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TETRAHEDRON

Synthesis and X-Ray Crystallographic Study of 6,12-Epiiminodibenzo[*b,f*][1,5]diazocines

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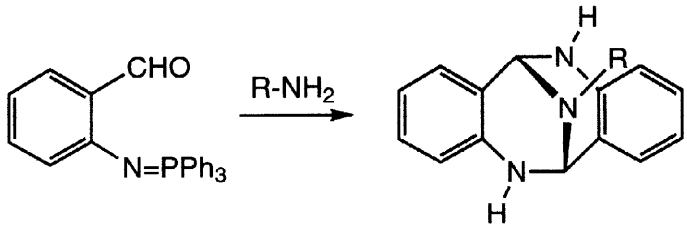
Abstract: *Seven 6,12-epiiminodibenzo[b,f][1,5]diazocines* **2** *with different substituents at position 13 have been prepared from o-(triphenylphosphoranylideneamino)benzaldehyde* **1** *and the corresponding aliphatic and aromatic primary amines in yields ranging from 40 to 80%. The molecular and crystal structures of componds* **2d** *(R = 4 H_3C-C_6H_4) and* **2e** *(R = 4 H_3CO-C_6H_4) have been determined by X-Ray analysis. Compound* **2d** *crystallizes as a racemate while compound* **2e** *crystallizes as a unique enantiomer (absolute configuration R,R).*

Although iminophosphorane **1**, available by Staudinger reaction between *o*-azidobenzaldehyde and triphenylphosphine,[1] contains the two reactive groups for an aza Wittig reaction, it has been reported that **1** itself undergoes neither intra- nor intermolecular aza Wittig reactions.[2] This lack of reactivity has been attributed to the formation of a resonance-stabilized chelate-ring involving the iminophosphorane and formyl groups.

We have found that iminophosphorane **1** reacts with primary amines (benzylamine, picolylamine, ferrocenylmethylamine[3] and anilines) in ethanol at room temperature in the presence of catalytic amounts of acetic acid to give the tricyclic compounds **2** containing the dibenzo[*b,f*][1,5]diazocine ring system in yields ranging from 40 to 80% (Scheme 1). The main interest of these compounds lies in their close analogy with Tröger's bases.[4-7]



1 **2**

a, R = C_6H_5-CH_2 (46%)
b, R = Fc-CH_2 (42%)
c, R = 3-C_5H_4N-CH_2 (28%)
d, R = 4 H_3C-C_6H_4 (50%)
e, R = 4 H_3CO-C_6H_4 (40%)
f, R = 4 Cl-C_6H_4 (80%)
g, R = 4 Br-C_6H_4 (52%)

Scheme 1

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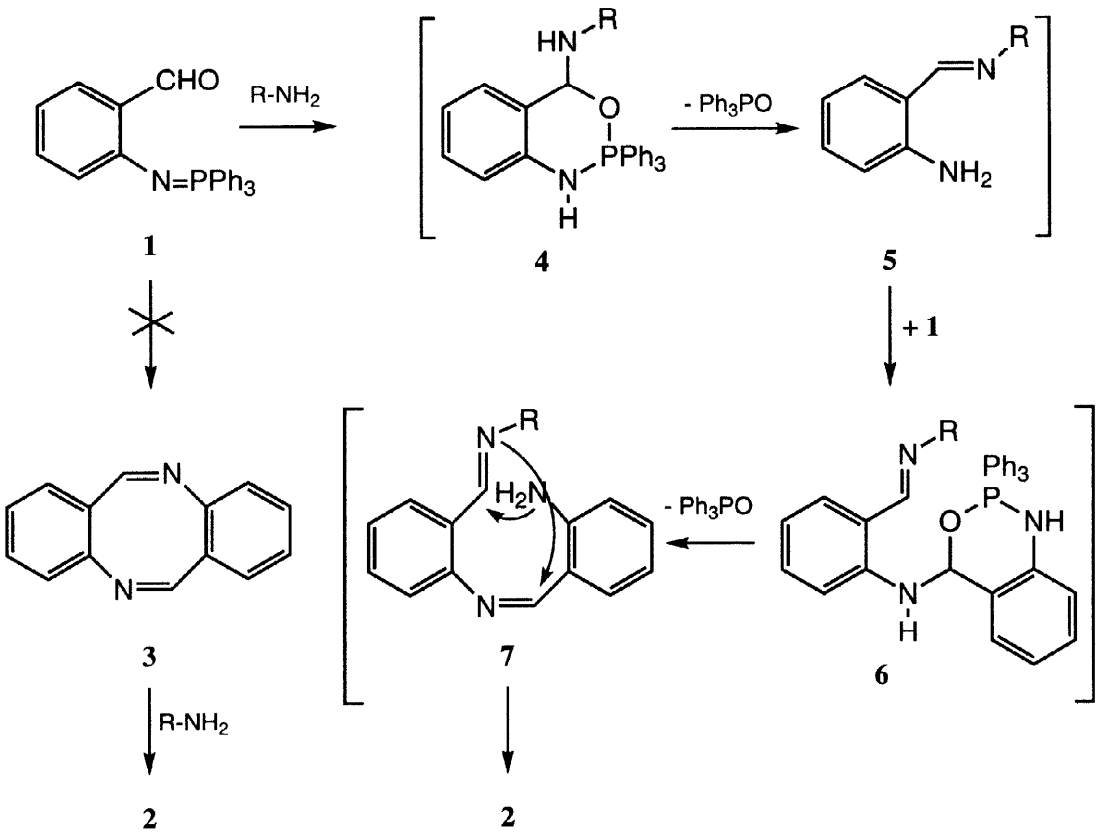
When an ethanolic solution of iminophosphorane **1** was treated with acetic acid at room temperature, the starting material was recovered unaltered. A similar result was obtained when it was heated in toluene at reflux and even at 220 °C in a sealed tube. These results clearly preclude that the conversion **1**→**2** involves the initial formation of the dibenzo[*b*,*f*][1,5]diazocine ring **3** via a double aza Wittig reaction followed by cross-addition of the amino group on the two aldimine groups of **3**. A tentative mechanism for the conversion **1**→**2** could involve the initial reaction of iminophosphorane **1** with the primary amino group to give the intermediate **4** which provides the aniline derivative **5** by loss of triphenylphosphine oxide. Compound **5** reacts with a second equi-



Scheme 2

valent of iminophosphorane **1** by the same way to give **6** which loses triphenylphosphine oxide to form **7**. This compound undergoes cyclization by attack of the amino group on the adjacent aldimine bond with concomitant attack of the resulting amino group on the other aldimine bond (Scheme 2).

It has only been described briefly that the reaction of o-tosylaminobenzaldehyde with ammonium acetate, methyl- and ethylamine afforded the corresponding 1,5-ditosyl-6,12-epimethyliminodibenzo[*b*,*f*][1,5]diazocines; the X-ray structure determination of the N-methyl derivative was reported.[7]

X-Ray Analysis.

The main features of the molecular (Fig. 1) and crystal structure of compounds **2d** and **2e** are listed in Table 1 according to the numbering scheme shown in Fig. 1. The most significant differences between both compounds are related to the conformation of the substituent at N3 and the bond distances and angles around it. The intermolecular N2-H2···N3 hydrogen bond interaction, in **2e**, can be responsible for the distortion of the N3 sp^3

hybridization [$\Sigma\alpha$(N3) = 339.0(2) and 343.1(5)° in **2d** and **2e** respectively]. In **2d**, where no hydrogen bonds are present, both pairs of N3-C4/C7 and C4-C3/C6-C7 distances are alike while in **2e** the shortening of the N3-C7, C3-C4 and the lengthening of the C6-C7 distances is observed together with a significant opening of the C12-N3-C7 angle. The angle of the two benzene rings fused to the bicycle system is quite constant [77.9(1) and 76.6(1)°] and similar to the compound described in ref. 7 (85.8°, an acetonitrile solvate, CSD refcode: VIFVIP)[8] The crystal packing in **2d** is only due to van der Waals contacts while in **2e** the molecules form chains along the **b** axis via N2-H2···N3 hydrogen bonds. These chains are then linked by N1-H1···O1 bonds along the **c** axis to give sheets.

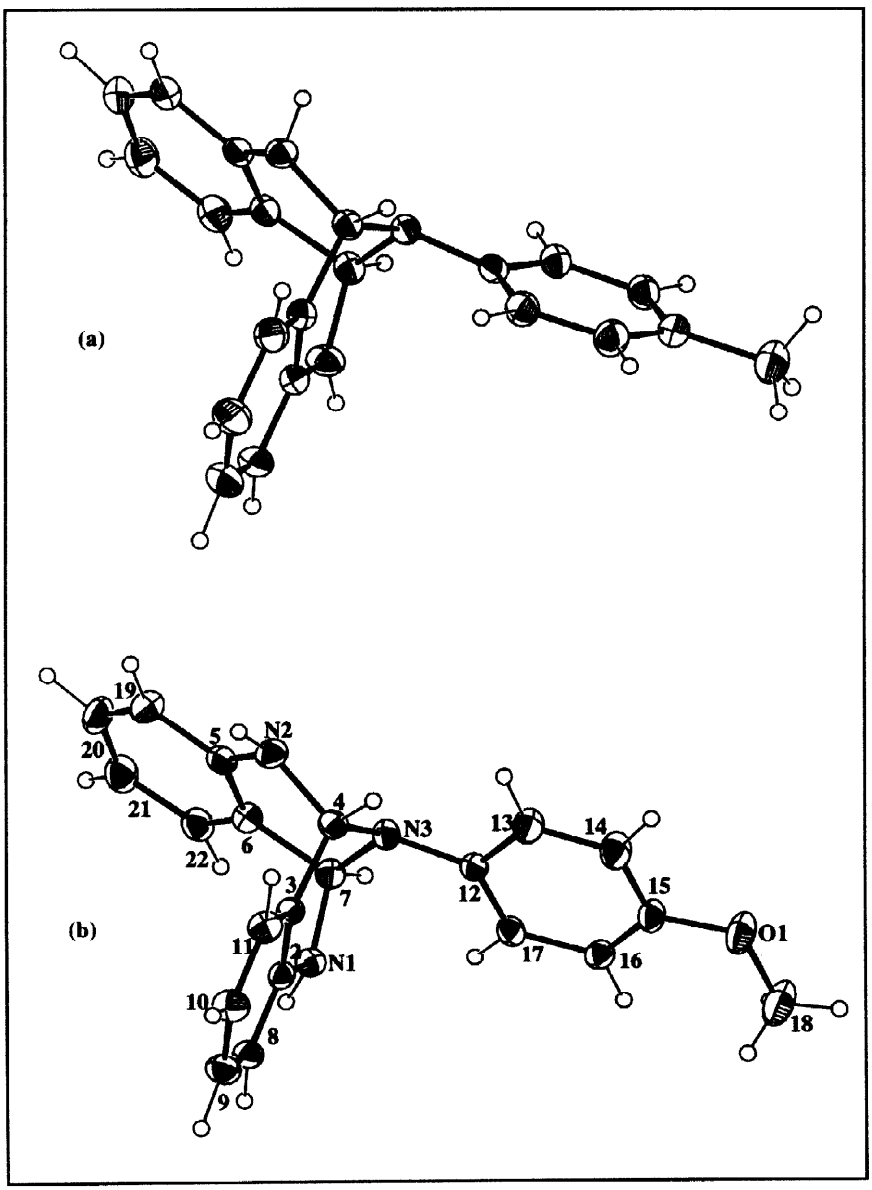


Figure 1. Views of the molecular structures of **2d** (a) and **2e** (b) showing the numbering scheme used in the crystallographic study. Ellipsoids are drawn at 30% probability level.

Table 1. Selected Geometrical Parameters for Compounds **2d** and **2e** (Å, °).

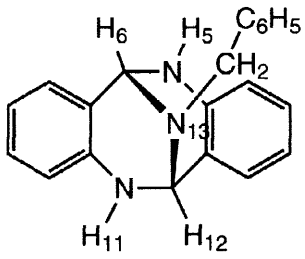
	2d	**2e**		**2d**	**2e**
N1-C2	1.388(3)	1.397(7)	C5-N2	1.403(2)	1.397(6)
N1-C7	1.450(3)	1.454(5)	C7-N3-C12	115.7(1)	118.2(2)
C7-N3	1.475(2)	1.447(5)	C4-N3-C12	116.4(1)	116.4(3)
C4-N3	1.477(2)	1.488(6)	C4-N3-C7	106.9(1)	108.5(3)
C12-N3	1.433(2)	1.433(4)	C4-N3-C12-C13	-169.4(2)	-51.1(5)
C4-N2	1.456(2)	1.444(4)			

Hydrogen interactions in **2e**

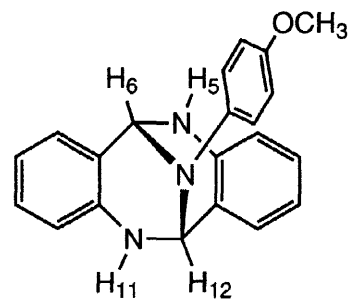
	X-H	H···Y	X···Y	X-H···Y
N1-H1···N3 (1-x, y-1/2, 1-z)	0.94(5)	2.45(6)	3.245(6)	143(5)
N2-H2···O1(x,y,1+z)	0.98(5)	2.28(5)	3.238(4)	163(4)

Structure of the pseudo-Tröger's bases 2 in the solid state and in solution.

For this discussion we have selected a representative of each class of compounds **2**, the *N*-CH_2R series (**2a-2c**) and the *N*-Ar series (**2d-2g**), the selected compounds being **2a** (*N*-benzyl) and **2e** (*N*-anisyl). The most characteristic feature of Tröger's bases and related compounds is their chiral nature which allow Tröger's bases to be resolved.[5,6]



2a



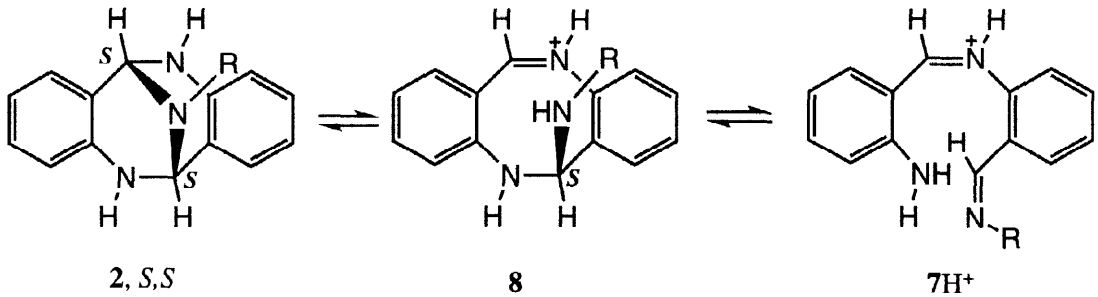
2e

The most interesting aspect of the ^1H NMR spectrum of compound **2a** is the appearance of the *N*-CH_2 at position 13: an AB system with δ_A = 3.62, δ_B = 3.97 ppm and $^2J_{AB}$ = 13.2 Hz, the anisochrony of the methylene protons reflecting the chiral nature of the **2** ring system. H6 and H12 appear as singlets at 4.88 ppm while the NH protons (H5 and H11) resonate at 4.52 ppm (slightly broad). In the region of saturated protons, compound **2e** shows the signals of the *para*-methoxy group (singlet at 3.63 ppm) and two doublets at 5.65 ppm (H6 and H12) and at 6.73 ppm (slightly broad, H5 and H11) with a $^3J_{NHCH}$ coupling constant of 3.3 Hz.

All reported X-ray structures of Tröger's bases,[5,6] compounds **2d** and **2e** (we have called pseudo-Tröger's bases) as well as 6,12-imino-6H,12H-dibenzo[*b,f*][1,5]-dithiocins[9] are centrosymmetrical crystals, *i.e.*, both enantiomers are present in the unit cell. On the other side, the unit cell of compound **2e** contains only one enantiomer whose absolute configuration was determined (*R,R*). Thus, for the first time a compound belonging to a family related to Tröger's bases presents spontaneous resolution. However, no compound of family **2** shows rotatory power (solvent: CH_2Cl_2) and preliminary attempts to use chiral HPLC columns (cyclodextrine, tria-

cetylcellulose) to separate both enantiomers failed with compounds **2d-2g**, including **2d** (a racemate) and **2e**. Another kind of ^{1}H NMR experiments which failed were the use of chiral LSR (with compound **2f**) and Pirkle's alcohol (with compound **2e**): in neither case was splitting of signals observed.

The most reasonable explanation is that **2e** is probably a racemate consisting in R,R and S,S crystals, the molecular structure have been determined on an R,R one. These enantiomers quickly racemize in solution (this being consistent with spontaneous resolution)[10] by a mechanism similar to the one we have proposed in Scheme 2 for the formation of epiiminodibenzo[b,f][1,5]diazocines. The rapid racemization is necessary to explain the HPLC and NMR experiments, not so the absence of optical rotation which could be due to the presence of the same amount of R,R and S,S crystals in the sample.



2, *S,S* **8** **7H**$^+$

Scheme 3

Scheme 3 shows how an *S,S* derivative could racemize by two succesive ring-openings, in **8** the first S center loses its stereogenicity and in **7H**$^+$ the same happens for the second one.

EXPERIMENTAL SECTION

General Methods.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 (200MHz) or a Varian Unity 300 (300MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin Elmer 240C instrument. HPLC experiments were carried out on home-built Waters instrument (Laboratory of Prof. J. Irrure, Barcelona) using cyclodextrine (LiChroCART 250-4, Chiradex, eluent methane:water 40:60) and triacetylcellulose (ET 250/8/4 CHIRAL TRIACEL, Macheray-Nagel, eluent ethanol) columns. The absence of optical rotation for all epiiminodibenzo[b,f]]1,5]diazocines **2** was determined with a Perkin Elmer 241 MC polarimeter using CH_2Cl_2 as solvent (compounds **2** absorb at 295 nm, ε = 5000).

*Preparation of o-(Triphenylphosphoranylidene)aminobenzaldehyde **1**.*

To a solution of triphenylphosphine (1.78 g, 6.7 mmol) in dry dichloromethane (10 mL) at 0°C, a solution of *o*-azidobenzaldehyde (1.0 g, 6.7 mmol) was added dropwise in the same solvent (20 mL) under nitrogen and the reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column, eluting with ethyl acetate/n-hexane

(3:1) to afford **1** as yellow prisms in 30% yield; m.p. 175.°C; IR (Nujol) 1676, 1593, 1549, 1439, 1379, 1342, 1266, 1182, 1109, 829, 756, 720, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.45 (d, 1H, ^3J=8.3 Hz), 6.62 (t, 1H, ^3J = 7.5 Hz), 7.01 (ddd, 1H, ^3J = 8.3, 7.3, ^4J = 1.9 Hz), 7.39-7.58 (m, 9H), 7.75 (ddd, 7H, ^3J = 12.2, 8.1, ^4J =1.7 Hz), 11.10 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 116.9, 122.9 (^3J = 11.1 Hz), 127.9 (^4J = 2.4 Hz), 128.7 (^3J = 12.1 Hz), 129.4 (^3J =19.6 Hz), 130.3 (^1J = 100.6 Hz), 132.0 (^4J = 2.8 Hz), 132.4 (^2J = 9.9 Hz), 134.5, 155.9, 193.8; EI MS m/z (%): 381 (M^+, 33), 353 (21), 352 (83), 277 (23), 199 (17), 198 (53), 183 (100), 152 (36), 108 (26), 107 (42), 77 (75). Anal Calcd. for $C_{25}H_{20}NOP$: C, 78.73; H, 5.29; N, 3.67. Found: C, 78.56; H, 5.44; N, 3.54.

General Procedure for the Preparation of 13-Aryl-5,11-iminodibenzo [b,f][1,5]-5,6,11,12-tetrahydrodiazocines **2**.

To a suspension of 2-triphenylphosphoranylideneaminobenzaldehyde **1** (0.5 g, 1.31 mmol) in dry ethanol (10 mL), the appropriate amine (1.64 mmol) and acetic acid (0.5 mL) were added. The reaction mixture was stirred at room temperature for 16 h but the work up for the isolation of the products was dependent on the amine used in the reaction. Thus, compounds **2d-g** precipitated from the reaction mixture and were recrystallized from ethanol, while for isolation of compounds **2a**, **2b** and **2c** it was necessary to concentrate the resulting solutions to dryness and the resulting crude products were then chromatographed on a silica gel column using dichloromethane/ethyl acetate (10/1) as eluent.

13-Benzyl-5,11-iminodibenzo[b,f][1,5]-5,6,11,12-tetrahydrodiazocine ***2a***. 46% yield; R_f = 0.84; m.p. 167-169 °C, yellow prisms; IR (Nujol) 3370, 1603, 1493, 1463, 1376, 1264, 1114, 1090, 1012, 756, 722, 699 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.62 (d, 1H, ^2J = 13.2 Hz), 3.97 (d, 1H, ^2J = 13.2 Hz), 4.52 (s, 2H), 4.88 (s, 2H), 6.59 (d, 2H, ^3J = 7.8 Hz), 6.72 (t, 2H, ^3J = 7.3 Hz), 7.01-7.05 (m, 4H), 7.25-7.33 (m, 3H), 7.41 (d, 2H, ^3J = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 54.5, 65.8, 116.2, 118.8, 124.2, 127.4, 128.1, 128.5, 128.6, 129.3, 137.9, 141.2; EI MS m/z (%): 313 (M^+, 7), 223 (17), 222 (100), 129 (12), 92 (13), 91 (76), 77 (15), 65 (30). Anal Calcd. for $C_{21}H_{19}N_3$: C, 80.48; H, 6.11; N, 13.41. Found: C, 80.35; H, 5.96; N, 13.23.

13-Ferrocenylmethyl-5,11-iminodibenzo[b,f] [1,5]- 5, 6, 11, 12-tetrahydrodiazocine ***2b***. 42% yield; R_f = 0.69; m.p. 196-197 °C, yellow plates; IR (Nujol) 3393, 1608, 1495, 1329, 1270, 1117, 1082, 1036, 1009, 890, 825, 754 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.48 (d, 1H, ^2J = 12.3 Hz), 3.58 (d, 1H, ^2J = 12.3 Hz), 4.06 (s, 5H), 4.08 (t, 2H, ^3J = 1.4 Hz), 4.13 (t, 2H, ^3J = 1.4 Hz), 4.28 (s, 2H), 4.84 (s, 2H), 6.54 (d, 2H, ^3J = 8.0 Hz), 6.70 (t, 2H, ^3J = 7.3 Hz), 6.96-7.01 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 49.8, 65.1, 68.0, 68.2, 68.5, 70.1, 70.2, 82.9, 116.0, 118.5, 123.8, 127.9, 128.3, 141.0; EI MS m/z (%): 421 (M^+, 7), 223 (17), 222 (20), 199(82), 121 (100), 77 (21), 65 (14), 56 (45). Anal Calcd. for $C_{25}H_{23}FeN_3$: C, 71.27; H, 5.50; N, 9.97. Found: C, 71.42; H, 5.35; N, 9.70.

13-(3-Picolyl)-5,11-iminodibenzo[b,f][1,5]-5,6,11,12-tetrahydrodiazocine ***2c***. 28% yield; R_f = 0.89; m.p. 158-159 °C, yellow prisms; IR (Nujol) 3404, 1612, 1497, 1268, 1116, 1040, 893, 754 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.67 (d, 1H, ^2J = 13.2 Hz), 3.87 (d, 1H, ^2J = 13.2 Hz), 4.24 (bs, 2H), 4.82 (s, 2H), 6.58 (d, 2H, ^3J = 8.1 Hz), 6.72 (t, 2H, ^3J = 7.5 Hz), 7.00-7.01 (m, 4H), 7.23 (t, 1H, ^3J = 7.3 Hz), 7.79 (d, 1H, ^3J = 7.8 Hz), 8.52-8.57 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 51.6, 65.5, 115.9, 118.6, 123.5, 123.6, 127.8, 128.3, 136.9, 140.8, 148.6, 150.2; EI MS m/z (%): 314 (M^+, 3), 222 (21), 149(60), 119 (50), 107 (15), 92 (100), 77 (39), 65 (55). Anal Calcd. for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.12; H, 5.60; N, 17.94.

13-(4-Methylphenyl)-5,11-iminodibenzo[b,f][1,5]-5,6,11,12-tetrahydrodiazocine ***2d***. 50% yield; m.p. 177 °C, colourless prisms; IR (Nujol) 3401, 1613, 1577, 1492, 1299, 1114, 1043, 955, 816, 758 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.16 (s, 3H), 5.77 (d, 2H, ^3J = 3.3 Hz), 6.48 (d, 2H, ^3J = 7.9 Hz), 6.56 (t, 2H, ^3J = 7.3 Hz), 6.78 (d, 2H, ^3J = 3.3 Hz), 6.92 (t, 2H, ^3J = 7.5 Hz), 6.98 (s, 4H), 7.14 (d, 2H, ^3J = 7.7 Hz); ^{13}C-NMR ($CDCl_3$) δ 20.0, 63.3,

114.6, 116.3, 117.2, 124.1, 127.7, 127.9, 128.4, 129.2, 142.1, 144.4; EI MS m/z (%): 313 (M^+, 100), 312(6), 222(5), 207 (18), 194 (4). Anal Calcd. for $C_{21}H_{19}N_3$: C, 80.48; H, 6.11; N, 13.41. Found: C, 80.32; H, 6.24; N, 13.28.

13-(4-Methoxyphenyl)-5,11-iminodibenzo[b,f][1,5]-5,6,11,12-tetrahydrodiazocine **2e**. 40% yield; m.p. 208-209°C, yellow prisms; IR (Nujol) 3346, 1607, 1583, 1510, 1495, 1270, 1245, 1028, 758, 744 cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ 3.63 (s, 3H), 5.65 (d, 2H, ^3J = 3.3 Hz), 6.47 (d, 2H, ^3J = 8.0 Hz), 6.55 (t, 2H, ^3J = 7.2 Hz), 6.73 (d, 2H, ^3J = 3.3 Hz), 6.76 (d, 2H, ^3J = 8.8 Hz), 6.91 (t, 2H, ^3J = 7.6 Hz), 6.99 (d, 2H, ^3J = 9.0 Hz), 7.12 (d, 2H, ^3J = 7.4 Hz); ^{13}C-NMR (DMSO-d_6) δ 55.2, 64.0, 114.2, 114.7, 116.4, 118.9, 124.2, 127.7, 127.9, 140.7, 142.1, 153.2; EI MS m/z (%): 329 (M^+, 93), 314(7), 237 (5), 222(13), 207 (100), 196 (26), 167 (10), 123 (50), 108 (14), 77 (14). Anal Calcd. for $C_{21}H_{19}N_3O$: C, 76.63; H, 5.77; N, 12.76. Found: C, 76.75; H, 5.60; N, 12.88.

13-(4-Chorophenyl)-5,11-iminodibenzo[b,f][1,5]-5,6,11,12-tetrahydrodiazocine **2f**. 80% yield; m.p. 207-208 °C, yellow prisms; IR (Nujol) 3392, 1612, 1492, 1232, 1116, 1015, 960, 821, 759, 739, 716 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.84 (d, 2H, ^3J = 3.4 Hz), 6.50 (d, 2H, ^3J = 7.9 Hz), 6.57 (t, 2H, ^3J = 7.3 Hz), 6.84 (d, 2H, ^3J = 3.4 Hz), 6.93 (t, 2H, ^3J = 7.1 Hz), 7.09-7.24 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 63.1, 114.8, 116.5, 118.7, 123.2, 123.8, 127.8, 128.0, 128.5, 141.9, 145.6; EI MS m/z (%): 336(26), 335 (M^++2, 19), 334 (M^++1, 100), 333 (M^+, 5), 222(8), 208 (8), 207 (31), 206 (15). Anal Calcd. for $C_{20}H_{16}ClN_3$: C, 71.96; H, 4.83; N, 12.59. Found: C, 71.82; H, 4.76; N, 12.66.

13-(4-Bromophenyl)-5,11-iminodibenzo[b,f][1,5]-5,6,11,12-tetrahydrodiazocine **2g**. 52% yield; m.p. 210-211°C, yellow prisms; IR (Nujol) 3386, 1610, 1586, 1495, 1232, 1114, 1012, 957, 821, 758, 742, 713 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.79 (s, 2H), 6.38 (s, 2H), 6.45 (m, 4H), 6.76 (s, 2H), 6.91 (t, 2H, ^3J = 7.5 Hz), 7.04 (d, 2H, ^3J = 8.1 Hz), 7.14 (d, 2H, ^3J = 7.4 Hz), 7.29 (d, 2H, ^3J = 8.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 63.2, 111.0, 114.7, 116.5, 119.1, 123.6, 127.7, 127.8, 131.3, 141.7, 145.9; EI MS m/z (%): 380(22), 379 (M^++2, 100), 378 (M^++1, 28), 377 (M^+, 94), 276 (6), 275 (7), 274 (6), 273 (6). 258 (3), 222(3), 208 (2), 207 (7). Anal Calcd. for $C_{20}H_{16}BrN_3$: C, 63.63; H, 4.24; N, 20.94. Found: C, 63.42; H, 4.36; N, 20.85.

X-ray Analysis.

Crystal data for **2d**: Triclinic, P-1, a = 11.8973(13), b = 11.3979(18), c = 6.5799(2) Å, α = 87.449(6), β = 96.779(5), γ= 115.417(10)°. A transparent, colorless crystal of 0.05 x 0.17 x 0.37 mm was used to collect 2709 reflexions up to θ = 65° using CuKα radiation on a Philips PW1100 diffractometer. The refinement of 293 parameters using 2176 [2σ(I) criterion] observed reflexions converged to R and Rw values of 0.040 and 0.043 respectively. The highest peak in the final difference Fourier synthesis was 0.16 e $Å^{-3}$.

Crystal data for **2e**: Monoclinic, $P2_1$, a = 11.5677(18), b = 8.1502(7), c = 9.1132(8) Å, β = 107.311(7)°. A crystal of dimensions 0.10 x 0.10 x 0.33 mm was used to measure 1515 Friedel pairs of which 1384 were considered as observed according to the conditions given for **2a**. 303 variables were refined including the secondary extinction [0.10(2) x 10^4] and the Flack parameters[11] [-0.07(60)] in order to determine the absolute configuration. According to this method, the enantiomer present in the crystal is the (*R,R*) as shown in Fig. 1. The final R and Rw values were 0.039 and 0.044. The highest peak in the final difference Fourier synthesis was 0.23 e $Å^{-3}$.

The structures were solved by direct methods, Sir92.[12] The non-hydrogen atoms were refined anisotropically and the hydrogen ones were included as isotropic. Most of the calculations were performed on a VAX6410 computer using the XTAL System.[13] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. IV.[14]

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References and notes.

1. Luheshi, A.-B.; Salem, S. M.; Smalley, R. K.; Kennewell, P. D.; Westwood, R. *Tetrahedron Lett.* **1990**, 6561. Molina, P.; Arques, A.; Cartagena, I.; Obón, R. *Tetrahedron Lett.* **1991**, 2521.
2. Nomura, Y.; Kikuchi, Y.; Takeuchi, Y. *Chem. Lett.*, **1974**, 575.
3. Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc. Perkin Trans 2* , **1991**, 751.
4. Tröger, J. *J. Prakt. Chem.* , **1877**, *36*, 225.
5. a) Wilcox, C. S. *Tetrahedron Lett.*, **1985**, *26*, 5749; b) Wilcox, C. S.; Cowart, M. D. *Tetrahedron Lett..*, **1986**, *27*, 5563; c) Cowart, M. D.; Sucholeiki, I.; Bukownik, R. R.; Wilcox, C. S. *J. Am. Chem. Soc.*, **1988**, *110*, 6204; d) Adrian Jr, J. C.; Wilcox, C. S. *J. Am. Chem. Soc.*, **1989**, *111*, 8055; e) Bond, D. R.; Scott, J. L. *J. Chem. Soc., Perkin Trans. 2* , **1991**, 47; f) Yashima, E.; Akashi, M.; Miyauchi, N. *Chem. Lett.* , **1991**, 1017; g) Adrian Jr, J. C.; Wilcox, C. S. *J. Am. Chem. Soc.*, **1992**, *114*, 1398; h) Crossley, M. J.; Hambley, T. W.; Mackay, L. G.; Try, A. C.; Walton, R. *J. Chem. Soc., Chem. Comm.*, **1995**, 1077.
6. Cerrada, L.; Cudero, J.; Elguero, J.; Pardo, C. *J. Chem. Soc., Chem. Comm.*, **1993**, 1713. Cudero, J.; Elguero, J.; Fruchier, A.; Jimenez, P.; Marcos, C.; Pardo, C.; Ramos, M. *Magn. Reson. Chem.*, **1996**, *34*, 318. Pardo, C.; Ramos, M.; Fruchier, A.; Elguero, J. *Magn. Reson. Chem.*, **1996**, *34*, 708. Cudero, J.; Pardo, C.; Ramos, M.; Gutierrez-Puebla, E.; Monge, M.; Elguero, J. *Tetrahedron*, **1997**, *53*, 2233.
7. Ukhin, L. Yu.; Komissarov, V. N.; Litvinov, I. A.; Piven, V. A.; Litvinova, N. A. *Dokl. Akad. Nauk SSSR* **1988**, *303*, 646.
8. Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.
9. Toste, F. D.; Lough, A. J.; Still, I. W. J. *Tetrahedron Lett.* **1995**, *36*, 6619.
10. Jacques, J.; Collet, A.; Wilen, S. H. Enantiomers, Racemates and Resolutions, Krieger, Florida, 1994.
11. Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
12. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. Sir92, *J. Appl. Crystallogr.* **1994**, 435.
13. Hall, S. R.; Flack, H. D.; J.M. Stewart, J. M. Xtal3.2, 1994, Eds. Univ. of Western Australia. Lamb: Perth.
14. *International Tables for X-Ray Crystallography*, Birmingham, Kynoch Press, England, 1974, Vol. IV.