# Synthesis and Structure of New Hosts Related to 9,9′-Biianthryl

**Gérard Boyer,[a] Rosa M. Claramunt,*[,a] José Elguero,[a] Mohamed Fathalla,[c]
Concepción Foces-Foces,*[,b] Carlos Jaime[c] and Antonio L. Llamas-Saiz[b]**
[a] *Departamento de Química Orgánica y Biología, Facultad de Ciencias, UNED, Ciudad Universitaria, E-28040 Madrid, Spain*
[b] *UEI de Cristalografía, Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, E-28006 Madrid, Spain*
[c] *Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Barcelona, 08193 Bellaterra, Spain*

The molecular structures of 10,10′-biacridinyl-9,9′-dione (**5**), 9-(10′-bromo-9′-anthryl)carbazole (**9**) and 9,9′-bicarbazyl (**12**) have been solved by X-ray crystallography. Proton and carbon-13 NMR studies of these and related compounds, show that in solution their conformations are also 'scissor-like'. AM1 semi-empirical calculations provide a rationale for the geometries of these compounds.

Toda,[1] Weber[2] and their coworkers introduced simultaneously the use of 9,9′-biianthryl as a 'scissor host without functional groups'.[3] We describe here the synthesis, NMR spectroscopy, X-ray structures (for compounds **5**, **9** and **12**) and molecular mechanics (MM2) and semi-empirical (AM1) calculations of related heterocyclic hosts, resulting from the replacement of one of the two 9-anthryl residues by either 10-acridinone or 9-carbazyl substituents.

## Results and Discussion

### *Chemistry*

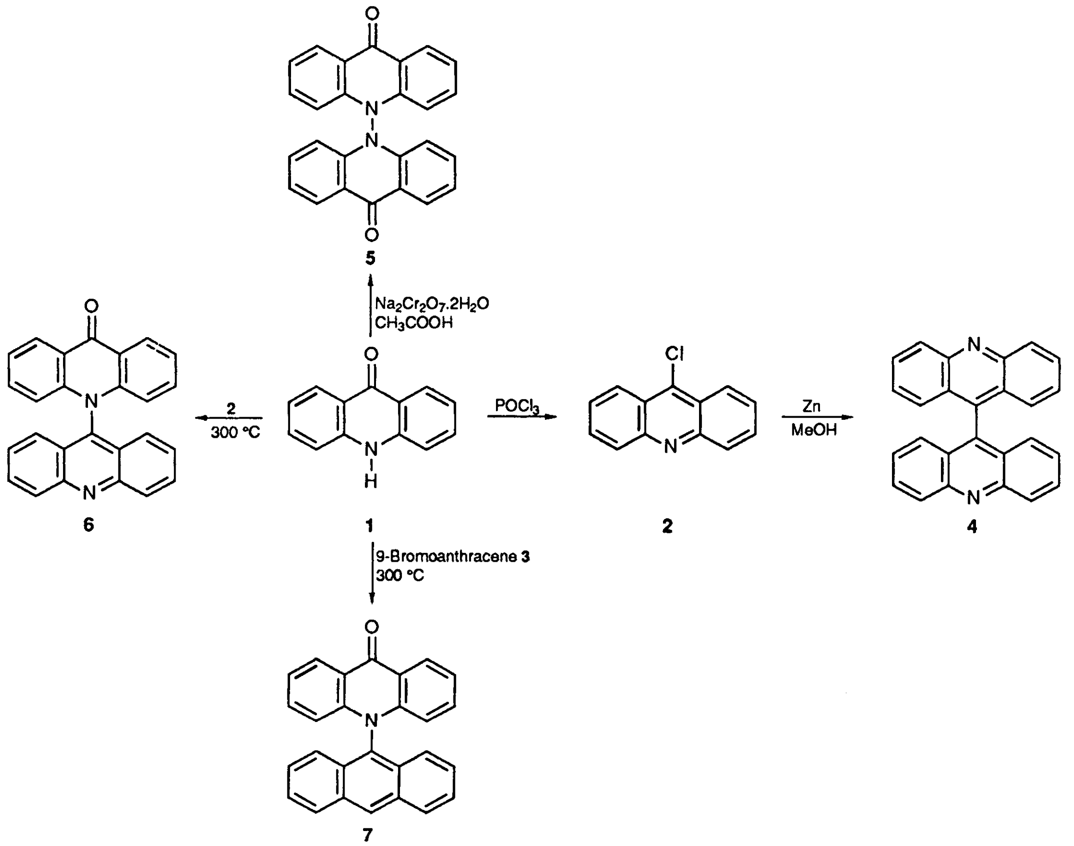
Synthetic procedures used for compounds **1–12** are summarized in Schemes 1 and 2. Symmetrical derivatives **4** and **5** (Scheme 1) are obtained by reduction or oxidation from acridin-9(10*H*)-one (**1**) and/or 9-chloroacridine (**2**). Asymmetrical compounds **6** and **7** were prepared by fusion at 300 °C of acridin-9(10*H*)-one with 9-chloroacridine or 9-bromoanthracene (**3**).

Carbazole (**8**) was used to prepare compounds **9–12** (Scheme 2). 9-(9′-Anthryl)carbazole (**10**) was obtained by fusion of carbazole and 9-bromoanthracene, since the method previously described by Zander[4] to prepare **10** when repeated, yielded instead 9-(9′-bromo-10′-anthryl)carbazole (**9**). Compound **11** was obtained by fusion using 9-chloroacridine (**2**) as solvent.

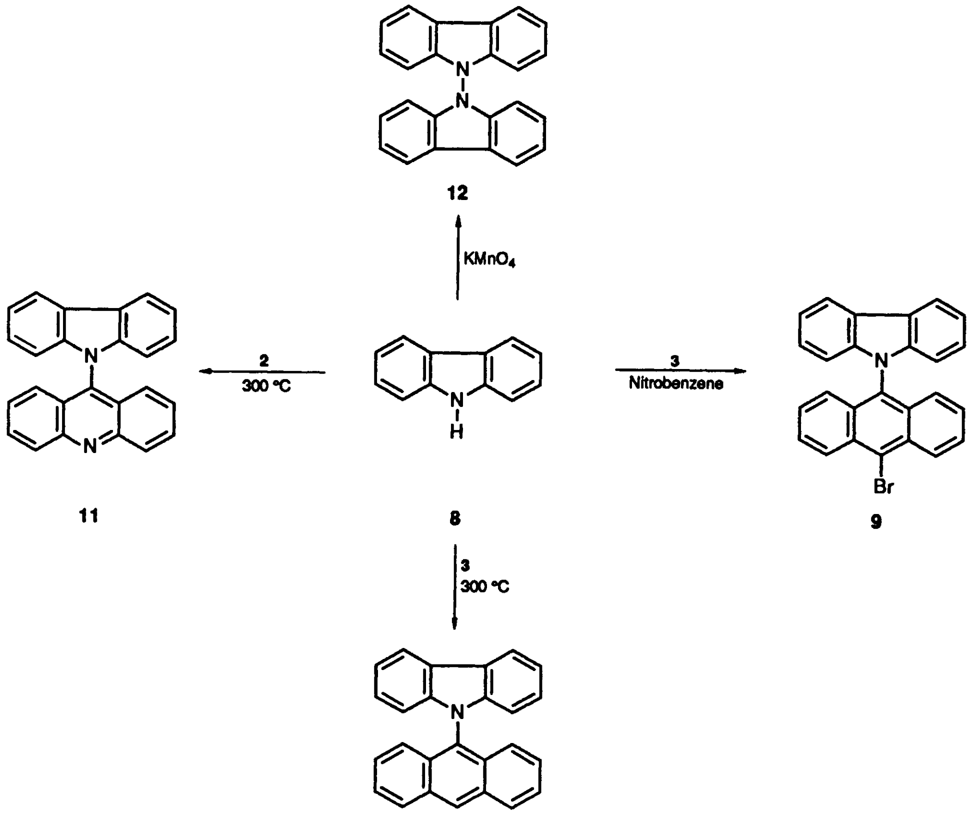
### *NMR Spectroscopy*

The chemical shifts of compounds **1–13** are given in Tables 1 and 2.

$^1$H *NMR Study*.—Analysis of the chemical shifts of bi-



**Scheme 1**



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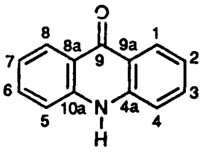
Scheme 2



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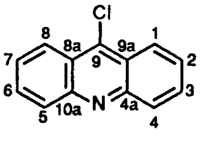

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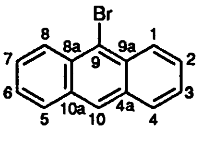

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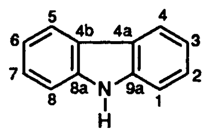

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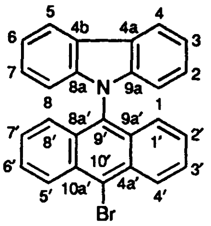

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acridinyl (**4**) and biacridinyldione (**5**) (see Scheme 1), revealed characteristic pattern spectra with a signal which appears as a 'doublet' (only an *ortho* coupling) at *ca.* 7 ppm, (H-1 of **4** = H-4 of **5**), this shielding being due to the proximity of the second ring. The other 'doublet' resonates downfield at 8.5 ppm, (H-4 of **4** = H-1 of **5**). Use of these results and COSY experiments allowed us to assign the signals of compounds **6** and **7** (Table 1). In both cases, H-1 and H-4 of the acridinone part are shifted respectively to 8.70 and 6.30 ppm. Next, two signals corresponding to the acridinic or anthracenic ring can be noted, the protons H-4′ and H-3′. The protons H-2, H-3, H-1′, H-2′ appear as a complex multiplet in a narrow range of frequencies, and are assigned by heteronuclear 2D experiments. In the case of 10-(9′-anthryl)acridin-9-one (**7**), one singlet characteristic of H-10′ is clearly identifiable (8.70 ppm). The complete analysis is difficult, since in $CDCl_3$ these compounds give an ABMX system with a deceptively simple spectrum; for this reason, $^1H$–$^1H$ coupling constants are not reported.

Concerning the derivatives of carbazole, compound **10** is easily differentiable from its homologue **9** by the appearance of a singlet at 8.65 ppm (see Table 1) [8.68 ppm for bianthryl (**13**)]; furthermore, it can be noted that H-3′ is deshielded by 0.19 ppm when there is a bromine in position 10′. Protons H-1′, H-2′, H-2, H-3 appear as a complex multiplet which was partially assigned using heteronuclear COSY experiments: H-1′ and H-2 resonate at 7.25 ppm, H-2′ and H-3 at *ca.* 7.30 ppm (in bianthryl, H-1′ and H-2′ appear at 7.10 and 7.14 ppm respectively).

In the case of compound **11**, acridine chemical shifts are very similar to those of its homologue **6**, with only the acridine proton H-2′, which appears shielded at 7.34 ppm, being significantly different. The protons H-2, H-3, H-1′ and H-2′ were assigned in the following order: $\delta$(H-1′) > $\delta$(H-2′) > $\delta$(H-3) >

**Table 1** 1H chemical shift ($\delta$) values of compounds **1–13** in $CDCl_3$ solution

| Compound | H-1 | H-2 | H-3 | H-4 | H-10 | H-1′ | H-2′ | H-3′ | H-4′ | H-10′ |
|---|---|---|---|---|---|---|---|---|---|---|
| **1**[a,b] | 8.22 | 7.24 | 7.71 | 7.53 | 9.38 | — | — | — | — | — |
| **2**[c] | 8.44 | 7.64 | 7.82 | 8.24 | — | — | — | — | — | — |
| **3** | 7.99 | 7.50 | 7.60 | 8.52 | 8.42 | — | — | — | — | — |
| **4** | 7.08 | 7.30 | 7.81 | 8.44 | — | — | — | — | — | — |
| **5** | 8.67 | 7.40 | 7.54 | 6.77 | — | — | — | — | — | — |
| **6** | 8.70 | 7.46[g] | 7.32[g] | 6.24 | — | 7.32[g] | 7.46[g] | 7.87 | 8.46 | — |
| **7** | 8.70 | 7.27[g] | 7.27[g] | 6.31 | — | 7.39[g] | 7.39[g] | 7.52 | 8.20 | 8.70 |
| **8**[d] | 8.08 | 7.24[g] | 7.24[g] | 7.42 | — | — | — | — | — | — |
| **9** | 6.71 | 7.25[g] | 7.31[h] | 8.28 | — | 7.25[g] | 7.28[h] | 7.63 | 8.71 | — |
| **10** | 6.71 | 7.22[f] | 7.27[g] | 8.27 | — | 7.22[f] | 7.28[g] | 7.44 | 8.11 | 8.65 |
| **11** | 6.76 | 7.29[h] | 7.34[g] | 8.29 | — | 7.38[h] | 7.34[g] | 7.82 | 8.43 | — |
| **12**[e] | 6.91 | 7.34[g] | 7.34[g] | 8.21 | — | — | — | — | — | — |
| **13**[f] | 7.10[h] | 7.14[h] | 7.45 | 8.15 | 8.68 | — | — | — | — | — |

[a] Values in $[^2H_6]$DMSO, the compound is insoluble in $CDCl_3$. [b] Values had been previously reported in the literature.[5] [c] Values had been previously reported in the literature.[6] [d] The values had been previously reported in the literature.[7] [e] Values in $CDCl_3$ calculated by iterative analysis had been previously reported in the literature.[8] [f] Values in $CDCl_3$ had been previously reported in the literature.[9] [g] These protons appear together as a complex multiplet. [h] Values obtained from the $2D(^1H-^{13}C)$ correlation spectra.

$\delta$(H-2) (see Table 1). As in compounds **6** and **7**, the coupling constants of **9–11** were not measurable, owing to their deceptively simple ABMX spectra.

$^{13}C$ *NMR Study*.—To simplify the discussion, two groups of compounds will be considered separately, one derived from acridin-9(10*H*)-one (**1**) (as parent compound, see Scheme 1), and the other derived from carbazole (**8**) (Scheme 2) (the $^1H-^{13}C$ coupling constants are reported in Table 3).

*First group.* Since acridin-9(10*H*)-one itself was insoluble in $CDCl_3$, its values in $[^2H_6]$DMSO were used to analyse spectra of compounds **5–7**. Biacridinyl (**4**) signals were assigned using acridine chemical shifts in $CDCl_3$,[14] and 9-chloroacridine (**2**) chemical shifts (see Table 2).

Substitution of acridin-9(10*H*)-one at the heterocyclic nitrogen produced normally a shielding of C-4, very strong in the case of biacridinyldione (**5**) (see Table 4, $\Delta_1$ **6**/**1**) and a small deshielding for C-1, C-2 and C-3. Reciprocally, the C-1 carbon signal of biacridinyl (**4**) is shielded (see $\Delta_3$ **4**/acridine in Table 5). For comparison, chemical shifts values of **5** in $[^2H_6]$DMSO relative to acridin-9(10*H*)-one are given in Table 4: $\Delta$ **5**/**1** values are very close to values calculated for $\Delta_1$ **5**/**1** (Table 5), with a small difference of 1 ppm ($[^2H_6]$DMSO) in the case of C-1 due to the proximity of the carbonyl group.

To characterize the mixed compounds **6** and **7**, heteronuclear $(^1H-^{13}C)$2D correlation spectroscopy experiments were used. For compound **6**, C-1′ and C-2 were differentiated using a COLOC experiment (C-1′: 122.74 ppm and C-2: 122.31 ppm). In every case, the C-1′ of the acridinyl rings is highly shielded (see $\Delta_3$ values in Table 5). Finally, a DEPT experiment was used to assign the chemical shift of C-10′ of compound **7** at 129.14 ppm, which is deshielded by *ca.* 3 ppm relative to anthracene.

*Second group.* Using carbazole (**8**) as reference compound, the bicarbazyl (**12**) was easily characterized, showing slight shielding of C-1 (see $\Delta_2$ values in Table 5).

Heteronuclear $(^1H-^{13}C)$2D correlation experiments were performed to assign the chemical shifts of the asymmetric compounds **9–11**; $^{13}C$ chemical shifts of bianthryl (**13**) were also used (see Table 2). For 9-(9′-acridyl)carbazole (**11**), the acridine ring was used as substituent residue to avoid different numberings. Table 5 shows similar effects consisting of a large shielding of C-1′ when carbazole or acridin-9(10*H*)-one is used as reference compound (see $\Delta_3$ **6**/acridine and $\Delta_3$ **11**/acridine in Table 5). On the other hand, the substituent effects are increased in the case of 10-(9′-acridyl)acridin-9-one (**6**) regarding C-1′ and C-2′. 9-(10′-Bromo-9′-anthryl)carbazole **9** was characterized by comparison with its homologue **10**; examination of its chemical shifts revealed that, owing to the presence of a bromine atom at position 9, C-10′ and C-3′ were deshielded by respectively 3.7 and 1.85 ppm, whereas C-4a′ appeared downfield at 130.57 ppm. Using heteronuclear experiments, it is possible to determine, even for a small range of frequencies, that the typical chemical shift order is $\delta$(C-2′) > $\delta$(C-2) > $\delta$(C-3′) > $\delta$(C-1′) > $\delta$(C-3) for non-substituted compound **10**, and $\delta$(C-3′) > $\delta$(C-2′) > $\delta$(C-2) > $\delta$(C-1′) > $\delta$(C-3) for compound **9** (see $^1H$ NMR study) [the same order of frequencies being observed for 9-(9′-acridyl)carbazole (**11**)].

$^{13}C-^1H$ *Coupling Constants*.—The coupling constants of the heterocyclic moieties (Table 3) showed that there is no significant change of $^1J$ values with changes in the other half-substituent (within 1–3 Hz).

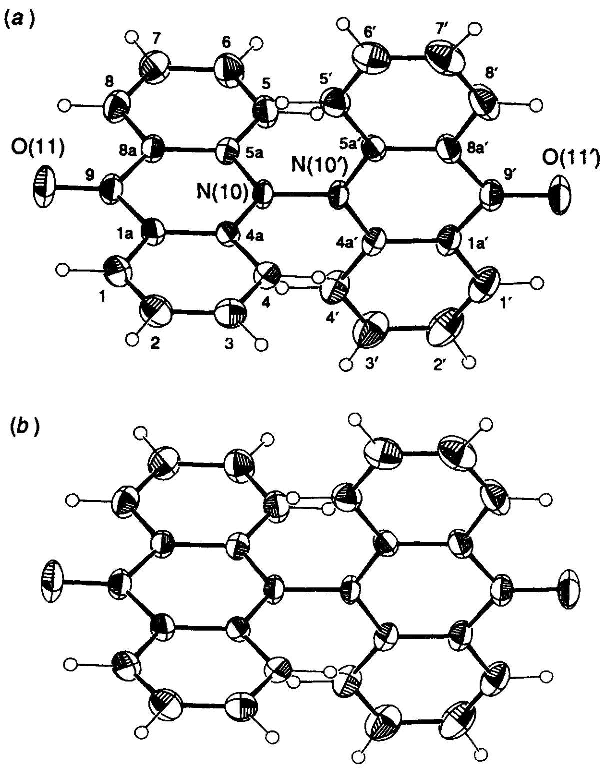


Fig. 1 Molecular structure of compound **5** showing the numbering system

**Table 2** $^{13}C$ Chemical shift ($\delta$) values of compounds **1**–**13** in $CDCl_3$ solution

| Compound | C-1 | C-2 | C-3 | C-4 | C-9 | C-10 | C-1′ | C-2′ | C-3′ | C-4′ | C-9′ | C-10′ | C-4a | C-9a | C-4a′ | C-9a′ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1**[a,b] | 125.99 | 120.96 | 133.41 | 117.30 | 176.99 | — | — | — | — | — | — | — | 140.86 | 120.46 | — | — |
| **2**[c] | 124.30 | 126.62 | 130.34 | 129.40 | 140.95 | — | — | — | — | — | — | — | 148.44 | 123.91 | — | — |
| **3**[d] | 127.58 | 127.15 | 125.60 | 128.56 | 122.31 | 127.07 | — | — | — | — | — | — | 132.11 | 130.54 | — | — |
| **4** | 126.20 | 126.75 | 130.58 | 129.80 | 141.18 | — | — | — | — | — | — | — | 148.47 | 125.74 | — | — |
| **5** | 128.43 | 123.62 | 135.14 | 123.57 | 177.37 | — | — | — | — | — | — | — | 140.82 | 122.55 | — | — |
| **6**[e] | 127.65 | 122.31 | 134.05 | 116.46 | 178.15 | — | 122.74 | 128.33 | 131.10 | 130.49 | 140.00 | — | 142.64 | 122.01 | 150.42 | 124.35 |
| **7**[f] | 128.11 | 122.55 | 133.81 | 116.88 | 178.38 | — | 121.87 | 126.18 | 127.43 | 129.09 | 127.90 | 129.14 | 143.35 | 122.14 | 132.31 | 129.43 |
| **8**[g] | 110.55 | 125.80 | 119.40 | 120.30 | — | — | — | — | — | — | — | — | 123.32 | 139.45 | — | — |
| **9**[f] | 110.18 | 126.22 | 120.07 | 120.46 | — | — | 123.87 | 127.34 | 127.62 | 128.35 | 129.32 | 124.53 | 123.17 | 142.54 | 130.57 | 131.06 |
| **10**[f] | 110.29 | 126.07 | 119.83 | 120.39 | — | — | 123.48 | 126.99 | 125.78 | 128.71 | 128.78 | 128.23 | 123.14 | 142.56 | 132.07 | 129.89 |
| **11**[e] | 110.24 | 126.35 | 120.48 | 120.54 | — | — | 123.80 | 127.05 | 130.67 | 130.13 | 139.40 | — | 123.46 | 142.14 | 150.10 | 124.43 |
| **12** | 109.06 | 126.56 | 121.20 | 120.60 | — | — | — | — | — | — | — | — | 121.95 | 139.78 | — | — |
| **13** | 126.82 | 125.80 | 125.30 | 128.52 | 133.06 | — | — | — | — | — | — | 127.21 | 131.52[h] | 131.60[h] | — | — |

[a] Values in [$^2H_6$]DMSO, the compound is insoluble in $CDCl_3$. [b] Values in [$^2H_6$]DMSO had been previously reported in the literature.[10] [c] Values in $CDCl_3$ had been previously reported in the literature.[11] [d] Values in $CDCl_3$ had been previously reported in the literature.[12] [e] These carbons belong to the acridine ring. [f] These carbons belong to the anthracene ring. [g] Values in $CDCl_3$ had been previously reported in the literature.[13] [h] These signals may be reversed.

**Table 3** ${}^1J$ (${}^1H$–${}^{13}C$) coupling constants (Hz) of compounds **4**–**7** and **9**–**13** in $CDCl_3$ solution

| Compound | C-1/1-H<br>C-1′/1′-H | C-2/2-H<br>C-2′/2′-H | C-3/3-H<br>C-3′/3′-H | C-4/4-H<br>C-4′/4′-H | C-10/10-H<br>C-10′/10′-H |
|---|---|---|---|---|---|
| **4** | 162.8 | 162.8 | 160.4 | 162.9 | — |
| | — | — | — | — | — |
| **5** | 165.0 | 164.6 | 161.9 | 163.3 | — |
| | — | — | — | — | — |
| **6** | 164.8 | 164.0 | 161.4 | 161.8 | — |
| | 164.0 | 164.8 | 162.7 | 164.0 | — |
| **7** | 162.3 | 163.0 | 160.6 | 161.6 | — |
| | 163.7 | 160.8 | 163.9 | 160.8 | *a* |
| **9** | 160.2 | 159.0 | 160.2 | 157.9 | — |
| | 163.9 | 163.3 | 161.7 | 162.9 | — |
| **10** | 161.0 | 159.0 | 160.2 | 159.3 | — |
| | 163.0 | 161.8 | 160.9 | 160.5 | 159.6 |
| **11** | 160.4 | 159.0 | 160.5[b] | 160.5[b] | — |
| | 163.9 | 161.8 | 159.8 | 163.7 | — |
| **12** | 158.5 | 158.8 | 160.5 | 144.6 | — |
| | — | — | — | — | — |
| **13** | 161.5 | 161.5 | 160.5 | 159.4 | 158.8 |
| | — | — | — | — | — |

[a] Coupling constant not observed. [b] Values not differentiable.

**Table 4** Comparison of substituent effects: $\Delta_1$ [$\delta$ compounds **5**, **6**, **7** − $\delta$ acridin-9(10*H*)-one (**1**)],[a] $\Delta_2$ [$\delta$ compounds **9**, **10**, **11**, **12** − $\delta$ carbazole (**8**)]; $\Delta_3$ ($\delta$ compounds **4**, **6**, **11** − $\delta$ acridine);[17] $\Delta_4$ ($\delta$ compounds **7**, **9**, **10** − $\delta$ anthracene)[15]

| | C-1 | C-2 | C-3 | C-4 | C-9 | C-10 |
|---|---|---|---|---|---|---|
| $\Delta_1$ **5/1** | +2.44 | +2.66 | +1.74 | −3.73 | — | — |
| $\Delta_1$ **6/1** | +1.66 | +1.35 | +0.64 | −0.84 | — | |
| $\Delta_1$ **7/1** | +2.12 | +1.59 | +0.40 | −0.42 | — | — |
| $\Delta_2$ **9/8** | −0.37 | +0.42 | +0.67 | +0.16 | — | — |
| $\Delta_2$ **10/8** | −0.26 | +0.27 | +0.43 | +0.09 | — | — |
| $\Delta_2$ **11/8** | −0.31 | +0.55 | +1.08 | +0.24 | — | — |
| $\Delta_2$ **12/8** | −1.49 | +0.76 | +1.80 | +0.30 | — | — |
| $\Delta_3$ **4**/acridine | −4.30 | +1.05 | +2.08 | +0.10 | +5.08 | — |
| $\Delta_3$ **6**[b]/acridine | −7.76 | +2.63 | +2.60 | +0.79 | +3.90 | — |
| $\Delta_3$ **11**[b]/acridine | −6.70 | +1.35 | +2.17 | +0.43 | +3.30 | — |
| $\Delta_4$ **7**[b]/anthracene | −6.26 | +0.86 | +2.11 | +0.96 | +1.70 | +2.94 |
| $\Delta_4$ **9**[b]/**3** | −4.70 | +1.75 | +0.47 | +0.74 | +2.24 | +2.20 |
| $\Delta_4$ **10**[b]/anthracene | −4.65 | +1.67 | +0.46 | +0.58 | +2.58 | +2.03 |

[a] Values of acridin-9(10*H*)-one (**1**) refer to [$^2H_6$]DMSO. [b] Marked carbons as in Table 2.

**Table 5** ${}^{13}C$ Chemical shift ($\delta$) values of biacridinyldione (**5**) in [$^2H_6$]DMSO solution, and $\Delta$ 5/1 values[a]

| | C-1 | C-2 | C-3 | C-4 | C-9 | C-4a | C-9a |
|---|---|---|---|---|---|---|---|
| $\delta$ | 127.49 | 123.46 | 135.39 | 113.90 | 176.50 | 140.55 | 122.16 |
| $\Delta$ 5/1 | +1.5 | +2.50 | +1.98 | −3.4 | — | — | — |

[a] $\Delta$ [$\delta$ biacridonyl (**5**)–$\delta$ acridin-9(10*H*)-one (**1**)].

## *X-Ray Crystallography*

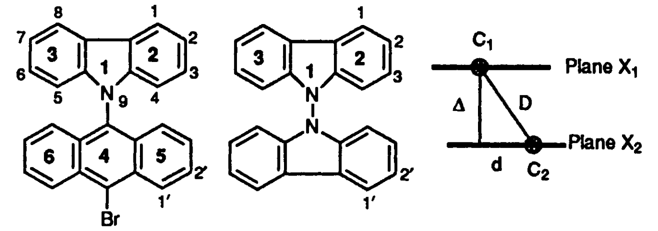
Recently,[15] the structure of 9,9′-bianthryl (**13**) has been reported. The averaged torsion angle between the anthracene rings (calculated from the atomic coordinates) is 74.2°. A view of the molecular structure of compound **5** with the numbering scheme used for atom labelling is shown in Fig. 1. For the labelling scheme of compounds **9** and **12**, see the heading of Table 6.

The conformation of each moiety of the molecule (tricyclic system) was characterized by a significant lack of planarity. The overall bend can be described by the angles between the mean least-squares planes of the central ring and each lateral phenyl ring, Table 6. Each half molecule is twisted with respect to the other by 85.3(3), 82.9(7) and 69.9(7), 70.2(8)° for **5**, **9** and the two molecules of **12** respectively. The corresponding Newman projections along the bond joining the two halves are displayed in Fig. 2. The molecules do not show any remarkable differences (bond distances and angles) with those moieties previously reported (Cambridge Structural Database).[16] The IR spectral data of the 9,9′-bicarbazyl molecule (**12**),[17] in the solid state, have been interpreted in terms of a $D_{2d}$ geometry (dihedral angle, 90°). The twisted $D_2$ geometry (dihedral angle ≠ 90°) was excluded. The results here reported show that these conclusions were erroneous and that the vibrational spectra of 9,9′-bicarbazyl must be re-interpreted on the basis of $D_2$ geometry (dihedral angle = 70°). The fluorescence of bianthryl (**13**) in the gas phase has been analysed assuming a dihedral angle between the two rings of 80°, which is reasonable considering the value (74.2°) in the crystal.[18]

The structures consist of discrete molecular units packed at approximately the van der Waals distances. The shortest intermolecular distances are given in Table 6. The packings are illustrated in Fig. 3, showing the local stacking (Table 6). Although in compound **12**, the distance between almost parallel phenyl rings is less than 3.0 Å, the glide between their centroids prevents any π interaction.

Smoothing of the van der Waals surface by rolling a sphere of 1.4 Å,[19] reveals that, in spite of the scissor-like conformation displayed by these molecules,[3] they are so closely packed that no voids are found in the crystal structures. The overall packing coefficient values are 0.69, 0.67 and 0.66 for **5**, **9** and **12**, values

**Table 6** Selected geometrical parameters. $C_1$–$C_6$ stand for the centroids of the corresponding rings



(*a*) Bond distances, angles and torsion angles (Å, °)

| | | | | |
|---|---|---|---|---|
| **5** | C(4a)–N(10) | 1.394(3) | C(5a′)–N(10′) | 1.390(3) |
| | C(4a′)–N(10′) | 1.392(3) | C(9)–O(11) | 1.232(4) |
| | C(5a)–N(10) | 1.393(3) | C(9′)–O(11′) | 1.238(4) |
| | N(10)–N(10′) | 1.393(3) | | |
| | C(4a)–N(10)–C(5a) | 123.5(2) | C(5a)–N(10)–N(10′) | 118.3(2) |
| | C(4a)–N(10)–N(10′) | 118.1(2) | C(4a′)–N(10′)–C(5a′) | 123.5(2) |
| | N(10)–N(10′)–C(5a′) | 118.3(2) | N(10)–N(10′)–C(4a′) | 118.2(2) |
| | C(5a)–N(10)–N(10′)–C(4a′) | −85.3(3) | | |
| **9** | C(4a)–N(9) | 1.391(7) | C(5a)–N(9) | 1.395(7) |
| | Br–C(9′) | 1.895(6) | N(9)–C(10′) | 1.432(7) |
| | C(4a)–N(9)–C(5a) | 108.4(4) | C(5a)–N(9)–C(10′) | 124.0(4) |
| | C(4a)–N(9)–C(10′) | 127.5(4) | C(4a′)–C(10′)–C(5a′) | 122.2(5) |
| | N(9)–C(10′)–C(5a′) | 118.8(5) | N(9)–C(10′)–C(4a′) | 119.0(5) |
| | C(5a)–N(9)–C(10′)–C(4a′) | 82.9(7) | | |
| **12** | C(4a)–N(9) | 1.382(9) | C(15a)–N(19) | 1.388(8) |
| | C(14a)–N(19) | 1.403(8) | N(9)–N(9′) | 1.372(6) |
| | C(5a)–N(9) | 1.365(7) | N(19)–N(19′) | 1.367(6) |
| | C(4a)–N(9)–C(5a) | 109.7(4) | C(5a)–N(9)–N(9′) | 124.8(2) |
| | C(4a)–N(9)–N(9′) | 125.5(3) | C(14a)–N(19)–C(15a) | 109.9(4) |
| | C(15a)–N(19)–N(19′) | 124.6(5) | C(14a)–N(19)–N(19′) | 125.6(5) |
| | C(4a)–N(9)–N(9′)–C(4a′) | 69.9(7) | C(14a)–N(19)–N(19′)–C(14a′) | 70.2(8) |

(*b*) Angles between planes ($X_1$,$X_2$)

| Compound | 1,2 | 1,3 | 4,5 | 4,6 |
|---|---|---|---|---|
| **5** | 1.1(1) | 0.6(1) | 3.2(1) | 1.3(1) |
| **9** | 0.3(2) | 1.1(2) | 1.4(2) | 0.8(1) |
| **12** Mol.1 | 2.7(2) | 1.7(2) | | |
| **12** Mol.2 | 1.9(2) | 0.6(2) | | |

| (*c*) C–H ⋯ Centroid contacts | C–H | C ⋯ Cent. | H ⋯ Cent. | C–H ⋯ Cent. |
|---|---|---|---|---|
| **5** C(2)–H(2) ⋯ $C_{4_i}$ | 1.03(4) | 3.705(3) | 2.69(4) | 164(3) |
| **12** C(6)–H(6) ⋯ $C_{3_{ii}}$ Mol.2 | 0.98(13) | 3.727(10) | 2.89(13) | 144(9) |
| **12** C(13)–H(13) ⋯ $C_{3_{iii}}$ Mol.2 | 1.18(10) | 3.699(11) | 2.72(10) | 140(6) |
| **12** C(16)–H(16) ⋯ $C_{3_{iv}}$ Mol.1 | 1.17(12) | 3.637(11) | 2.69(10) | 137(6) |

| (*d*) Compound | $X_1$,$X_2$ | D | Δ | *d* | $X_1 \wedge X_2$ |
|---|---|---|---|---|---|
| **5** | $5,5_v$ | 3.907(2) | 3.412(1) | 1.903(2) | 2.0(1) |
| **9** | $5,6_{vi}$ | 3.674(4) | 3.431(3) | 1.314(3) | 3.0(2) |
| **12** | 3 Mol.2, $2_{vii}$ Mol.1 | 5.745(5) | 2.737(4) | 5.051(4) | 3.3(3) |

i: $1 + x, y, z$. ii: $\frac{1}{2} - x, \frac{1}{2} - y, z$. iii: $x, -y, -\frac{1}{2} + z$. iv: $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$. v: $1 - x, y, \frac{1}{2} - z$. vi: $\frac{1}{2} - x, \frac{1}{2} + y, z$. vii: $1 - x, y, \frac{1}{2} + z$.

in agreement with the calculated density (see Experimental section).

### *Mechanical and Semi-empirical Calculations*

To rationalize the experimental dihedral angles and to determine if they are near the values for the molecules in their free form (*i.e.* to determine if the rotation about the central bond is due to crystal packing effects) we have tried to calculate molecules **5**, **9**, **12** and **13** by molecular mechanics (different versions of Allinger's force field method) and by the AM1 semi-empirical approximation[20] (MOPAC package).[21] Both methods are well suited for this kind of problem. For instance, in the case of biphenyl,[22] the experimental twist angle (electron diffraction) is 44.4 ± 1.2°, the HF/6-31G** is 46.26°, and those calculated by different methods are 42.9° (MM2′),[23] 37.1° (MM2 + V4),[24] 36.1° (MMP2),[23] 46.2° (MM3)[25] and 47.9° (AM1, this work). The latest version of Allinger's MM2 force field[26] [MM2(91)][27] and its newest MM3 force field[28] [MM3(92)][29] were used throughout this work to compute the structure of molecules **5**, **9**, **12** and **13**, using the conjugated π-system option in all cases.

*AM1 Semi-empirical Calculations.*—The values obtained with this method are reported in Table 7. Compared with the crystallographic data, the calculated values are in good agreement for the pivot bond lengths, $d_0(\text{exp}) = 0.012 + 1.01d_0$ (AM1), $n = 4$, $R = 0.97$, but for the dihedral angles the

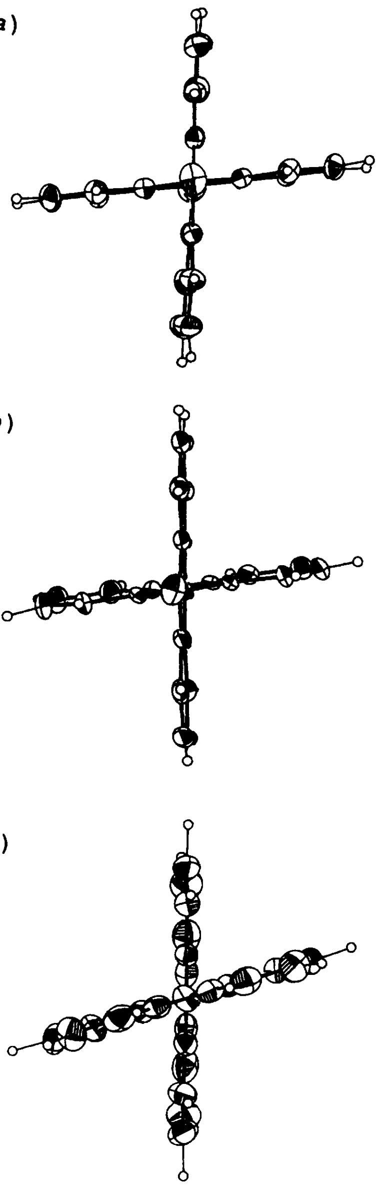


**Fig. 2** Newman projections along the central bond, (*a*), (*b*) and (*c*) for compounds **5**, **9** and **12** (Mol. 2) respectively

corresponding relationship shows a low correlation coefficient $R = 0.71$. The reason is the dihedral angle of bianthryl (**13**) which is either overestimated in the AM1 calculation (86.0°) or, more probably, 'flattened' in the crystal (74.2°). Removal of the point corresponding to **13** considerably improves the correlation: $\omega^\circ(\text{exp}) = 17.8 + 0.875\,\omega^\circ(\text{AM1}), n = 3, R = 0.999$. It is thus possible to conclude that the experimental geometries, with the possible exception of bianthryl, are representative of these molecules and not due to crystal packing effects. The $\omega^\circ$(AM1) dihedral angles are related to the geometry (hexagonal or pentagonal) of the central ring and not to the nature of the pivotal atoms: $\omega^\circ(\text{AM1}) = 68.8 + 9.25\,h, n = 4, R = 0.95$, $h$ being the number of central six-membered rings, 0 for compound **12**, 1 for compound **9** and 2 for compounds **5** and **13**. This reflects the fact that steric effects are larger for central six-membered rings than for central five-membered rings.

*Molecular Mechanics Calculations.*—For bianthryl (**13**) no changes in the MM2(91) or MM3(92) calculations were necessary. Both the MM2(91) with block-diagonal optimization and the MM3(92) with Newton–Raphson optimization yield satisfactory results, justifying our confidence in Allinger's force field

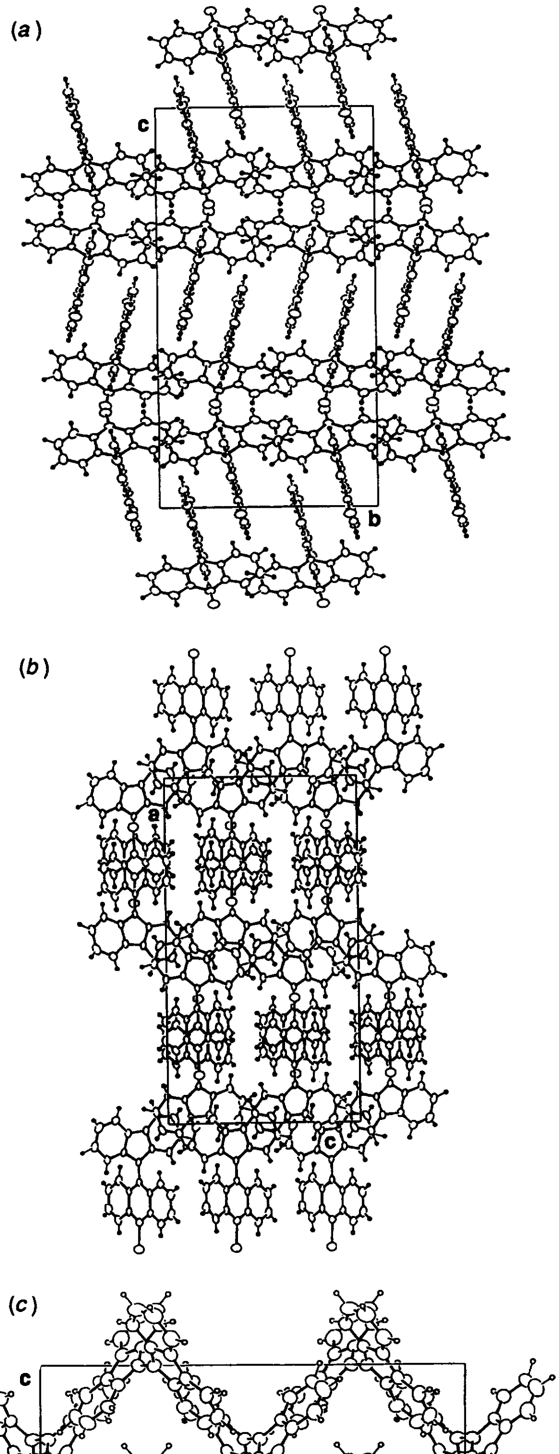


**Fig. 3** Packing diagrams as viewed along the **a**,**b**,**a** axis for compounds **5**, **9** and **12** [(*a*), (*b*) and (*c*) respectively]

**Table 7** Experimental and calculated characteristics of 'scissor-like' derivatives. Pivot bond lengths ($d_0$ in Å), 'scissoring' dihedral angles ($\omega$, in degrees) and energies (steric energies for MM2 and MM3 and heats of formation for AM1 in kcal mol$^{-1}$)[a]

| | Experimental | | AM1 | | | MM2(91) | | | MM3(92) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $d_0$ | $\omega$ | $d_0$ | $\omega$ | $\Delta H_f$ | $d_0$ | $\omega$ | S.E. | $d_0$ | $\omega$ | S.E. |
| **5** | 1.393 | 85.3 | 1.35 | 86.4 | 113.9 | — | — | — | — | — | — |
| **9** | 1.432 | 82.9 | 1.41 | 82.4 | 161.8 | — | — | — | — | — | — |
| **12** | 1.372 | 70.0 | 1.36 | 66.6 | 187.3 | — | — | — | — | — | — |
| **13** | 1.502 | 74.2 | 1.47 | 86.0 | 139.0 | 1.46 | 83.3 | −28.02 | 1.51 | 90.0 | 6.33 |

[a] 1 cal. = 4.184 J.

methods for this kind of molecule. For **5**, **9** and **12**, the necessary parameters are not available. To use these methods, some hypotheses are necessary concerning the type of atoms used to replace those which are missing. This led to grossly underestimated values for the dihedral angles, for instance $\omega^\circ = 14.5°$ for **12** [MM3(92)]; to reproduce the experimental values, the torsional constant $V_2$ has to be modified considerably. This, in turn, produces unwanted variations in the pivotal bond length, which become abnormally long. It can be concluded that molecular mechanics calculations are presently unsuitable for molecules derived from bianthryl having pivotal nitrogen atoms.

## Experimental

Melting points were determined on a Büchi 530 apparatus and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded either on a Bruker AC-200 and at 50.323 MHz, using $CDCl_3$ or [$^2H_6$]DMSO as solvents and $SiMe_4$ as internal standard; all chemical shifts ($\delta$) are reported in parts per million (ppm). The $^1$H and $^{13}$C chemical shifts are accurate to 0.01 ppm, and the digital resolution of coupling constants is ±0.6 Hz for $^{13}$C NMR. The data acquisition parameters for the heteronuclear ($^1$H–$^{13}$C)2D correlation experiments were F$_1$ domain (SI1, 512 W; SW1, 1282 Hz; relaxation delay D1, 1 s), F$_2$ domain (SI2, 2 K; SW2, 10 204 Hz), number of transients per FID, NS, 128; number of preparatory dummy transients per FID, DS, 0 and $J$ value of 160 Hz, ($J$ = 9 Hz for the COLOC experiment). Parameters for ($^1$H–$^1$H) COSY experiments were F$_1$ domain (SI1, 512 W; SW1, 1200 Hz; relaxation delay D1, 1 s), F$_2$ domain (SI2, 1 K; SW2, 2500 Hz), number of transients per FID, NS, 64; number of preparatory dummy transients per FID, DS, 2. All the 2D experiments were processed with a sine bell window (WDW1 = WDW2 = S, SSB1 = 0, SSB2 = 0). Electron impact mass spectra (MS) were obtained at 70 eV ionizing power, on a Hewlett-Packard 5993C spectrometer. Commercial reagents from Aldrich Chimica were used without further purification. Column chromatography was run on silica gel. Literature procedures were used to prepare 9-chloroacridine (**2**);[30] 9,9′-biacridinyl (**4**);[31] 10,10′-biacridinyl-9,9′-dione (**5**);[32] 10-(9′-acridyl)acridin-9-one (**6**);[33] 9-(10′-bromo-9′-anthryl)carbazole (**9**);[4] 9,9′-bicarbazyl (**12**);[34] and 9,9′-bianthryl (**13**)[35] with some modifications described below. Compounds **5** and **9** were recrystallized from ethanol–chloroform and compound **12** from mesitylene to obtain suitable crystals for X-ray diffraction analysis.

*Materials*.—9,9′-Biacridinyl (**4**) was purified by column chromatography using 50:50 ethyl acetate–hexane as the eluent ($R_f$: 0.40), 48% yield, m.p. > 360 °C (lit.,[31] 392 °C); $m/z$ 356 (M$^+$, 100) and 177 (21).

10,10′-Biacridinyl-9,9′-dione (**5**) was purified[32] by column chromatography with 95:5 chloroform–ethanol as the eluent ($R_f$: 0.60), yield: 25%, as green prisms from ethanol–chloroform, m.p. 268–270 °C (lit.,[32] m.p. 251 °C); $m/z$ 388 (M$^+$, 25), 194 (M/2, 100), 166 (22) and 140 (6).

10-(9′-Acridyl)acridin-9-one (**6**) was purified using a 90:10 mixture of chloroform–ethanol as eluent ($R_f$: 0.63). Yield: 21%, m.p. > 360 °C (lit.,[21] m.p. 383–384 °C); $m/z$ 372 (M$^+$, 100), 343 (8) and 170 (17).

10-(9′-Anthryl)acridin-9-one (**7**) was prepared by the same method described[33] for the preparation of compound **6**, but using acridin-9(10$H$)-one (0.5 g, 0.0025 mol) and 9-bromoanthracene (0.70 g, 0.0027 mol). The mixture was heated at 300 °C for 2 h and chromatographed on silica gel using 95:5 chloroform–ethanol as the eluent ($R_f$: 0.63), to yield 3% of compound **7**, m.p. 265 °C from ethanol; $m/z$ 371 (M$^+$, 100), 352 (11) and 341 (9).

9-(10′-Bromo-9′-anthryl)carbazole **9** was isolated using the method described[4] for preparation of 9-(9′-anthryl)carbazole (**10**). After purification by column chromatography using 90:10 hexane–chloroform as the eluent ($R_f$: 0.16), compound **9** was obtained in 2% yield, as yellow prisms from ethanol–chloroform, m.p. 267 °C; $m/z$ 421, 422, 423 (M$^+$, 100) and 339 (20).

9-(9′-Anthryl)carbazole **10** was prepared by fusion between carbazole (1 g, 0.006 mol) and 9-bromoanthracene (1.8 g, 0.007 mol), heating at 300 °C for 2.5 h, and purified by column chromatography (60:40 hexane–chloroform, $R_f$: 0.46). Yield 24% as prisms from ethanol–chloroform, m.p. 252 °C; $m/z$ 343 [(M + 1)$^+$, 100], 342 [(M + 1)$^+$, 24] and 341 (M$^+$, 22).

9-(9′-Acridyl)carbazole (**11**) (for the sake of homogeneity we have chosen carbazole as parent compound) was prepared by fusion between carbazole (1 g, 0.006 mol) and 9-chloroacridine (1.5 g, 0.007 mol), heated at 300 °C for 3 h. Purification by column chromatography using 50:50 ethyl acetate–hexane ($R_f$: 0.40), yielded 16% of **11**, as yellow prisms from benzene, m.p. 270 °C; $m/z$ 344 (M$^+$, 60), 171 (25) and 129 (32).

9,9′-Bicarbazyl (**12**) was purified by column chromatography using 90:10 hexane–chloroform as the eluent ($R_f$: 0.14), 18% yield as prisms from ethanol, m.p. 228 °C (lit.,[27] 220–221 °C); $m/z$ 332 (M$^+$, 97), 331 (16), 166 (M/2, 100), 167 (16) and 140 (12).

*Crystal-structure Determination of Compounds* **5**, **9** *and* **12**.—Table 8 contains the main crystal analysis parameters. Compound **12** crystallizes in an orthorhombic cell with two halves of the molecule in the asymmetric unit. A two-fold axis at ($\frac{1}{4}$, $\frac{1}{4}$, $z$) and ($\frac{1}{2}$, 0, $z$) passing through the midpoint of the N(9)–N(9′) bond completes the molecule. Most of the calculations have been performed with the XRAY80 SYSTEM,[36] on a VAX6410 computer. The structures were solved by Patterson and direct methods[37,38] and were refined by least-squares procedures, with an empirical weighting scheme.[39] Absorption correction was carried out by means of the DIFABS program.[40] Finally, the PARST program[41] was used for geometrical calculations and the atomic scattering factors were taken from the International Tables for X-Ray Crystallography.*[,42]

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* Supplementary data [see 'Instructions for Authors (1993),' *J. Chem. Soc., Perkin Trans. 2*, 1993, January issue]. Lists of the atomic coordinates, thermal components, hydrogen parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

**Table 8** Crystal analysis parameters at room temperature

| | **5** | **9** | **12** |
|---|---|---|---|
| Crystal data | | | |
| Formula | $C_{26}H_{16}N_2O_2$ | $C_{26}H_{16}NBr$ | $C_{24}H_{16}N_2$ |
| Crystal habit | Colourless prism | Yellow prism | Colourless octahedron |
| Crystal size (mm) | 0.07 × 0.14 × 0.33 | 0.14 × 0.28 × 0.60 | 0.27 × 0.27 × 0.50 |
| Symmetry | Monoclinic, *C*2/*c* | Orthorhombic, *Pbca* | Orthorhombic, *Ccc*2 |
| Unit cell determination: | Least-squares fit from 61 reflections ($\theta < 45°$) | Least-squares fit from 77 reflections ($\theta < 45°$) | Least-squares fit from 80 reflections ($\theta < 45°$) |
| Unit cell dimensions (Å, °) | $a = 9.3332(4)$ | $a = 24.2348(10)$ | $a = 11.8206(4)$ |
| | $b = 14.8341(8)$ | $b = 11.5757(2)$ | $b = 20.3869(12)$ |
| | $c = 27.6721(36)$ | $c = 13.5108(4)$ | $c = 14.6430(6)$ |
| | 90, 97.728(6), 90 | 90, 90, 90 | 90, 90, 90 |
| Packing: *V*(Å), *Z* | 3786.8(6), 8 | 3790.3(2), 8 | 3528.8(3), 8 |
| *Dc*(g/cm$^3$), *M*, F(000) | 1.363, 388.43, 1616 | 1.480, 422.32, 1712 | 1.251, 332.40, 1392 |
| $\mu$(cm$^{-1}$) | 6.58 | 30.28 | 5.35 |
| Experimental data | | | |
| Technique | | Four circle diffractometer: Philips PW1100, Bisecting geometry<br>Graphite oriented monochromator: Cu-Kα<br>Detector apertures 1 × 1°. 1 min/reflex, $\theta_{max} = 65°$<br>$\omega/2\theta$ scans | |
| Scan width | 1.5° | 1.4° | 1.6° |
| Number of reflections: | | | |
| Independent | 3224 | 3221 | 1573 |
| Observed | 2127 [$3\sigma(I)$ criterion] | 2228 [$3\sigma(I)$ criterion] | 1254 [$3\sigma(I)$ criterion] |
| Standard reflections: | | 2 reflections every 90 min. No variation | |
| Max.-min. transmission factors | — | 2.005–0.545 | |
| Solution and refinement | | | |
| Solution | Sir88 | Patterson + Dirdif | Sir88 |
| Refinement: Least-squares on Fo | | Full-matrix | |
| Parameters: | | | |
| Number of variables | 327 | 317 | 298 |
| Degrees of freedom | 1800 | 1971 | 956 |
| Ratio of freedom | 6.5 | 7.2 | 4.2 |
| H atoms | | From difference synthesis | |
| Final shift/error | 0.02 | 0.07 | 0.22 |
| Weighting-scheme | | Empirical as to give no trends in $\langle \omega\Delta^2F \rangle$ vs. $\langle \lvert F_o \rvert \rangle$ and $\langle \sin\theta/\lambda \rangle$ | |
| Max. thermal value | $U_{22}$[O(11)] = 0.118(2) Å$^2$ | $U_{11}$[*C*(2′)] = 0.105(6) Å$^2$ | $U_{11}$[C(2)] = 0.142(8) Å$^3$ |
| Final $\Delta F$ peaks | 0.14 e/Å$^3$ | 0.48 e/Å$^3$ | 0.15 e/Å$^3$ |
| Final *R* and *R*w | 0.044, 0.051 | 0.065, 0.078 | 0.053, 0.068 |

*Calculations.*—AMI and molecular mechanics calculations were carried out on a VAX6610 computer in the Computer Center of the Universidad Autònoma de Barcelona.

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