Unexpected Rearrangements of Bicyclic Pyrazolines Derived from 6,6-Diphenylpentafulvene

Francis Djapa,[a] Moncef Msaddek,[c] Kabula Ciamala,*[a] Joël Vebrel,[b] and Claude Riche[d]

Keywords: Diphenylpentafulvene / Diarylnitrilimines / Regiochemistry / Quinolines / Pyrazole

New quinoline and pyrazole derivatives are obtained after the acid-promoted intramolecular rearrangement of regioisomeric pyrazolines resulting from the cycloaddition of 6,6-diphenylpentafulvene with diarylnitrilimines.

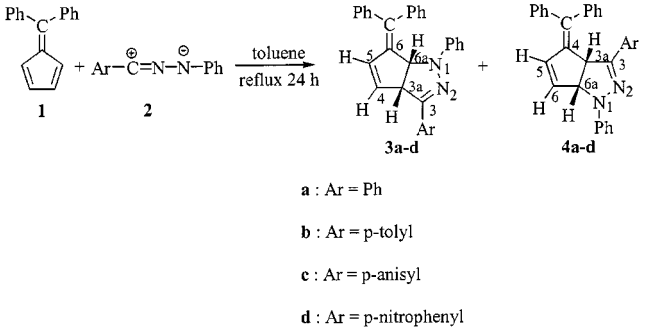
Introduction

As part of our research during the last decade, we have shown that some bicyclic spiropyrazolines rearrange into new heterocycles or polyheterocycles in the presence of trifluoroacetic acid. Thus, we have reported that the cycloaddition of diarylnitrilimines with 3-arylidene-4-isothiochromanones yielded 1,3,4-triarylspiropyrazoline[5:3]4′-isothiochromanones, which immediately and quantitatively transformed to 1,2,4-triphenyl-4,10-dihydro-10-thia-3,4-diazaphenanthrene derivatives in acidic medium. Under the same reaction conditions, 3-arylidene-2*H*-1,2-benzothiazine-4(3*H*)-one 1,1-dioxides led to spiro[1,3,4-triaryl-Δ^2-pyrazoline-5:2′-benzothiazinine-1′-one] derivatives; in the presence of trifluoroacetic acid, these adducts were converted into sulfamides after the opening of the intermediate spiroheterocycles.

Very recently, we have reported an efficient and original synthesis of pyridazin-3(2*H*)-ones by way of 1,3-dipolar cycloaddition. This synthesis was particularly interesting because the separation of the *(Z)* and *(E)* stereoisomers of the starting materials [3-arylidenebenzofuran-2(3*H*)-ones] appeared unnecessary. Indeed, although each stereoisomeric enone gave a different spiroadduct, the same pyridazinone was obtained upon acidic treatment of their admixture.

As we are interested in the rearrangement of fused pyrazolines, we have chosen to study the behaviour of such heterocycles obtained by the action of diarylnitrilimines **2** on the 6,6-diphenylpentafulvene **1** (Scheme 1).

We report herein the rearrangements of 1,3-diaryl-6-diphenylmethylene-3a,6a-dihydrocyclopenta[*c*]pyrazoles **3** and 1,3-diaryl-4-diphenylmethylene-3a,6a-dihydrocyclopenta[*c*]pyrazoles **4** in trifluoroacetic acid.



Scheme 1. Reaction of 6,6-diphenylpentafulvene **1** with diarylnitrilimines **2**

Results and Discussion

The 1,3-dipolar cycloaddition of diphenylnitrilimine **2a** with 6,6-diphenylpentafulvene **1** has been reported in the literature.[1] However, no experimental details were given. Dhan et al.[2] carried out this reaction in refluxing benzene for 40 h. After purification of the crude reaction mixture by chromatography on silica gel with petroleum ether (60–80 °C) as eluent, the authors isolated only one pure regioisomer **3a**. We have generalised this reaction to dipoles **2b–d** by refluxing them separately with **1** in toluene for 24 h. Contrary to Dhan's results, we isolated in each case a crude mixture of *two* regioisomeric adducts, i.e. 1,3-diaryl-6-diphenylmethylene-3a,6a-dihydrocyclopenta[*c*]pyrazole **3** (major, 70%) and 1,3-diaryl-4-diphenylmethylene-3a,6a-dihydrocyclopenta[*c*]pyrazole **4** (minor, 30%) as shown in Scheme 1. The regiochemistry of these adducts was established from their ^{1}H NMR spectra (300 MHz) wherein the signal of proton 6a-H of the major regioisomers appeared as a doublet around δ = 5.65–5.90. It was coupled only to proton 3a-H (^3J = 7.9–8.5 Hz).

In the minor adducts **4**, proton 6a-H resonated at 5.50 ppm (ddd signal) and was coupled with protons 3a-H, 6-H and 5-H (Experimental Section). The regiochemistries

[a] Laboratoire de Chimie et Electrochimie Moléculaire, UFR des Sciences et Techniques, Université de Franche-Comté, 16 Route de Gray, F-25030 Besançon Cedex, France
[b] Centre de Spectrométrie, UFR des Sciences et Techniques, Université de Franche-Comté, 16 Route de Gray, F-25030 Besançon Cedex, France
[c] Département de Chimie, Faculté des Sciences de Monastir, 5000 Monastir, Tunisie
[d] Institut de Chimie des Substances Naturelles, CNRS, F-91198 Gif-sur-Yvette, France

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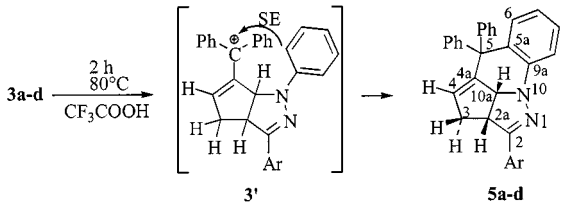
thus established were confirmed by an X-ray study of the rearrangement products of these adducts in acidic medium.

Transformation of Condensed Pyrazolines 3

When boiled in trifluoroacetic acid for 2 h, pyrazolines **3** quantitatively rearranged through an unexpected pathway into a complex tetracyclic molecule **5** (Scheme 2).



Scheme 2. Transformation of condensed pyrazolines **3**

The mass spectrum of the compound **5b** (Ar = *p*-tolyl) showed a molecular ion ($M^{+\bullet}$) at 438 amu, identical to that of the starting adduct **3b** (M = 438 g/mol). The exact structure of **5b** was established by an X-ray study (Figure 1). The latter corroborated the spectroscopic data (Experimental Section) and allowed us to suggest the reaction mechanism shown in Scheme 2, in which the two phenyl groups stabilise the resonance structure of the intermediate benzylic carbocation **3**′. The latter then leads to intramolecular electrophilic substitution on the neighbouring phenyl group.[3,4]

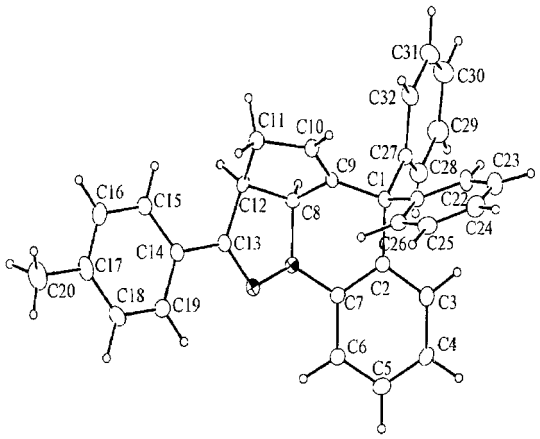
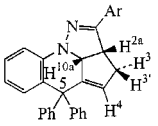


Figure 1. Molecular structure of compound **5b** (Ar = *p*-tolyl) in the crystal

The DQF-COSY[5,6] NMR spectrum of **5d** (Figure 2, Ar = *p*-nitrophenyl) allowed us to identify each proton. This assignment has been generalised to all compounds **5**.

In the spectrum of Figure 2, the most important correlation was found at the intersection of the signals at δ = 4.30 (2a-H) and 3.10 (ddd signal). The latter chemical shift was attributed to 3′-H, whereas 3-H resonated at δ = 2.75 (dddd). Indeed, the dihedral angles 2a-H–C-2a–C-3–3-H (10.4°) and 2a-H–C-2a–C-3–3′-H (115°) indicated that the coupling constant between 3′-H and 2a-H was higher than that between 3-H and 2a-H (Karplus rule). Thus, protons 3-H, 3′-H, 2a-H and 4-H constituted a clearly identifiable ABXX′ system.



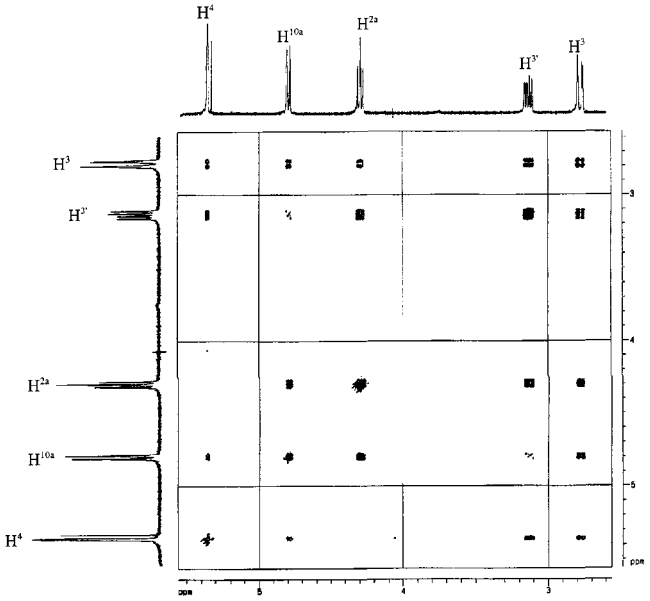
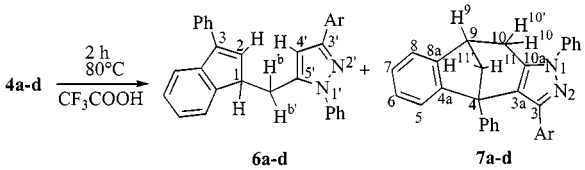


Figure 2. DQF-COSY spectrum of compound **5d** (Ar = *p*-nitrophenyl)

In the ^{13}C NMR spectrum of **5d**, the weak signal at 56.5 ppm was unambiguously attributed to the quaternary sp^3 carbon (C-5), which carried two phenyl groups. C-2a resonated at δ = 47.7, whilst C-3 showd a signal at δ = 39.6. C-10a was linked to nitrogen and gave a deshielded signal at δ = 69.0.

Transformation of Condensed Pyrazolines 4

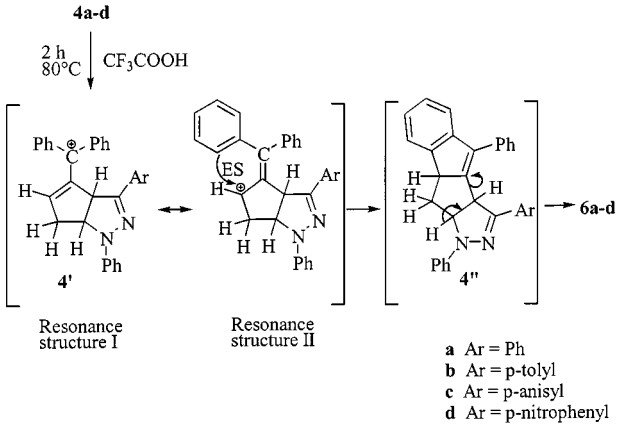
Under the same reaction conditions, the minor regioisomeric pyrazolines **4** led quantitatively to a mixture of two rearrangement products: 1,3-diphenyl-5-[1-(3-phenylidenyl)methyl]pyrazoles **6** (70%) and 1,3,4-triaryl-4,9-dihydro-10*H*-4,9-methanobenzo[4,5]cyclohepta[1,2-*c*]pyrazoles **7** (30%). These structures (Scheme 3) have been established on the basis of their spectroscopic data and an X-ray study of **7c** (Ar = *p*-anisyl).



a Ar = Ph
b Ar = p-tolyl
c Ar = p-anisyl
d Ar = p-nitrophenyl

Scheme 3. Transformation of condensed pyrazolines **4**

The reaction leading to compound **6** was initiated by the protonation of the conjugated π-system of **4** (C-5 and C-6), leading to a positive delocalized charge (see Scheme 4 below, resonance structures I and II). In structure I, the phenyl group carried by the nitrogen is too far from the positive charge to react as before. In structure II, one phenyl nucleus of the fulvene is susceptible to intramolecular electrophilic substitution; the position carrying a partial positive charge might thus contribute to construction of the intermediate cyclic structure **4"** (Scheme 4).



Scheme 4. Intramolecular electrophilic substitution leading to **6**

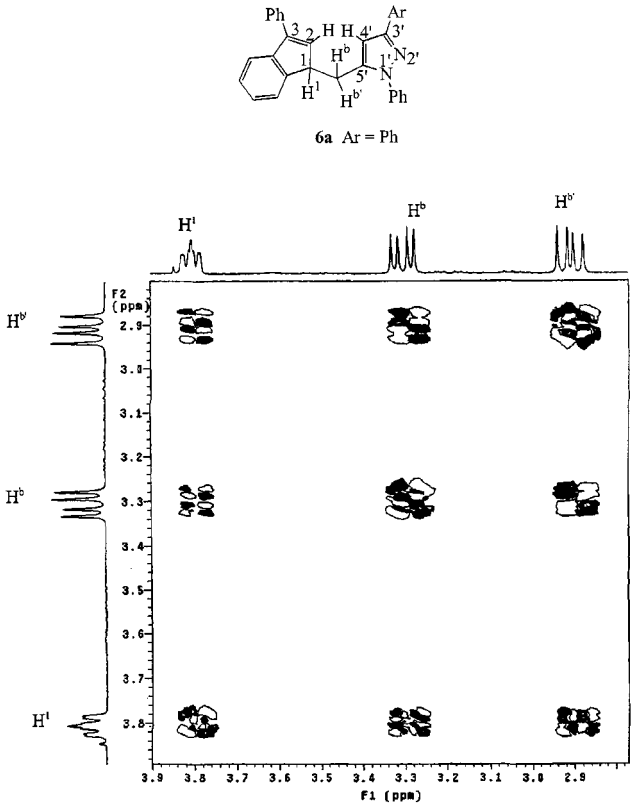


Figure 3. Partial DQF-COSY spectrum of compound **6a** (Ar = Ph)

Such a polycyclic structure is very constrained due to the presence of three fused pentagonal rings. Since the pyrazoline nucleus tends to heteroaromatise into pyrazole, the central ring is easily opened *via* a deprotonation–protonation reaction, leading to compound **6** (Scheme 4).

The ^{1}H NMR spectrum of compound **6a** (Ar = Ph) clearly indicated that there were three protons carried by sp^3 carbons and two ethylenic protons. The HSQC spectrum of this same compound showed that among the three protons linked to sp^3 carbons, two (2.90 and 3.30 ppm) were carried by the same carbon atom (28.5 ppm), the latter proton (3.80 ppm) being linked to the carbon at 48.2 ppm. The ethylenic protons (6.50 and 6.70 ppm) were linked to the sp^2 carbon atoms at 104.0 and 135.0 ppm, respectively. The DQF-COSY spectrum revealed the proton–proton interactions and allowed us to attribute 4′-H, 2-H and 1-H. The 4′-H proton (6.70 ppm) was not correlated with any other proton; the 2-H proton (6.50 ppm, doublet) was coupled with 1-H (3.80 ppm, ddd). We have also observed interactions between this last proton and the diastereotopic protons H^b and $H^{b'}$.

The expansion of the DQF-COSY spectrum between 2.80 and 3.90 ppm (Figure 3) showed that the most intense correlation was located at the intersection of the signal at 3.80 ppm and that at 2.90 ppm. This indicated the most important link (1-H and H^b) because these two protons formed a dihedral angle close to 173°, whereas the dihedral angle 1-H–C-1–C^b–$H^{b'}$ was 27°.

It can be seen that the ^{1}H NMR spectrum confirms the chemical shifts of H^b and $H^{b'}$ by way of the following coupling constants: $J_{H1\text{-}Hb}$ = 9.3 Hz and $J_{H1\text{-}Hb'}$ = 6.3 Hz. On the HMBC spectrum we noticed correlations between C^b and 1-H, C-1 with H^b, $H^{b'}$ and 2-H, C-4′ with H ^{b}, $H^{b'}$ and 2-H. Furthermore, the correlations of 1-H with C-2 and C^b were clearly observed.

The mass spectrum of compound **6a** (Ar = Ph) was obtained by electron impact at 70 eV (NERMAG R10/10 H). This was of great interest because two competitive fragmentation schemes were evident. The identification of the main positive fragments of *m*/*z* = 191 amu and *m*/*z* = 233 amu allowed the reconstitution of the original structure **6a** (Figure 4).

The retention of the positive charge on the indenic system is facilitated because it leads to a well stabilised benzylic carbocation. However, it should be noted that the homolytic break of the same σ bond creates a benzylic radical, also stabilised by resonance. For this alternative fragmentation scheme, the positive charge was corroborated by the methylenepyrazole cation at *m*/*z* = 233 amu.

The minor products **7** did not originate from carbocations **4′**. We verified experimentally that they derived from compounds **6**. Indeed, when a solution of pure **6b** (or **6d**) was refluxed for 4 h in trifluoroacetic acid, **7b** (or **7d**) was obtained in 30% yield (**7d**, 50%). Unfortunately, after prolonged heating at 80 °C, we observed a complete degradation of **6b** (or **6d**). It was consequently impossible to obtain

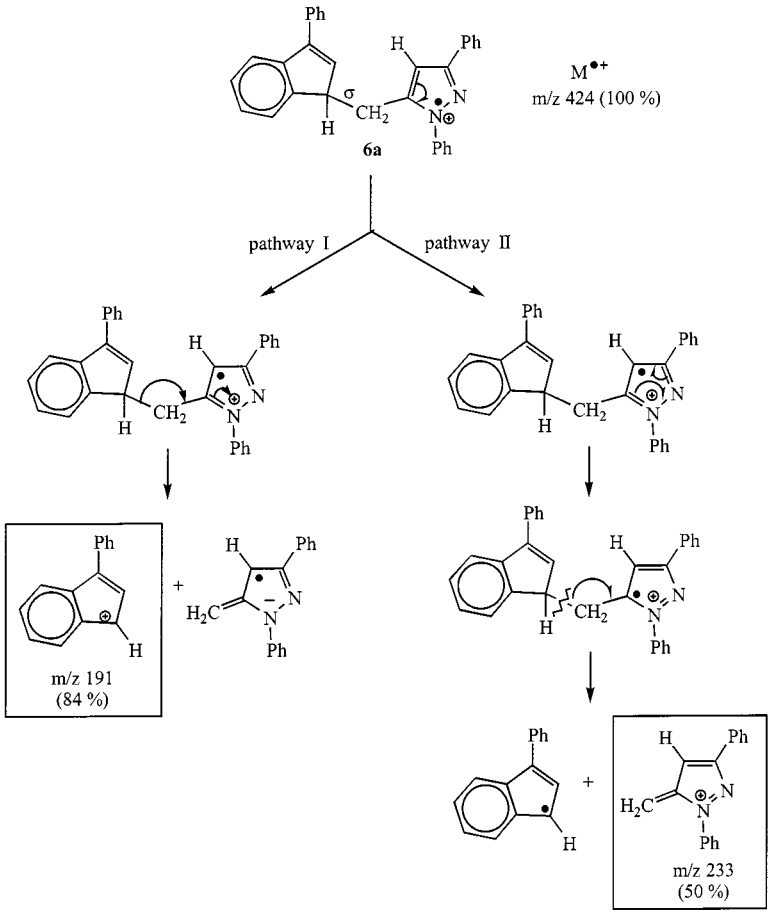
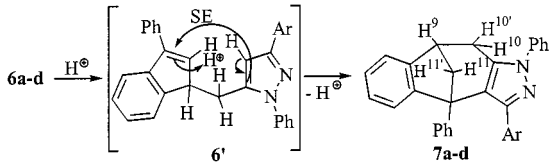


Figure 4. Two fragmentation schemes of molecular ion M^+ 424 of **6a**

7 with better yields than those indicated. In both cases, physical characteristics, IR and NMR spectroscopic data of isolated products were identical to those of compounds **7b** (or **7d**) obtained from the initial reaction medium. To explain this phenomenon, we have hypothesised that the protonation of position 2 of the indenic derivatives **6** first generates a benzylic carbocation; an intramolecular electrophilic substitution then leads to compounds **7** (Scheme 5).

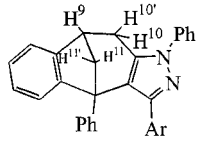


Scheme 5. Formation of **7** from **6**

Compounds **7** thus bear two methylenic groups (10-H, 10′-H, 11-H, 11′-H) separated by one –CH (9-H). The HSQC spectrum of compound **7c** confirmed the (–CH_2–CH–CH_2–) linking because each carbon at 31.2 and 55.2 ppm carried two protons, whereas the carbon at 39.0 ppm carried only one proton. This spectrum gave the following additional information: among the two methylenic carbons, the most shielded one (31.2 ppm) carried the less shielded protons (11-H and 11′-H) whereas the carbon at 55.2 ppm carried the most shielded ones (10-H and 10′-H).

This observation was confirmed by a computational calculation performed with the PM3 method which showed that C-11 had a charge of –0.10 au whereas C-10 had a charge ten times smaller (–0.010 au). The charge and the chemical shift were opposed because we observed that C-11 was more shielded than C-10. Proton 9-H (multiplet) appeared at 3.80 ppm. The COSY spectrum of this same compound **7c** (Figure 5) allowed us to complete the assignment.

We have seen that 11-H and 11′-H were the less shielded protons (2.80 or 3.45 ppm). Proton 9-H at 3.80 ppm was strongly coupled (intense correlation) with the signal at 3.45 ppm which corresponded to 11′-H. The observed coupling 9-H–11-H (weak correlation) suggested that 11-H appeared at 2.80 ppm. We observed the following coupling constants: $J_{H11'\text{-}H9} = 5.1$ Hz, $J_{H11\text{-}H9} \approx 0$ Hz. These values were theoretically confirmed from a Dreiding molecular model of **7c**; the observed dihedral angles were 40° and 80°, respectively.



7c Ar = p-anisyl

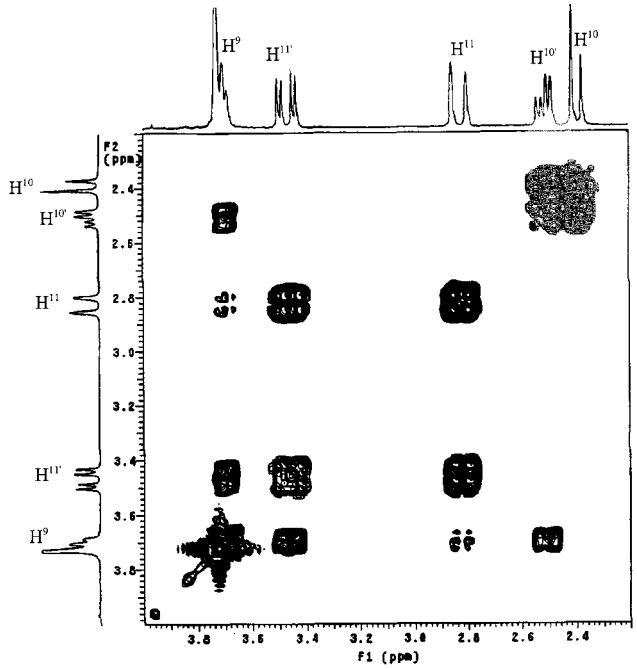


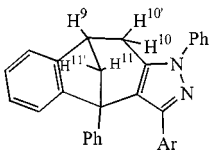
Figure 5. COSY spectrum of **7c** (Ar = *p*-anisyl)

The Karplus relation gave the theoretical coupling constants $J_{H11'\text{-}H9}$ = 4.7 Hz and $J_{H11\text{-}H9}$ = 0 Hz. The same reasoning was used in the case of 10-H and 10′-H. The signal at 2.40 ppm, which did not give any correlation with 9-H, was thus due to 10-H. Proton 10′-H resonated at 2.50 ppm. We found $J_{H9\text{-}H10}$ = 0 Hz and $J_{H9\text{-}H10'}$ = 5.0 Hz, in good agreement with the theoretical values of $J_{H9\text{-}H10}$ = 0 Hz and $J_{H9\text{-}H10'}$ = 4.5 Hz.

An X-ray study of a monocrystal of **7c** (Figure 6, Ar = *p*-anisyl) has facilitated the structural attribution of pyrazole derivatives **7**.

Conclusion

The pyrazolines produced by the reaction of 6,6-diphenylpentafulvene with diarylnitrilimines have a particular behaviour departing on the regiochemistry of the cycloaddition. They rearrange in acidic medium to give, quantitatively, new polyheterocyclic products. The mechanisms which explain these transformations are different from those known until now in that they are not initiated by protonation of the sp^3 nitrogen atom but by that of an sp^2 carbon.



7c Ar = p-anisyl

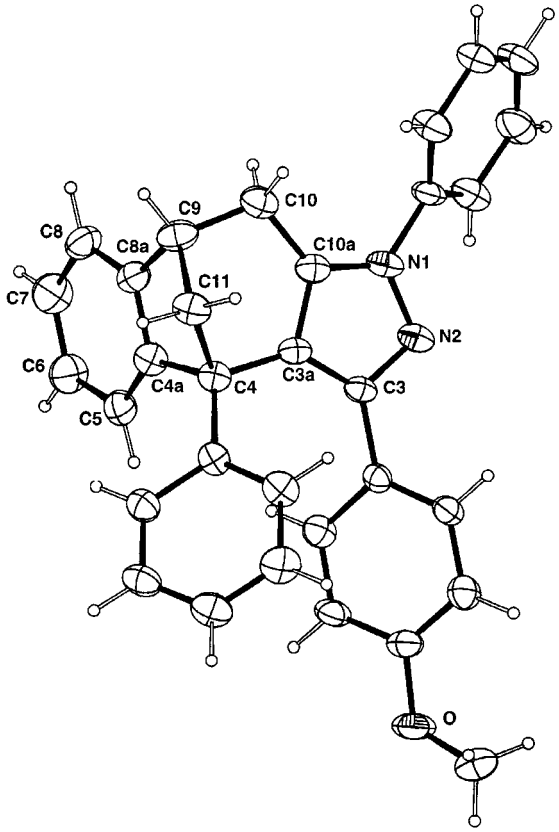


Figure 6. The molecular structure of **7c** (Ar = *p*-anisyl)

Experimental Section

Melting points were carried out on an Electrothermal IA 9200 instrument and are uncorrected. IR spectra (KBr) were recorded on a Bio-Rad FTS-7 spectrophotometer. H^1 and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz for ^1H and 50.3 MHz for ^{13}C) or AVANCE 300 (300 MHz for ^1H and 75 MHz for ^{13}C) spectrometers in $CDCl_3$ and TMS as internal standard. Analytical data were obtained by the CNRS Vernaison (France) and were satisfactory (C, H, N ± 0.4% from theoretical).

X-ray Crystal Structure of 5b: Crystal data: $C_{32}H_{26}N_2$, M_W = 438.55, crystal of 0.425 × 0.275 × 0.037 mm, monoclinic, space group *P*21/*c*, *Z* = 4, *a* = 15.268(6), *b* = 9.9222(14), *c* = 16.030(7) Å, *β* = 109.535(17)°, *V* = 2327.7 Å^3, d_{calc} = 1.251 g.cm^{-3}, *F*(000) = 928, λ = 0.71073 Å (Mo-K_α), Nonius CAD4 diffractometer, theta range: 1.42–24.93, 4236 collected reflections, 4074 unique (R_{int} = 0.0423), full-matrix least-squares (SHELXL93), *R* = 0.0628, *wR*2 = 0.1097 for 4074 unique reflections, residual electron density between –0.307 and 0.226 e.A^{-3}. For further information see ref.[7]

X-ray Crystal Structure of 7c: Crystal data: $C_{32}H_{26}N_2O$, M_W = 454.55, colourless crystal of 0.40 × 0.40 × 0.05 mm, monoclinic, space group $P2_1$, *Z* = 4, *a* = 10.282(4), *b* = 12.652(7), *c* =

18.570(9) Å, β = 91.360(10)°, V = 2415.1(20) Å^3, d_{calc} = 1.250 g.cm^{-3}, $F(000)$ = 960, λ = 1.54180 Å (Cu-K_α), μ = 0.587, Nonius CAD4 diffractometer, theta range: 4.23–66.96, 6412 collected reflections, 6206 unique (R_{int} = 0.0691), 4307 observed [$I > 2\sigma(I)$], full-matrix least-squares (SHELXL93), R = 0.0739 for 4307 observed reflections, $wR2$ = 0.2049 for 6206 unique reflections, residual electron density between –0.354 and 0.301 e.A^{-3}. For further information see ref.[7]

The diarylnitrilimines **2** were prepared in situ by dehydrohalogenation of 1-aryl(chloro)methylene-2-phenylhydrazines.[8,9,10] 6,6-Diphenylpentafulvene **(1)** was synthesised by condensation of cyclopentadiene with benzophenone in a solution of CH_3COONa according to G. Kresze et al.[11]

Cycloadducts 3 and 4. – General Procedure: To a magnetically stirred solution of fulvene **1** (10 mmol) and 1-aryl(chloro)methylene-2-phenylhydrazine **2** (10 mmol) in toluene (60 mL), was added a solution of triethylamine (6 mL) in the same solvent (10 mL) during 5 min. The mixture was stirred and refluxed for 24 h. After filtration of triethylamine chlorohydrate, the solvent was evaporated in vacuo. The reaction product was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether (bp. 40–60 °C); analytical samples were obtained after recrystallization from ethanol.

***cis*-1,3-Diphenyl-6-diphenylmethylene-3a,6a-dihydrocyclopenta-[*c*]pyrazole (3a):** Chromatographic separation with CH_2Cl_2/petroleum ether (60:40) gave **3a** in 42% yield. – R_f = 0.5. – M.p. 190 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (ddd, J = 7.9 Hz, J = 2.1 Hz, J = 2.1 Hz, 1 H, 3a-H), 5.65 (d, J = 7.9 Hz, 1 H, 6a-H), 6.05 (dd, J = 5.8 Hz, J = 2.1 Hz, 1 H, 4-H), 6.55 (dd, J = 5.8 Hz, J = 2.1 Hz, 1 H, 5-H), 6.60–8.00 (m, 20 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 56.2 (C-5), 66.5 (C-1). – $C_{31}H_{24}N_2$ (424.5): calcd. C 87.73, H 5.69, N 6.59; found C 87.47, H 5.65, N 6.64.

***cis*-6-Diphenylmethylene-3-(4-methylphenyl)-1-phenyl-3a,6a-dihydrocyclopenta[*c*]pyrazole (3b):** Chromatographic separation with CH_2Cl_2/petroleum ether (50:50) gave **3b** in 27% yield. – R_f = 0.7. – M.p. 231 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 4.70 (ddd, J = 8.1 Hz, J = 2.1 Hz, J = 2.1 Hz, 1 H, 3a-H), 5.65 (d, J = 8.1 Hz, 1 H, 6a-H), 6.05 (dd, J = 5.8 Hz, J = 2.1 Hz, 1 H, 4-H), 6.55 (dd, J = 5.8 Hz, J = 2.1 Hz, 1 H, 5-H), 6.50–7.60 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.3 (CH_3), 56.4 (C-5), 66.4 (C-1). – $C_{32}H_{26}N_2$ (438.5): calcd. C 87.65, H 5.97, N 6.38; found C 87.86, H 6.05, N 6.43.

***cis*-6-Diphenylmethylene-3-(4-methoxyphenyl)-1-phenyl-3a,6a-dihydrocyclopenta[*c*]pyrazole (3c):** Chromatographic separation with CH_2Cl_2/petroleum ether (80:20) gave **3c** in 40% yield. – R_f = 0.5. – M.p. 213 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 4.75 (ddd, J = 8.2 Hz, J = 2.1 Hz, J = 2.1 Hz, 1 H, 3a-H), 5.65 (d, J = 8.2 Hz, 1 H, 6a-H), 6.05 (dd, J = 5.8 Hz, J = 2.1 Hz, 1 H, 4-H), 6.60 (dd, J = 5.8 Hz, J = 2.1 Hz, 1 H, 5-H), 6.70–7.90 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 55.2 (C-5), 56.5 (OCH_3), 66.4 (C-1). – $C_{32}H_{26}N_2O$ (454.5): calcd. C 84.56, H 5.76, N 6.16; found C 84.26, H 5.83, N 6.21.

***cis*-6-Diphenylmethylene-3-(4-nitrophenyl)-1-phenyl-3a,6a-dihydrocyclopenta[*c*]pyrazole (3d):** Chromatographic separation with CH_2Cl_2/petroleum ether (60:40) gave **3d** in 34% yield. – R_f = 0.6. – M.p. 228 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (ddd, J = 8.5 Hz, J = 2.1 Hz, J = 1.8 Hz, 1 H, 3a-H), 5.90 (d, J = 8.5 Hz, 1 H, 6a-H), 6.05 (dd, J = 5.5 Hz, J = 2.1 Hz, 1 H, 4-H), 6.65 (dd, J = 5.5 Hz, J = 1.8 Hz, 1 H, 5-H), 6.70–8.40 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 55.3 (C-5), 66.9 (C-1). – $C_{31}H_{23}N_3O_2$ (469.5): calcd. C 79.30, H 4.94, N 8.95; found C 79.20, H 4.97, N 8.77.

***cis*-1,3-Diphenyl-4-diphenylmethylene-3a,6a-dihydrocyclopenta-[*c*]pyrazole (4a):** Chromatographic separation with CH_2Cl_2/petroleum ether (60:40) gave **4a** in 8% yield. – R_f = 0.6. – M.p. 176 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.45 (d, J = 8.4 Hz, 1 H, 3a-H), 5.60 (ddd, J = 8.4 Hz, J =1.8 Hz, J = 1.1 Hz, 1 H, 6a-H), 6.15 (dd, J = 5.9 Hz, J = 1.8 Hz, 1 H, 6-H), 6.60 (dd, J = 5.9 Hz, J = 1.1 Hz, 1 H, 5-H), 7.00–7.40 (m, 20 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 52.2 (C-5), 68.0 (C-1). – $C_{31}H_{24}N_2$ (424.5): calcd. C 87.71, H 5.69, N 6.59; found C 87.40, H 5.62, N 6.64.

***cis*-4-Diphenylmethylene-3-(4-methylphenyl)-1-phenyl-3a,6a-dihydrocyclopenta[*c*]pyrazole (4b):** Chromatographic separation with CH_2Cl_2/petroleum ether (50:50) gave **4b** in 9% yield. – R_f = 0.8. – M.p. 179 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 5.40 (d, J = 8.4 Hz, 1 H, 3a-H), 5.60 (ddd, J = 8.4 Hz, J = 1.8 Hz, J = 1.1 Hz, 1 H, 6a-H), 6.15 (dd, J = 5.9 Hz, J = 1.8 Hz, 1 H, 6-H), 6.60 (dd, J = 5.9 Hz, J = 1.1 Hz, 1 H, 5-H), 6.70–7.70 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.3 (CH_3), 52.2 (C-5), 67.8 (C-1). – $C_{32}H_{26}N_2$ (438.5): calcd. C 87.65, H 5.97, N 6.38; found C 87.73, H 6.15, N 6.33.

***cis*-4-Diphenylmethylene-3-(4-methoxyphenyl)-1-phenyl-3a,6a-dihydrocyclopenta[*c*]pyrazole (4c):** Chromatographic separation with CH_2Cl_2/petroleum ether (80:20) gave **4c** in 13.5% yield. – R_f = 0.6. – M.p. 204 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 5.40 (d, J = 8.4 Hz, 1 H, 3a-H), 5.55 (ddd, J = 8.4 Hz, J = 1.8 Hz, J = 1.6 Hz, 1 H, 6a-H), 6.15 (dd, J = 5.8 Hz, J = 1.8 Hz, 1 H, 6-H), 6.60 (dd, J = 5.8 Hz, J = 1.6 Hz, 1 H, 5-H), 6.60–7.50 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 56.4 (OCH_3), 51.2 (C-5), 67.9 (C-1). – $C_{32}H_{26}N_2O$ (454.5): calcd. C 84.56, H 5.76, N 6.16; found C 84.82, H 5.72, N 6.18.

***cis*-4-Diphenylmethylene-3-(4-nitrophenyl)-1-phenyl-3a,6a-dihydrocyclopenta[*c*]pyrazole (4d):** Chromatographic separation with CH_2Cl_2/petroleum ether (50:50) gave **4d** in 30% yield. – R_f = 0.6. – M.p. 206 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.50 (d, J = 8.7 Hz, 1 H, 3a-H), 5.70 (ddd, J = 8.7 Hz, J = 1.8 Hz, J = 1.5 Hz, 1 H, 6a-H), 6.15 (dd, J = 5.8 Hz, J = 1.8 Hz, 1 H, 6-H), 6.60 (dd, J = 5.8 Hz, J = 1.5 Hz, 1 H, 5-H), 6.70–8.00 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 51.4 (C-5), 68.6 (C-1). – $C_{31}H_{23}N_3O_2$ (469.5): calcd. C 73.30, H 4.94, N 8.95; found C 73.46, H 4.87, N 8.94.

Acidic Treatment of Cycloadducts 3 and 4. – General Procedure:[12,13,14] Cycloadduct **3** or **4** (0.1 g) in trifluoroacetic acid (10 mL) was refluxed for 2 h and then poured into an ice-water mixture (50 mL). After extraction with CH_2Cl_2 (2 × 30 mL), the layers were separated, and the organic phase was washed with saturated aqueous $NaHCO_3$ (20 mL), then with water (3 × 20 mL), and finally dried (Na_2SO_4), and the solvents evaporated in vacuo. In the case of **3**, compounds **5** precipitated and were purified by recrystallization from EtOH. The crude powdery product obtained after the treatment of **4** (which contained both **6** and **7**) was purified by column chromatography on silica gel with CH_2Cl_2 as eluent.

The same procedure was used for the synthesis of **7a** and **7c** from **6a** and **6c**. Reaction time: 4 h.

***cis*-2,5,5-Triphenyl-2a,3,5,10a-tetrahydrocyclopent[*cd*]pyrazolo-[1,5-*a*]quinoline (5a):** Yield quantitative. – M.p. 245 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.80 (dddd, J = 17.1 Hz, J = 2.2 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 3-H), 3.10 (ddd, J = 17.1 Hz, J = 8.3 Hz, J = 2.0 Hz, 1 H, 3′-H), 4.30 (ddd, J = 10.4 Hz, J = 8.3 Hz, J = 2.0 Hz, 1 H, 2a-H), 4.70 (ddd, J = 10.4 Hz, J = 2.3 Hz, J = 2.0 Hz,

1 H, 10a-H), 5.30 (ddd, J = 2.0 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 4-H), 6.60–7.80 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 39.2 (C-3), 48.6 (C-2a), 56.4 (C-5), 67.9 (C-10a). – $C_{31}H_{24}N_2$ (424.5): calcd. C 87.71, H 5.69, N 6.59; found C 87.62, H 5.74, N 6.56.

***cis*-2-(4-Methylphenyl)-5,5-diphenyl-2a,3,5,10a-tetrahydrocyclopent[*cd*]pyrazolo[1,5-*a*]quinoline (5b):** Yield quantitative. – M.p. 230 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3) 2.75 (dddd, J = 17.0 Hz, J = 2.1 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 3-H), 3.00 (ddd, J = 17.0 Hz, J = 8.5 Hz, J = 2.0 Hz, 1 H, 3′-H), 4.25 (ddd, J = 10.2 Hz, J = 8.5 Hz, J = 2.0 Hz, 1 H, 2a-H), 4.70 (ddd, J = 10.3 Hz, J = 2.1 Hz, J = 2.0 Hz, 1 H, 10a-H), 5.30 (ddd, J = 2.0 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 4-H), 6.60–7.80 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.3 (CH_3) 39.3 (C-3), 48.6 (C-2a), 56.4 (C-5) 67.9 (C-10a). – $C_{32}H_{26}N_2$ (438.5): calcd. C 87.65, H 5.97, N 6.38; found C 87.92, H 6.08, N 6.34.

***cis*-2-(4-Methoxyphenyl)-5,5-diphenyl-2a,3,5,10a-tetrahydrocyclopent[*cd*]pyrazolo[1,5-*a*]quinoline (5c):** Yield quantitative. – M.p. 258 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.80 (dddd, J = 16.6 Hz, J = 2.0 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 3-H), 3.10 (ddd, J = 16.6 Hz, J = 8.4 Hz, J = 2.0 Hz, 1 H, 3′-H), 3.80 (s,3 H, OCH_3), 4.25 (ddd, J = 10.2 Hz, J = 8.5 Hz, J = 2.0 Hz, 1 H, 2a-H), 4.70 (ddd, J = 10.3 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 10a-H), 5.30 (ddd, J = 2.0 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 4-H), 6.60–7.80 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 39.3 (C-3), 48.8 (C-2a), 55.2 (OCH_3), 56.5 (C-5) 67.9 (C-10a). – $C_{32}H_{26}N_2O$ (454.5): calcd. C 84.56, H 5.76, N 6.16; found C 84.63, H 5.74, N 6.09.

***cis*-2-(4-Nitrophenyl)-5,5-diphenyl-2a,3,5,10a-tetrahydrocyclopent[*cd*]pyrazolo[1,5-*a*] quinoline (5d):** Yield quantitative. – M.p. 262 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.80 (dddd, J = 16.6 Hz, J = 2.0 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 3-H), 3.10 (ddd, J = 16.6 Hz, J = 8.4 Hz, J = 2.0 Hz, 1 H, 3′-H), 3.80 (s,3 H, OCH_3), 4.25 (ddd, J = 10.2 Hz, J = 8.5 Hz, J = 2.0 Hz, 1 H, 2a-H), 4.70 (ddd, J = 10.3 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 10a-H), 5.30 (ddd, J = 2.0 Hz, J = 2.0 Hz, J = 2.0 Hz, 1 H, 4-H), 6.60–7.80 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 39.6 (C-3), 47.7 (C-2a), 56.5 (C-5), 69.0 (C-10a),. – $C_{31}H_{23}N_3O_2$ (469.5): calcd. C 79.30, H 4.94, N 8.95; found C 79.66, H 5.01, N 8.90.

1,3-Diphenyl-5-[1-(3-phenylindenyl)methyl]pyrazole (6a): Yield 90%. – M.p. 72–74 °C. – R_f = 0.7. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.90 (dd, J = 15.2 Hz, J = 9.3 Hz, 1 H, H^b), 3.30 (dd, J = 15.2 Hz, J = 6.3 Hz, 1 H, $H^{b'}$), 3.80 (ddd, J = 9.3 Hz, J = 6.3 Hz, J = 2.0 Hz, 1 H, 1-H), 6.50 (d, J = 2.0 Hz, 1 H, 2-H), 6.70 (s, 1 H, 4-H), 7.00–8.00 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 28.5 (C-b), 48.2 (C-1). – $C_{31}H_{24}N_2$ (424.5): calcd. C 87.71, H 5.69, N 6.59; found C 88.07, H 5.71, N 6.57.

3-(4-Methylphenyl)-1-phenyl-5-[1-(3-phenylindenyl)methyl]pyrazole (6b): Yield 70%. – M.p. 82 °C. – R_f = 0.4. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 2.85 (dd, J = 15.2 Hz, J = 9.1 Hz, 1 H, H^b), 3.30 (dd, J = 15.2 Hz, J = 6.7 Hz, 1 H, $H^{b'}$), 3.80 (ddd, J = 9.1 Hz, J = 6.7 Hz, J = 2.4 Hz, 1 H, 1-H), 6.50 (d, J = 2.4 Hz, 1 H, 2-H), 6.65 (s, 1 H, 4-H), 7.00–8.00 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.0 (CH_3), 28.5 (C-b), 48.2 (C-1). – $C_{32}H_{26}N_2$ (438.5): calcd. C 87.65, H 5.97, N 6.38; found C 87.39, H 5.82, N 6.07.

3-(4-Methoxyphenyl)-1-phenyl-5-[1-(3-phenylindenyl)methyl]-pyrazole (6c): Yield 70%. – M.p. 80 °C. – R_f = 0.6. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.90 (dd, J = 15.3 Hz, J = 9.4 Hz, 1 H, H^b), 3.30 (dd, J = 15.3 Hz, J = 6.2 Hz, 1 H, $H^{b'}$), 3.80 (ddd, J = 9.4 Hz, J = 6.2 Hz, J = 1.9 Hz, 1 H, 1-H), 3.80 (s, 3 H, OCH_3), 6.50 (d, J = 1.9 Hz, 1 H, 2-H), 6.70 (s, 1 H, 4-H), 6.30–8.00 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 28.4 (C-b), 48.0 (C-1), 55.2 (OCH_3). – $C_{32}H_{26}N_2O$ (454.5): calcd. C 84.56, H 5.76, N 6.16; found C 84.64, H 5.72, N 6.16.

3-(4-Nitrophenyl)-1-phenyl-5-[1-(3-phenylindenyl)methyl]pyrazole (6d): Yield 50%. – M.p. 135 °C. – R_f = 0.8. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.95 (dd, J = 15.3 Hz, J = 9.3 Hz, 1 H, H^b), 3.35 (dd, J = 15.3 Hz, J = 6.1 Hz, 1 H, $H^{b'}$), 3.80 (ddd, J = 9.3 Hz, J = 6.1 Hz, J = 2.1 Hz, 1 H, 1-H), 6.45 (d, J = 2.1 Hz, 1 H, 2-H), 6.75 (s, 1 H, 4-H), 7.00–8.00 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 28.4 (C-b), 48.0 (C-1). – $C_{31}H_{23}N_3O_2$ (469.5): calcd. C 79.30, H 4.94, N 8.95; found C 79.46, H 5.17, N 8.61.

1,3,4-Triphenyl-4,9-dihydro-10*H*-4,9-methanobenzo[4,5]cyclohepta-[1,2-*c*]pyrazole (7a): Yield 10%. – M.p. 200 °C. – R_f = 0.5. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (d, J = 10.7 Hz, 1 H, 10-H), 2.50 (dd, J = 10.7 Hz, J = 5.0 Hz, 1 H, 10′-H), 2.80 (d, J = 16.2 Hz, 1 H, 11-H), 3.45 (dd, J = 16.2 Hz, J = 5.0, 1 H, 11′-H), 3.70 (dd, J = 5.0 Hz, J = 5.0, 1 H, 9-H), 6.80–7.70 (m, 19 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.2 (C-11), 39.0 (C-9), 53.3 (C-4), 55.3 (C-10). – $C_{31}H_{24}N_2$ (424.5): calcd. C 87.71, H 5.69, N 6.59; found C 87.54, H 5.63, N 6.68.

3-(4-Methylphenyl)-1,4-diphenyl-4,9-dihydro-10*H*-4,9-methanobenzo[4,5]cyclohepta[1,2-*c*]pyrazole (7b): Yield 30%. – M.p. 235 °C. – R_f = 0.2. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3) 2.40 (d, J = 10.7 Hz, 1 H, 10-H), 2.50 (dd, J = 10.7 Hz, J = 5.0 Hz, 1 H, 10′-H), 2.80 (d, J = 16.2 Hz,1 H, 11-H), 3.45 (dd, J = 16.2 Hz, J = 5.0, 1 H, 11′-H), 3.70 (dd, J = 5.0 Hz, J = 5.0, 1 H, 9-H), 6.80–7.70 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.0 (CH_3), 31.2 (C-11), 39.0 (C-9), 53.3 (C-4), 55.3 (C-10). – $C_{32}H_{26}N_2$ (438.5): calcd. C 87.65, H 5.97, N 6.38; found C 87.53, H 6.25, N 6.41.

3-(4-Methoxyphenyl)-1,4-diphenyl-4,9-dihydro-10*H*-4,9-methanobenzo[4,5]cyclohepta[1,2-*c*]pyrazole (7c): Yield 30%. – M.p. 180 °C. – R_f = 0.5. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (d, J = 10.8 Hz, 1 H, 10-H), 2.50 (dd, J = 10.8 Hz, J = 5.0 Hz, 1 H, 10′-H), 2.80 (d, J = 16.2 Hz, 1 H, 11-H) 3.45 (dd, J = 16.2 Hz, J = 5.1, 1 H, 11′-H), 3.70 (dd, J = 5.1 Hz, J = 5.0, 1 H, 9-H), 3.80 (s, 3 H, OCH_3), 6.50–7.60 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.2 (C-11), 39.0 (C-9), 53.6 (C-4), 55.0 (OCH_3), 55.2 (C-10). – $C_{32}H_{26}N_2O$ (454.5): calcd. C 84.56, H 5.76, N 6.16; found C 84.75, H 5.69, N 6.32.

3-(4-Nitrophenyl)-1,4-diphenyl-4,9-dihydro-10*H*-4,9-methanobenzo[4,5]cyclohepta[1,2-*c*]pyrazole (7d): Yield 50%. – M.p. 260 °C. – R_f = 0.6. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (d, J = 10.8 Hz, 1 H, 10-H), 2.55 (dd, J = 10.8 Hz, J = 4.9 Hz, 1 H, 10′-H), 2.85 (d, J = 16.2 Hz, 1 H, 11-H), 3.45 (dd, J = 16.2 Hz, J = 5.0, 1 H, 11′-H), 3.75 (dd, J = 5.0 Hz, J = 4.9 Hz, 1 H, 9-H), 7.00–8.00 (m, 18 H, aromatic). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.0 (C-11), 38.8 (C-9), 53.5 (C-4), 54.9 (C-10). – $C_{31}H_{23}N_{23}O_2$ (469.5): calcd. C 79.30, H 4.94, N 8.95; found C 79.41, H 4.87, N 9.07.

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