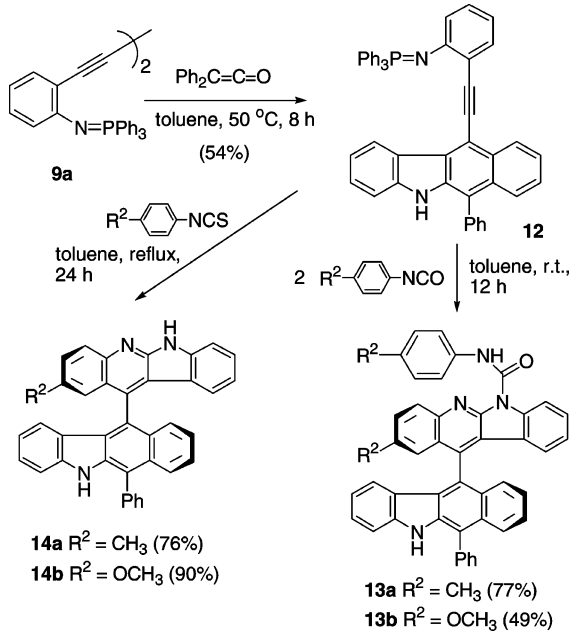
SCHEME 3. Preparation of Bis(benzocarbazoles) 10 and Bis(quinindolines) 11



The conversions **5** → **10** and **6** → **11** presumably occur by two independent biradical cyclizations of their two enyne−ketenimine or enyne−carbodiimide fragments via the tetraradicaloid canonical form **A** represented in Scheme 2.

Next, we approached the conversion of bis(iminophosphorane) **9a** into the benzocarbazole monoiminophosphorane **12**. This transformation was accomplished by slow addition of 1 equiv of diphenylketene, in toluene solution, to a 0.015 M solution of **9a** in the same solvent. When compound **12** was reacted with 1 equiv of an aryl isocyanate, the only isolable product, although in low yield (∼25−30%), was the corresponding benzocarbazole−quinindoline **13** incorporating two aryl isocyanate fragments, one forming part of the quinindoline ring system and the second linked to its indolic nitrogen atom (Scheme 4). In these reactions, nearly a 40% of the starting material **12** was recovered unchanged. Variations of the reaction conditions, such as slow addition of the aryl isocyanate to the solution containing the iminophosphorane **12**, led us to invariable results, with compounds **13** always being the only reaction products. Obviously, when we carried out the reactions of iminophosphorane **12** with 2 equiv of an aryl isocyanate, compounds **13** were obtained in higher yields (49−77%). The benzocarbazole−quinindoline skeleton of compounds **13** and the incorporation of a second molecule of aryl isocyanate into

SCHEME 4. Preparation of Benzocarbazole−Quinindolines 13 and 14



their structures was secured by an X-ray study of a monocrystal of **13a** ($R^1 = H$; $R^2 = CH_3$). This study was also definitive for establishing the place where the second molecule of aryl isocyanate was introduced, just at the indolic nitrogen atom of the quinindoline fragment instead of at the pyridinic nitrogen atom of the same unit or at the nitrogen atom of the benzocarbazole fragment. In the crystal, the value of the angle between the mean planes of the benzocarbazole and quinindoline units of **13a** is 83.5° (see the Supporting Information).

In contrast, the reaction of **12** with aryl isothiocyanates afforded the benzocarbazole−quinindolines **14** in 76−90% yield (Scheme 4) in a way that avoids the incorporation of a second unit of the heterocumulenic reactant into the structure of the final products. The lower reactivity of isothiocyanates when compared with isocyanates may well account for this remarkable difference.

It is noteworthy that up to now no synthetic pathways were known for preparing bis(benzocarbazoles), bis(quinindolines), or benzocarbazole−quinindolines in which their two heteroaryl fragments are linked by a single bond.

The quateraryls **10**, the biaryls **11**, and the teraryls **13** and **14** are constructed by two identical (**10** and **11**) or different (**13** and **14**) planar tetracyclic heterocyclic rings, connected by a biaryl bond. On the basis of their structures, with four "*ortho*-substituents" next to the biaryl axis (the aryl−aryl single bond linking both tetracyclic systems) it seems reasonable to assume that these compounds are axially chiral,[16] as the rotation around this axis should be notably hindered (see the X-ray structure of compound **11a** in Figure 1). The nonstereoselective method reported here for their preparation should produce racemic mixtures of the two possible atropoenantiomers of each indi-

(16) For reviews on axially chiral biaryls, see: (a) Baudoin, O. *Eur. J. Org. Chem.* **2005**, 4223−4229. (b) Bringmann, G.; Mortimer, A. J. P.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5384−5427. (c) Bringmann, G.; Tasler, S.; Pfeifer, R.-M.; Breuning, M. *J. Organomet. Chem.* **2002**, *661*, 49−65. (d) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809−3844. (e) Kamikawa, K.; Uemura, M. *Synlett* **2000**, 938−949.

vidual compound. To investigate this assumption by ^{1}H NMR spectroscopy, we carried out a gradual addition of optically pure (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol [(*S*)-TFAE][17] to a $CDCl_3$ solution of **11a**. After the addition of 4 equiv of (*S*)-TFAE the splitting of some signals was observed, probably due to the formation of the two expected diastereomeric association complexes in a 1:1 ratio.

In summary, we have disclosed here an amenable preparation of three new types of symmetric and nonsymmetric *C*,*C*-coupled heterobiaryls combining benzocarbazole and quinindoline structural units, which is based on the double biradical cyclization of bis(ketenimines) and bis(carbodiimides) derived from the 1,4-diphenyl-1,3-butadiyne framework. These heterobiaryls are apparently obtained as racemic mixtures of atropoenantiomers due to its presumed chiral biaryl axis.

Experimental

Sample Procedure for the Preparation of the Bis(benzocarbazoles) 10. To a heated solution at 50 °C of the bis(iminophosphorane) **9** (1 mmol) in anhydrous toluene (25 mL) was added diphenylketene (0.39 g, 2 mmol) in the same solvent (5 mL), and then the reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the resulting crude material was chromatographed on a silica gel column.

Bis(benzocarbazole) 10a (R^1 = H): eluent for column chromatography, hexanes/diethyl ether (2:3, v/v); yield 90%; mp 232 °C (colorless prism); IR (Nujol) 3424, 3391, 1607, 1574, 1353, 1313, 1251, 1231, 1176, 1148, 1108, 1021, 945, 788, 760, 742, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.23 (d, 2 H, J = 7.8 Hz), 6.52−6.57 (m, 2 H), 7.08−7.21 (m, 6 H), 7.37−7.42 (m, 2 H), 7.60−7.64 (m, 2 H), 7.70−7.75 (m, 4 H), 7.78−7.82 (m, 2 H), 7.85−7.87 (m, 2 H), 7.96 (s, 2 H), 8.01 (d, 2 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 109.7, 118.4 (q), 119.4, 123.1, 123.3 (q), 124.7, 125.4, 126.5, 126.9, 128.0 (q), 128.1, 129.3 (q), 129.4, 129.5, 131.0 (q), 131.1, 131.3, 137.1 (q), 137.7 (q), 142.1 (q); HRMS (EI): *m*/*z* calcd for $C_{44}H_{28}N_2$ 584.2252, found 584.2257.

Sample Procedure for the Preparation of the Bis(quinindolines) 11. To a suspension of the bis(iminophosphorane) **9** (1 mmol) in anhydrous toluene (25 mL) was added a solution of the aryl isothiocyanate (2 mmol) in the same solvent (5 mL), and then the reaction mixture was heated at reflux temperature for 20 h. After cooling, the solvent was removed to dryness and the resulting crude material was triturated with dichloromethane (15 mL), filtered, and dried under vacuum.

Bis(quinindoline) 11a (R^1 = H, R^2 = CH_3): yield 65%; mp >320 °C (yellow prism); IR (Nujol) 3124, 1606, 1579, 1400, 1348, 1244, 1230, 1138, 1109, 818, 744, 725 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 2.13 (s, 6 H), 6.08 (d, 2 H, J = 7.8 Hz), 6.60 (t, 2 H, J = 7.5 Hz), 7.05 (s, 2 H), 7.26 (t, 2 H, J = 7.5 Hz), 7.44 (d, 2 H, J = 8.0 Hz), 7.55 (d, 2 H, J = 8.9 Hz), 8.11 (d, 2 H, J = 8.6 Hz), 12.01 (s, 2 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 21.0, 111.0, 115.5 (q), 119.6, 121.6, 122.0 (q), 123.4, 127.7, 128.1, 131.5, 132.8 (q), 134.7 (q), 141.8 (q), 145.2 (q), 152. (q); HRMS (EI): *m*/*z* calcd for $C_{32}H_{22}N_4$ 462.1844, found 462.1847.

Sample Procedure for the Preparation of the Benzocarbazole−Quinindolines 14. To a solution of iminophosphorane **12** (0.67 g, 1 mmol) in anhydrous toluene (20 mL) was added a solution of the aryl isothiocyanate (1 mmol) in the same solvent. The reaction mixture was heated at reflux temperature for 24 h. After cooling, the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column, using hexanes/diethyl ether as eluent, or was triturated with dichloromethane (15 mL), filtered, and dried under vacuum.

Benzocarbazole−Quinindoline 14a (R^1 = H, R^2 = CH_3): eluent for column chromatography, hexanes/diethyl ether (1:9, v/v); yield 76%; mp 253 °C (yellow prisms); IR (Nujol) 3408, 1606, 1394, 1344, 1246, 1234, 1178, 1151, 1138, 1109, 821, 773, 744, 723, 704 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.15 (s, 3 H), 6.03 (d, 1 H, J = 7.9 Hz), 6.07 (d, 1 H, J = 7.9 Hz), 6.51 (t, 1 H, J = 7.6 Hz), 6.58 (t, 1 H, J = 7.6 Hz), 7.08−7.12 (m, 2 H), 7.17 (t, 1 H, J = 7.8 Hz), 7.22−7.28 (m, 2 H), 7.36−7.40 (m, 1 H), 7.42 (d, 2 H, J = 8.0 Hz), 7.56 (dd, 1 H, J = 8.7, 1.4 Hz), 7.61−7.65 (m, 1 H), 7.72−7.78 (m, 4 H), 7.86 (d, 1 H, J = 8.7 Hz), 8.12 (d, 1 H, J = 8.7 Hz), 10.88 (s, 1 H), 11.91 (s, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 21.0, 110.8, 111.2, 116.6 (q), 118.6, 118.9 (q), 119.4, 120.1 (q), 121.3, 121.4 (q), 121.9, 122.5 (q), 123.0, 123.2 (q), 123.8, 124.6, 125.1, 125.3, 125.6 (q), 125.7 (q), 127.1, 127.6, 127.8, 127.9, 129.2, 130.3 (q), 131.0, 131.3, 132.3 (q), 136.3 (q), 137.5 (q), 137.6 (q), 141.7 (q), 143.1 (q), 145.3 (q), 152.6 (q); HRMS (EI): *m*/*z* calcd for $C_{38}H_{25}N_3$ 523.2048, found 523.2050.

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Supporting Information Available: Experimental details for the synthesis of compounds **8b**, **9**, **12**, and **13**. Spectral data (NMR, IR, MS, elemental analyses) for compounds **8b**, **9**, **10b**, **11b**−**d**, **12**, **13**, and **14b**. CIF files of **11a** and **13a**. ^{1}H and ^{13}C NMR spectra of compounds **10**, **11**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For the use of (*S*)-TFAE for similar tasks, see: (a) Demir-Ordu, Ö.; Yilmaz, E. M.; Dogan, I. *Tetrahedron: Asymmetry* **2005**, *16*, 3752−3761. (b) Focante, F.; Leardini, R.; Mazzanti, A.; Mercandelli, P.; Nanni, D. *Organometallics* **2006**, *25*, 2166−2172.