Synthesis and Characterization of Some Aza[5]helicenes

Cristina Bazzini,[a] Sergio Brovelli,[b] Tullio Caronna,*[a] Cristian Gambarotti,[c] Matteo Giannone,[c] Piero Macchi,[d] Francesco Meinardi,[b] Andrea Mele,[c] Walter Panzeri,[e] Francesco Recupero,[c] Angelo Sironi,[d] and Riccardo Tubino[b]

Keywords: Helical structures / Fluorescence spectroscopy / Photochemistry

A systematic study on the synthesis and properties of aza[5]helicenes bearing one or two nitrogen atoms in selected ring positions is reported for the first time. This photochemical approach can be conveniently applied to the preparation of either mono- or diaza[5]helicenes. The aza[5]helicenes were characterized by NMR spectroscopy, X-ray crystallography, emission spectroscopy, and luminescence lifetime. The extremely long triplet lifetime observed (in the range of seconds) makes these molecules promising candidates for practical applications in photo- and optoelectronics.

Introduction

Helicenes constitute a class of molecules with many intriguing features such as extended aromaticity, chirality, a capability to self-assemble into columnar solid-state architectures, and an ability to behave as organic conductors. Potential applications of helicenes can be found in the fields of non-linear optics (NLO)[1] and circularly polarized luminescence.[2] Since the first synthesis of helicenes, reported by Newman in 1955,[3] a great deal of work has been carried out on helicenes with a backbone composed either of carbon atoms only[4] or containing selected heteroatoms.[4] In this latter case, particular interest has been paid to thiohelicenes, a class of molecules with alternating thiophene and benzene rings, which show interesting self-assembly behavior in the solid state,[5] and to bridged triarylamines, a particular kind of azahelicene.[6] Whenever the resolution of the enantiomers could be obtained, very high $[\alpha]_{500}{}^{23}$ values were found.[7] For the nine-membered thiohelicene, the two enantiomers show distinctive circular dichroism spectra,[8] the (+)-enantiomer having the absolute configuration of the right-handed helix.[9] Nitrogen-substituted heteroaromatic molecules are currently gaining increasing interest owing to the fact that their complexes with transition metal ions show interesting properties in harvesting (visible) light and reemitting it at a wavelength that depends on the metal ion used,[10] thus allowing the development of light-emitting devices, chemosensors, photovoltaic dye-sensitized devices, etc. Furthermore, if the heteroaromatic ligand has more than one nitrogen atom in its frame, large supramolecular complexes can be formed, and the properties of this kind of systems have been the focus of the research activities of many groups.[11] Few examples of aza[5]helicenes (the number in square brackets refers to the number of rings in the helicene) are known in the literature,[12] and a systematic study of their synthesis and properties is still missing. In a preliminary paper, we pointed out that the strategies for obtaining diaza[5]helicenes differ depending on the positions of the nitrogen atoms.[13] For these reasons, we decided to start an extensive and systematic study on aza[5]-helicenes. The motivations of this project are: a) to provide a possible general synthetic approach to this class of molecules, b) to provide a thorough characterization of the spectral and structural features of the newly synthesized molecules, and c) to provide promising building blocks for new materials. Indeed, aza[5]helicenes may act as ligands for transition metal ions and the complexes obtained, along with their supramolecular assemblies, are potential candidates for light emitters whose wavelength may be tuned by changing the complexing ion.

Results and Discussion

Figure 1 gives an example of the molecular formula and atom numbering of aza[5]helicene and its double-bond pre-

---

[a] Dipartimento di Ingegneria Industriale Università degli Studi di Bergamo,
Via G. Marconi, 5, 24044 Dalmine, Italy
Fax: +39-035-562-779
E-mail: tullio.caronna@unibg.it
[b] INFM and Dipartimento di Scienza dei Materiali, Università Milano-Bicocca,
Via Cozzi 53, 20125 Milano, Italy
[c] Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano,
Via Mancinelli 7, 20131 Milano, Italy
[d] Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Universita’ degli Studi di Milano,
Via Venezian 21, 20133 Milano, Italy
[e] CNR-Istituto di Chimica del Riconoscimento Molecolare,
Via Mancinelli 7, 20131 Milano, Italy

DOI: 10.1002/ejoc.200400648

cursor. A simple strategy that may be used for the synthesis of the aza[5]helicenes reported in this paper starts from the well-known photochemical ring-closure of 1,2-diarylethylenes, which yields the most crowded derivative as the major product. While the synthesis of carbohelicenes has been studied both from a synthetic and a theoretical point of view,[14] few azahelicenes are known in the literature and some reported theoretical approaches are not completely satisfactory.[15,16]

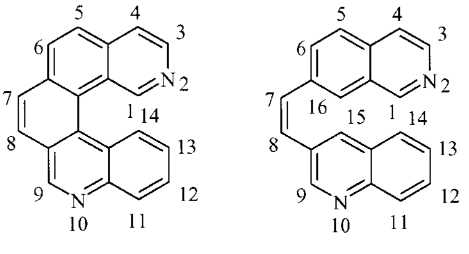


Figure 1. Molecular formulae and atom numbering for aza[5]helicenes and their precursors.

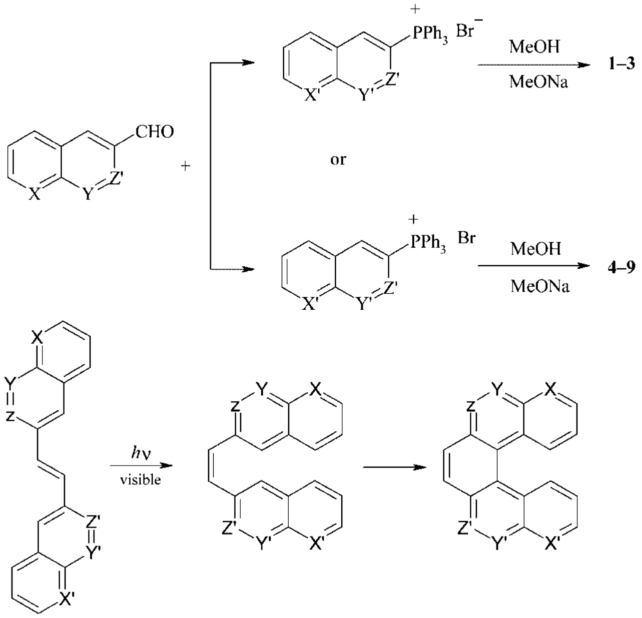
The key step of our syntheses of azahelicenes was thus the photolysis of differently nitrogen-substituted 1,2-diarylethylenes. The rationale for such a choice can be summarized in the following points: a) literature data indicated that photochemical cyclization could be exploited for the synthesis of substituted carbohelicenes[17] and more complex carbohelicenes ([11]-, [12]-, [13]-, and [14]helicenes);[18] b) in stilbene-like molecules, the presence of one or more nitrogen atoms does not alter the photochemical behavior of the 1,2-substituted ethylenes dramatically.[19] For these reasons, we synthesized some ethylenes substituted in the 1-position with quinoline or isoquinoline and in the 2-position with naphthalene, quinoline, or isoquinoline. The photochemical cyclization was carried out as shown in Scheme 1.

In all these cases the reaction gave the desired aza[5]helicenes or diaza[5]helicenes selectively without ring closure in other positions. GC analysis during the irradiation showed the presence of only three peaks, corresponding to the *cis* isomer (identified by GC-MS), the azahelicene, and the *trans* isomer, in that order.

The synthetic approach to the monoazahelicenes **1**–**3** starts with the preparation of the phosphonium salt of 2-(bromomethyl)naphthalene and its reaction with the heterocyclic aldehyde obtained by oxidation of the methyl derivative with SeO_2.

The synthesis of the diazadiarylethylenes **4**–**9** was achieved in a slightly different way. In these cases, some of the heterocyclic aldehydes were reduced to the corresponding alcohols and then transformed into the chloride derivatives, which, in turn, were used to obtain the corresponding phosphonium salts. A subsequent Wittig reaction gave the desired ethylenes.

It is interesting to note that 2-aza[5]helicene and 7-aza[5]helicene could not be obtained following this strategy (Scheme 2). All attempts to synthesise the 2-aza[5]helicene gave the 7-azabenzo[*ghi*]perylene **20** as the only product, whereas the photochemical cyclization leading to 7-aza[5]helicene was unsuccessful even under the most drastic conditions reported in the literature.[20] Furthermore, for this latter compound, attempts to repeat a published synthesis were unsuccessful.[21] We are currently exploring other possible synthetic strategies for their synthesis, as well as other monoazahelicenes. The synthesis of 6,9-diaza[5]helicene has already been reported by us[13] and others,[12g] although the present approach is simpler.



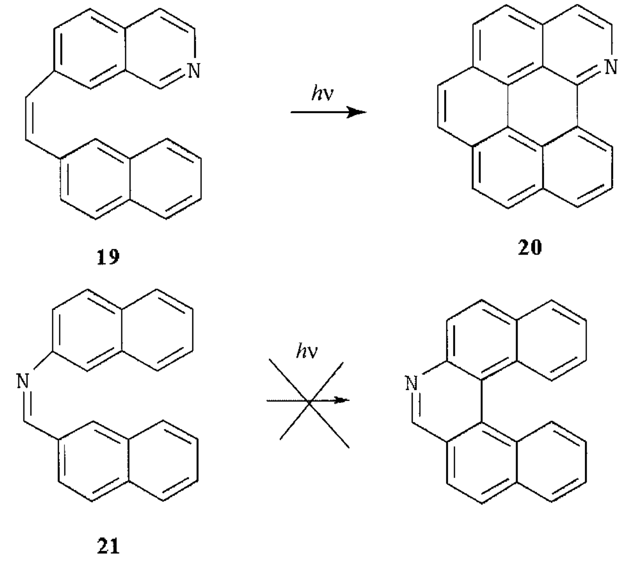
1) X = N, Y = Z = X' = Y' = Z' = CH
Yield: 85%
2) Y = N, X = Z = X' = Y' = Z' = CH
Yield: 70%
3) Z = N, X = Y = X' = Y' = Z' = CH
Yield: 70%
4) X = X' = N, Y = Z = Y' = Z' = CH
Yield: 78%
5) Y = Y' = N, X = Z = X' = Z' = CH
Yield: 83%
6) Z = Z' = N, X = Y = X' = Y' = CH
Yield: 68%
7) X = Z' = N, Y = Z = X' = Y' = CH
Yield: 78%
8) X = Y' = N, Y = Z = X' = Z' = CH
Yield: 72%
9) Y = Z' = N, X = Z = X' = Y' = CH
Yield: 89%

10) 4-Aza[5]helicene
Yield: 47% , AcOEt, 36 h
11) 5-Aza[5]helicene
Yield: 82% , AcOEt, 36 h
12) 6-Aza[5]helicene
Yield: 40% , AcOEt, 36 h
13) 4,11-diaza[5]helicene
Yield: 98% , AcOEt, 24 h
14) 5,10-diaza[5]helicene
Yield: 98% , AcOEt, 24 h
15) 6,9-diaza[5]helicene
Yield: 72% , AcOEt, 36 h
16) 4,9-diaza[5]helicene
Yield: 85% , AcOEt, 36 h
17) 4,10-diaza[5]helicene
Yield: 98% , AcOEt, 24 h
18) 5,9-diaza[5]helicene
Yield: 98% , AcOEt, 36 h

Scheme 1.

NMR Spectroscopy

The structural characterization of the target products in solution was achieved by ^1H NMR spectroscopy. The spectral assignment was based on the combined use of the following elements: a) the chemical-shift dependence of the ^1H signals as a function of *N*-substitution in heteroaromatic bases; b) ^3J and ^4J coupling constant values in N-containing heteroaromatic bases; c) $^1H\{^1H\}$ NOE difference and



Scheme 2.

2D-NOESY experiments. A detailed example of the use of the above-mentioned points has been reported previously.[13] The full assignment of the azahelicenes' spectra is summarized in Table 1. From a structural viewpoint, it is interesting to underline that the signal assigned to the proton in position 14 (see Figure 1) is remarkably deshielded in both mono- and diazahelicenes due to the effect of the π-electron ring-current of the opposite aromatic ring (e.g. the ring containing the proton in position 1), and that a long-range NOE due to the dipolar interaction of the protons in positions 1 and 14 is also detected in 2D-NOESY experiments. These findings are in full agreement with the nonplanar structure of the azahelicenes obtained by X-ray diffraction and discussed below.

Crystal Structures of Monoaza[5]helicenes

Of the nine helicenes reported above, we structurally characterized the three monoazahelicenes **10**, **11**, and **12** by single-crystal X-ray diffraction. The conformations of all these molecules closely resemble that of the "parent" [5]-helicene molecule, whose idealized molecular symmetry is C_2 and which crystallizes in two monoclinic forms, $P2_1/c$, with one molecule in a general position, and $C2/c$, with one molecule in a general position and one on a twofold axis[22] (see Figure 2, where labeling and a qualitative picture of long and short bonds is reported).

The helicene **11** crystallizes as a conglomerate of enantiomorphic crystals in the noncentrosymmetric space group $P2_1nb$. The helicene **10** is isomorphic with the parent [5]-helicene of $C2/c$, except for an orientational disorder which affects the molecule on the twofold axis. Finally, the space group of helicene **12** is $P2_1/n$.

We can compare the molecular geometries of helicene and monoaza[5]helicenes by investigating parameters such as the skeletal bond lengths and the dihedral angles at the unique central C–C bonds (Table 2). Experimentally determined distances have been corrected for thermal libration effects,[23] except for the [5]helicene, whose data are taken from the literature.[22] For **10**, only the (ordered) molecule in the general position is considered, while for [5]helicene the (unique) distances are obtained from the average between the two molecules of the $C2/c$ phase and the molecule of the $P2_1/c$ phase.

In Table 3 we report the same parameters obtained from a density functional gas-phase geometry optimization at the B3LYP/6-31G(d,p)[24] level of theory. For the two ordered structures, the agreement is within 0.03 Å and, in particular, the alternation of short and long bonds is correctly predicted. A significantly worse agreement (0.05 Å) is found for **10**, but this is probably due to the lower quality of the crystals and the orientational disorder that affects part of the structure, both of which clearly reduce the accuracy of the refined model, as can be seen from the poor agreement factors given in the table in the Experimental Section and the larger uncertainties in Table 3.

Somewhat at variance from our expectations, the effect of the heteroatom is limited to its nearest neighbor (shortening the bond); little difference is observed at greater distances.

The dihedral angles about the central C7–C8 and C14b–C14c bonds are quite constant in all structures at about 10° and 30°, respectively. Even though the molecules are significantly distorted from planarity (Figure 3), the two central bond lengths in all helicenes are quite close to those of phenanthrene[25] or other similar molecular fragments (in planar conformation) retrieved from the Cambridge Crystallographic Database,[26] where average values are 1.345(3) Å and 1.456(2) Å for C7–C8 and C14b–C14c, respectively.

The particular shape of the helicene molecules clearly influences the crystal packing (Figure 4). In the two centrosymmetric structures, stacks of enantiomers form embraces and produce chains elongated along given directions. In the acentric structure, however, no special stacking motif is observed, although the overall packing is no less efficient than that of the centrosymmetric forms (see, for example, the occupied volume per molecule, V/Z, in Table 3). The polymorphism shown by the parent helicene suggests that more than one supramolecular arrangement is energetically favored and the same could hold true for aza-helicenes. Preliminary analysis of diazahelicenes (not reported in this paper) seems to confirm this hypothesis. For each azahelicene, the reasons that lead to one arrangement instead of the others could be quite subtle. Electrostatic forces, for example, must certainly be considered: the molecular dipole moment magnitudes of azahelicenes are almost identical (about 2.5 D, against ca. 0 for [5]helicene), but their directions are quite different. On the other hand, weaker hydrogen bonds, with N atoms acting as acceptors, seem to be less-efficient driving forces, given that in all structures examined here all C–H···N contacts have H···N distances exceeding 2.7 Å, while many C–H···H–C contacts slightly below the van der Waals distances occur.

Table 1. ^{1}H NMR spectroscopic data[a] for the aza[5]helicenes.

	H1	H2	H3	H4	H5	H6	H7
10	8.83 dd, *J* = 1.8, 8.7	7.19 dd, *J* = 4.1, 8.7	8.90 dd, *J* = 1.8, 4.1	–	8.17[b] *J* = 8.9	8.12[c] *J* = 8.9	[d]
11	8.54 dd, *J* = 1.4, 8.7	7.35 ddd, *J* = 1.4, 6.9, 8.7	7.69 ddd, *J* = 1.4, 6.9, 8.3	8.25 dd, *J* = 1.4, 8.3	–	9.41 s	7.89[b,e] *J* = 8.7
12	8.51 d, *J* = 8.5	7.50 ddd, *J* = 1.4, 6.6, 8.5	7.63 ddd, *J* = 1.4, 6.6, 8.0	8.09 dd, *J* = 1.4, 8.0	9.40 s	–	8.15[b] *J* = 8.5
13	8.77 dd, *J* = 1.3, 8.5	7.26 dd, *J* = 4.1, 8.5	8.95 dd, *J* = 1.3 4.1	–	8.22[b] *J* = 8.8	8.16[c] *J* = 8.8	8.01 s
14	8.30 d, *J* = 8.4	7.45 ddd, *J* = 1.4, 6.9, 8.4	7.77 ddd, *J* = 1.4, 6.9, 8.3	8.66 br. d, *J* = 8.3	–	9.47 s	8.15 s
15	8.16 dd, *J* = 1.4, 8.3	7.58 ddd, *J* = 1.4, 6.9, 8.3	7.70 ddd, *J* = 1.4, 6.9, 8.3	8.55 d, *J* = 8.3	9.45 s	–	8.31 s
16	7.98 br. d, *J* = 8.0	7.28 dd, *J* = 4.2, 8.0	8.76 dd, *J* = 1.6, 4.2	–	[g]	[g]	[g]
17	8.95 dd, *J* = 1.8, 8.5	7.28 dd, *J* = 4.4, 8.5	8.97 dd, *J* = 1.8, 4.4	–	8.28[b] *J* = 8.4	8.15[c] *J* = 8.4	8.05[b,e] *J* = 8.0
18	8.53 br. d, *J* = 8.5	7.40 ddd, *J* = 1.4, 6.9, 8.5	7.74 ddd, *J* = 1.4, 6.9, 8.3	8.27 dd, *J* = 1.4, 8.3	–	9.42 s	8.15 d, *J* = 8.3

	H8	H9	H10	H11	H12	H13	H14
10	[d]	[d]	[d]	7.97 dd, *J* = 1.4, 8.1	7.54 ddd, *J* = 1.4, 6.9, 8.1	7.30 ddd, *J* = 1.4, 6.9, 8.1	8.46 br. d, *J* = 8.1
11	8.03[c,e] *J* = 8.7	[f]	[f]	7.98 dd, *J* = 1.4, 8.3	7.58 ddd, *J* = 1.4, 6.9, 8.3	7.36 ddd, *J* = 1.4, 6.9, 8.3	8.62 br. d, *J* = 8.3
12	8.01[c] *J* = 8.5	7.89[b] *J* = 8.5	7.96[c] *J* = 8.5	7.98 dd, *J* = 1.4, 8.0	7.56 ddd, *J* = 1.4, 6.9, 8.0	7.32 ddd, *J* = 1.4, 6.9, 8.5	8.50 br. d, *J* = 8.5
13	–	–	–	–	–	–	–
14	–	–	–	–	–	–	–
15	–	–	–	–	–	–	–
16	[g]	–	9.05 s	[g]	8.76 dd, *J* = 1.6, 4.2	7.28 dd, *J* = 4.2, 8.0	7.98 d, *J* = 8.0
17	8.08[c,e] *J* = 8.0	9.44 s	–	8.46 br. d, *J* = 8.4	7.72 ddd, *J* = 1.4, 6.9, 8.4	–	8.28[h]
18	8.26 d, *J* = 8.3	–	9.84 s	8.15[i]	7.72 ddd, *J* = 1.4, 6.9, 8.0	7.61 ddd, *J* = 1.4, 6.9, 8.5	8.62 br. d, *J* = 8.5

[a] Chemical shift (δ, ppm, reference internal TMS) and coupling constants (Hz). [b] A part of AB spin system. [c] B part of AB spin system. [d] δ = 7.97–7.89 (m, 4 H, H7, H8, H9, H10). [e] Assignments can be reversed. [f] δ = 7.97–8.01 (m, 2 H, H9, H10). [g] δ = 7.83–7.58 (m, 5 H, H5, H6, H7, H8, H11). [h] Overlapped with H5. [i] Partially overlapped with H7.

Optical Properties

Again, in the present work, we have concentrated on the monoaza derivatives. Figure 5 shows the absorption spectrum of **11** in ethanol in the region of the lowest electronic transition compared with the corresponding luminescence collected at 300 K and 77 K. The full absorption spectrum, up to 5 eV, is reported in the inset. The absorption onset is at about 3.14 eV and corresponds to the singlet–singlet $S_1 \leftarrow S_0$ 0–0 transition.[27] A well-defined vibronic progression with an energy separation of 1200 cm^{-1}, due to the C–H bond bend vibration mode, is also easily detectable.

The measured fluorescence quantum yield (Φ) is about 0.076. The oscillator strength f of the $S_1 \leftarrow S_0$ transition can be obtained from the Strickler–Berg equation [Equation (1)][27]

$$f = \frac{4.39 \cdot 10^{-9}}{n} \int \varepsilon d\tilde{\nu} \tag{1}$$

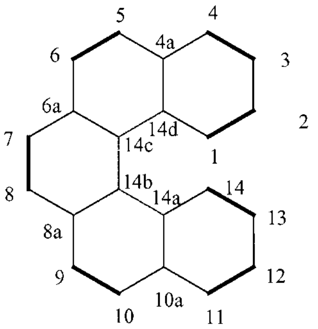


Figure 2. A Scheme showing the labeling system adopted. Shorter (<1.39 Å) and longer (>1.44 Å) distances in the parent [5]helicene molecule are drawn as bold and dashed lines respectively.

where n is the refraction index of the solution and the integral is calculated over the entire vibronic progression, which gives a value of 1.17×10^{-2}.

Similar to the absorption spectrum, the room-temperature photoluminescence is constituted by a single vibronic progression with an energy separation of about 1200 cm^{-1} and nearly perfect mirror symmetry. The small Stokes shift of about 36 meV between absorption and emission spectra suggests a negligible molecular relaxation upon excitation, thus indicating that, even though it is nonplanar, the helicene backbone does not undergo any planarization upon excitation.

Table 3. Experimental results for 10^{-5} M ethanol solutions of **10**, **11**, and **12**.

	f	τ^{S}_{TOT} [ns]	τ^{S}_{RAD} [ns]	τ^{T}_{TOT} [s]	Φ	$k_{ISC} \times 10^6$
10	–	3.4	–	1.91	0.2031	7.1
11	1.17×10^{-2}	3.5	45.8	2.4	0.0758	9.4
12	0.961×10^{-2}	3.0	50.1	0.95	0.0599	3.8

The emission spectra at low temperature show a second vibronic progression with the purely electronic transition at 2.48 eV, and the usual energy separation of 1200 cm^{-1}. This emission can be ascribed to a recombination of the first excited triplet state (populated by intersystem crossing, ISC) both because of the large Stokes shift and because of its very long lifetime (see below).

Photoluminescence time-resolved measurements allowed us to obtain deeper insight into the decay pathways involved in the de-excitation of **11**. The total fluorescence (τ^{S}_{TOT}) and phosphorescence (τ^{T}_{TOT}) lifetimes were measured as described in the Experimental Section. Both the decays are single exponential (Figure 6) and the obtained lifetimes are 3.5 ns and 2.4 s, respectively. From the mea-

Table 2. Skeletal bond lengths [Å] in helicene and aza-helicenes molecules, characterized by X-ray diffraction or DFT calculations. The bond lengths involving N atoms are in bold character. Molecular volume [Å^3] and torsion angles [°] at the central 7–8 and 14b–14c bonds are also reported. Standard uncertainties in experimentally determined distances are reported in parentheses (for [5]helicene the values in parentheses are the standard deviation from averaged parameters determined from the coordinates reported in ref.[22]).

	[5]Helicene		**10**		**11**		**12**	
	X-ray	DFT	X-ray	DFT	X-ray	DFT	X-ray	DFT
(1)–(2)	1.369(1)	1.3807	1.369(5)	1.379	1.376(3)	1.381	1.374(3)	1.381
(13)–(14)			1.361(5)	1.381	1.371(3)	1.381	1.377(2)	1.381
(2)–(3)	1.396(1)	1.4091	1.368(7)	1.409	1.384(4)	1.409	1.405(4)	1.410
(12)–(13)			1.401(6)	1.409	1.401(4)	1.409	1.398(3)	1.409
(3)–(4)	1.352(1)	1.3782	1.317(7)	1.320	1.350(4)	1.378	1.355(4)	1.378
(11)–(12)			1.331(8)	1.378	1.352(4)	1.378	1.36 (3)	1.378
(5)–(6)	1.324(2)	1.3607	1.343(9)	1.361	1.304(4)	1.302	1.299(3)	1.302
(9)–(10)			1.353(9)	1.361	1.335(4)	1.361	1.338(3)	1.361
(7)–(8)	1.328(3)	1.3647	1.358(11)	1.365	1.346(4)	1.365	1.346(3)	1.365
(4)–(4a)	1.408(1)	1.4169	1.403(7)	1.361	1.423(4)	1.415	1.415(3)	1.414
(11)–(10a)			1.412(7)	1.417	1.429(3)	1.416	1.421(2)	1.417
(5)–(4a)	1.434(1)	1.4295	1.394(8)	1.429	1.385(3)	1.379	1.434(3)	1.430
(10)–(10a)			1.465(8)	1.429	1.416(3)	1.430	1.428(2)	1.429
(6)–(6a)	1.420(1)	1.4313	1.433(7)	1.432	1.441(3)	1.433	1.376(3)	1.379
(9)–(8a)			1.385(9)	1.431	1.434(3)	1.432	1.431(3)	1.431
(7)–(6a)	1.426(2)	1.4237	1.388(7)	1.424	1.431(4)	1.420	1.426(3)	1.422
(8)–(8a)			1.447(8)	1.424	1.419(4)	1.425	1.422(2)	1.425
(14d)–(4a)	1.425(1)	1.4311	1.425(5)	1.430	1.416(3)	1.430	1.416(2)	1.425
(14a)–(10a)			1.410(5)	1.431	1.424(3)	1.431	1.426(2)	1.431
(14c)–(6a)	1.419(1)	1.4233	1.421(6)	1.423	1.411(3)	1.418	1.419(2)	1.423
(14b)–(8a)			1.417(6)	1.423	1.422(3)	1.424	1.421(2)	1.423
(1)–(14d)	1.410(1)	1.4195	1.407(5)	1.417	1.410(3)	1.418	1.418(2)	1.419
(14)–(14a)			1.419(5)	1.419	1.413(2)	1.419	1.413(2)	1.419
(14d)–(14c)	1.451(1)	1.4606	1.444(5)	1.458	1.466(3)	1.457	1.452(2)	1.456
(14b)–(14a)			1.459(5)	1.460	1.459(3)	1.459	1.461(2)	1.459
(14c)–(14b)	1.443(1)	1.4515	1.438(5)	1.451	1.444(3)	1.450	1.447(2)	1.450
(8a)–(8)–(7)–(6a)	9.7(3)	9.6	8.5(9)	9.4	10.2(4)	9.4	8.3(2)	8.9
(14a)–(14b)–(14c)–(14d)	32.3(3)	29.8	32.6(6)	29.1	29.8(3)	28.5	27.5(2)	30.0
V/Z	360–365		360		355		354	

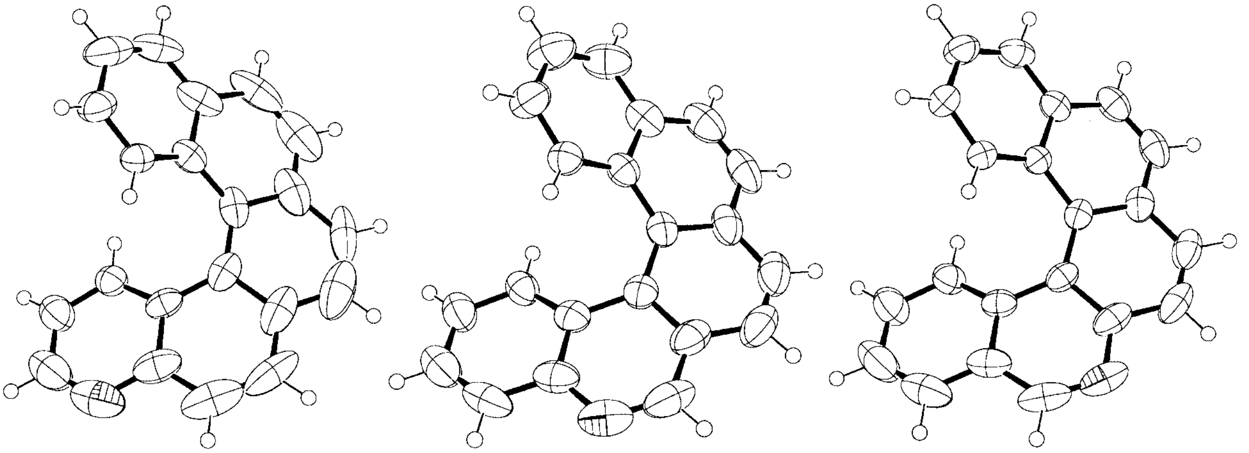


Figure 3. Molecular geometry of the three aza[5]helicenes (from left to right, **10**, **11**, and **12**), characterized by X-ray diffraction. Thermal ellipsoids are drawn at 50% probability level (N atoms are identified with the octant shaded format). For **10** the view represents the order conformation only.

sured Φ and $\tau^S{}_{TOT}$, the fact that $\Phi = \tau_{TOT}/\tau^S{}_{RAD}$, and the simple relationship between $\tau^S{}_{RAD}$ and the oscillator strength,[27] it is possible to recalculate the $S_1 \leftarrow S_0$ transition oscillator strength. The obtained $\tau^S{}_{RAD}$ value (49.8 ns) gives a value of f of 1.8×10^{-2}, which is close to previous estimates (the slightly larger value obtained is probably due to uncertainty in the evaluation of Φ). Moreover, the nonradiative lifetime ($\tau^S{}_{NR}$) can be calculated from the total and radiative lifetime values using the relationship $1/\tau_{TOT} = 1/\tau_{RAD} + 1/\tau_{NR}$. The rather short value obtained ($\tau^S{}_{NR}$ = 3.2 ns) suggests the presence of very efficient nonradiative decay pathways.

Finally, we evaluated the ISC rate in order to check its role among the other singlet nonradiative decay channels. As the singlet emission intensity is proportional to the fluorescence quantum yield, and the triplet emission intensity is proportional to the phosphorescence quantum yield times the ISC rate (k_{ISC}), it is possible to demonstrate [Equation (2)] that

$$k_{ISC} = \frac{I_T}{I_S} \times \frac{k_R^S}{\Phi_T} \tag{2}$$

Assuming that k_{ISC} and $k^S{}_{RAD}$ are not temperature dependent, from the I_T/I_S ratio observed at 77 K we obtain $k_{ISC} = 9.4 \times 10^6\ s^{-1}$ in the case of $\Phi_T = 1$ or larger if Φ_T is smaller than 1 even at 77 K (reliable Φ_T data are not available at present). The corresponding upper limit for τ_{ISC} is therefore around 10^{-7} s, thus demonstrating that the ISC is one of the more efficient nonradiative channels for the singlet de-excitation.

Similar results were also obtained for the other monohelicenes. The data summarized in Table 2 demonstrate that the optical properties of these molecules are almost unaffected by the position of the nitrogen atom.

In summary, the small $S_0 \leftarrow S_1$ transition oscillator strength, coupled with the large k_{ISC}, makes these helicenes good candidates for applications as ligands in metal-organic energy-transfer complexes. Table 2 summarizes the experimental results obtained for 10^{-5} M ethanol solutions of **10**, **11**, and **12**.

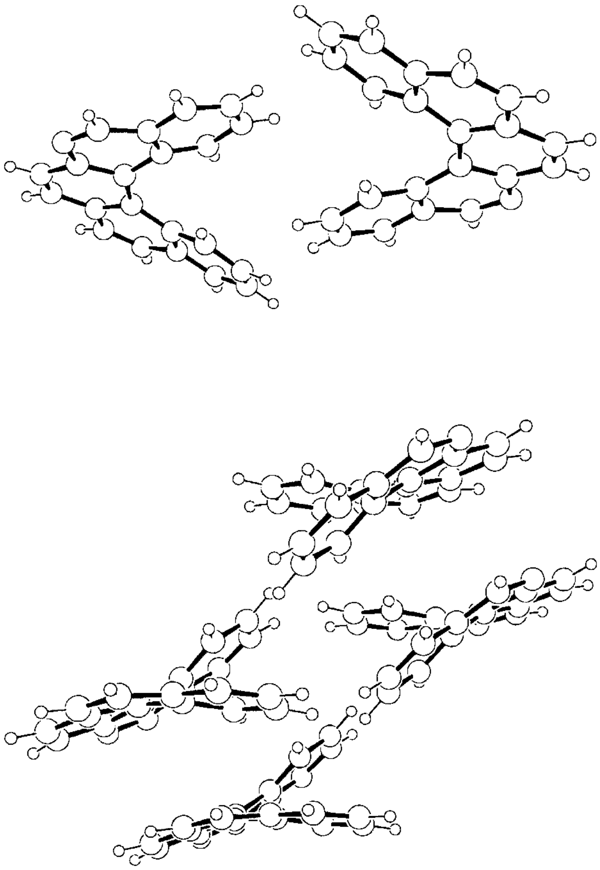


Figure 4. Embrace of two enantionmers (top) and of stacks of enantiomers (bottom).

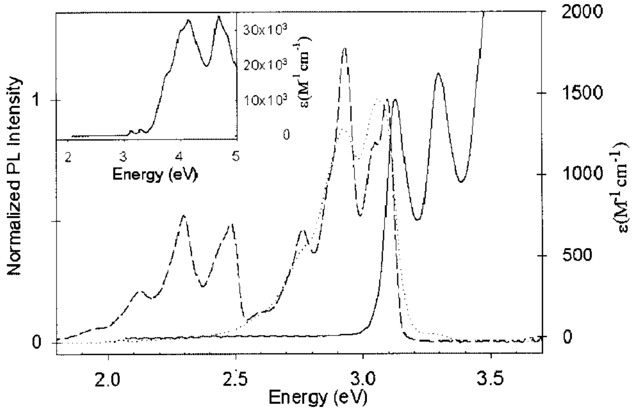


Figure 5. Low-energy tail of the absorption spectrum (solid line) and emission spectra at 298 K and 77 K (dotted and short dashed line, respectively) for a 10^{-5} M ethanol solution of **11**.

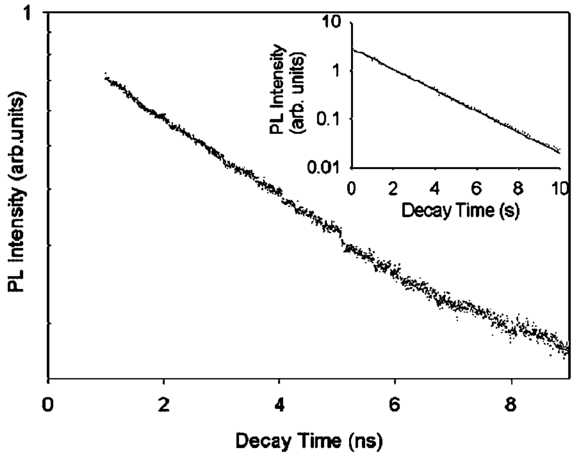


Figure 6. Fluorescence and phosphorescence (see inset) decay time of a 10^{-5} M ethanol solution of **11** with the corresponding single exponential fit.

Conclusions

A series of aza[5]helicenes bearing one or two nitrogen atoms in selected positions has been synthesized and characterized structurally (X-ray crystallography), and spectroscopically (NMR spectroscopy, absorption, emission, and lifetime of the excited states). On the basis of the behaviors of the studied molecules, we can conclude that aza[5]helicenes may be promising systems for practical applications in photo- and optoelectronics.

Experimental Section

General Remarks: All solvents were distilled and dried before use. 2-Methylnaphthalene, 3-methylisoquinoline, 6-methylquinoline, quinoline-3-carbaldehyde, selenium(IV) oxide, triphenylphosphane, and 1-bromopyrrolidine-2,5-dione (*N*-bromosuccinimide) are commercial products and were used without further purification. NMR spectra were recorded either on Bruker ARX 400 or Bruker Avance 500 spectrometers operating at proton resonance frequencies of 400 and 500 MHz, respectively. The products were dissolved in $CDCl_3$ and tetramethylsilane (TMS) was added as reference. $^1H\{^1H\}$ NOE difference and two-dimensional NOESY spectra were recorded by using standard literature pulse sequences. Electron ionization mass spectra were recorded on a Finnigan MAT TSQ 70 instrument (70 eV); the samples were introduced into the spectrometer source by direct probe insertion. Irradiations were carried out on a Rayonet RPR-100 photochemical reactor equipped with 16 lamps irradiating in the visible range.

Absorption measurements were carried out with a Perkin–Elmer Lambda 900 spectrophotometer. Continuous wave PL and PLE measurements as well as time-resolved ones in the time range of a few seconds were performed with an Aminco Bowman Series 2 spectrofluorimeter. All the optical measurements were performed with a spectral resolution of 1 nm and all the spectra were corrected for the instrumental spectral response. For the low-temperature measurements the solutions were directly frozen in liquid nitrogen. The quantum yield (Φ) was determined by comparison with a standard solution of quinine sulfate in 1.0 N sulfuric acid.[28] Time-resolved measurements were performed with a streak-camera-based set-up with a temporal resolution better than 20 ps.

2-(Bromomethyl)naphthalene: This compound was prepared, as reported in the literature,[29] from 2-methylnaphthalene, *N*-bromosuccinimide, and benzoyl peroxide in CCl_4 under irradiation in 90% yield; m.p. 52–54 °C (ref. 54 °C).

(2-Naphthylmethyl)triphenylphosphonium Bromide: This compound was prepared, as reported in the literature,[29] from 2-(bromomethyl)naphthalene and triphenylphosphane in boiling xylene in 92% yield; m.p. 248–251 °C (dec.; ref. 248–251 °C).

6-Quinolinecarbaldehyde and 3-Isoquinolinecarbaldehyde: These compounds were prepared, as reported in the literature,[30] by mixing the corresponding methyl-substituted heterocycle with selenium(IV) oxide and heating the solid mixture at 250 °C.
6-Quinolinecarbaldehyde: Yield: 96%; m.p.74–76 °C (ref. 75–76 °C).[31]
3-Isoquinolinecarbaldehyde: Yield: 30%; m.p. 47–49 °C (ref. 49.6–50 °C).[32]

(X-Heterocycle)methanol. General Procedure: These compounds were prepared, as reported in the literature, by treatment of the corresponding aldehydes with $NaBH_4$ in EtOH.
3-Quinolylmethanol: Yield: 94%; m.p. 81–83 °C (ref. 83–84 °C).[33]
6-Quinolylmethanol: Yield: 96%; m.p. 80–82 °C (ref. 79–80 °C).[34]
3-Isoquinolylmethanol: Yield: 82%; m.p. 78–82 °C (ref. 81 °C).[35]

(X-Heterocyclemethyl) Chloride. General Procedure: These compounds were prepared, as reported in the literature,[36] by precipitating the chlorohydrate salt of the methanol heterocycle from benzene with gaseous HCl. The solid was dissolved in thionyl chloride and refluxed for 1 h. After evaporation of the unreacted thionyl chloride, the solid was collected, dissolved in ice-water, and basified with ammonia. The precipitate was collected and dried to give the appropriate chloro derivative.
3-Quinolylmethyl Chloride: Yield: 78%; m.p. 30–32 °C (ref. 33–34 °C).[36]
6-Quinolylmethyl Chloride: Yield: 80%, 69–71 °C (ref. 70.5–71 °C).[36]
3-Isoquinolylmethyl Chloride: Yield: 64% oil (ref. oil).[36]

(X-Heterocyclemethyl)triphenylphosphonium Chloride. General Procedure: The X-Heterocyclemethyl chloride (0.177 g, 1 mmol) was dissolved in toluene (10 mL) and triphenylphosphane (0.262 g, 1 mmol) was added. The mixture was refluxed for 4 h. The solid was filtered, washed well with toluene, and dried. It was then used directly without particular characterization.

(3-Quinolylmethyl)triphenylphosphonium Chloride: Yield: 76%; m.p. 262–264 °C.
(6-Quinolylmethyl)triphenylphosphonium Chloride: Yield: 62%; m.p. 201–203 °C.
(3-Isoquinolylmethyl)triphenylphosphonium Chloride: Yield: 67%; m.p. 206–208 °C.

1-(2-Naphthyl)-2-(X-heterocycle)ethene. General Procedure: NaOMe (0.065 g, 1.2 mmol) was added, whilst stirring, to a flask containing a mixture of X-heterocyclic aldehyde (0.157 g, 1 mmol) and (2-naphthylmethyl)triphenylphosphonium bromide (0.483 g, 1 mmol) or the appropriate (X-heterocyclic methyl)triphenylphosphonium chloride (0.439 g, 1 mmol) in methanol (15 mL). The mixture was gently refluxed for 3 h. After cooling, water was added, and the solution extracted many times with a large amount of CH_2Cl_2. After drying and solvent evaporation, the residue was chromatographed on silica gel. The numbering used is the same as for the helicene, with the addition of the two hydrogens (15 and 16) borne by the carbon atoms were the closure occurs.

1-(2-Naphthyl)-2-(6-quinolyl)ethene (1):[37] R_f = 0.30 (CH_2Cl_2/AcOEt, 5:1). Yield: 85%; m.p. 211–212 °C (ref. 209.5 °C). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.40 (dd, $J_{2,3}$ = 4.4, $J_{2,1}$ = 8.0 Hz, 1 H, H2), 7.87–7.37 (various multiplets containing unassigned signals, 10 H), 7.92 (X of ABX, 1 H, H16), 8.02 (B of ABX, $J_{6,16}$ = 1.8, $J_{6,5}$ = 8.9 Hz, 1 H, H6), 8.11 (A of ABX, $J_{5,6}$ = 8.9 Hz, 1 H, H5), 8.15 (dd, $J_{1,3}$ = 1.4, $J_{1,2}$ = 8.0 Hz, 1 H, H1), 8.88 (dd, $J_{3,1}$ = 1.4, $J_{3,2}$ = 4.4 Hz, 1 H, H3) ppm.

1-(2-Naphthyl)-2-(3-quinolyl)ethene (2): R_f = 0.43 (AcOEt/hexane, 1:1). Yield: 70%; m.p. 200–202 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.37 (B of AB, $J_{8,7}$ = 16.2 Hz, 1 H, H8), 7.52 (A of AB, $J_{7,8}$ = 16.2 Hz, 1 H, H7), 8.30–7.47 (various multiplets containing unassigned signals, 12 H), 8.22 (d, $J_{16,6}$ = 2.2 Hz, 1 H, H16), 9.18 (d, $J_{6,16}$ = 2.2 Hz, 1 H, H6) ppm. MS: m/z = 281 [M^+], 280. $C_{21}H_{15}N$ (281.4): calcd. C 89.65, H 5.37, N 4.98; found C 89.74, H 5.37, N 4.89.

2-(3-Isoquinolyl)-1-(2-naphthyl)ethene (3): R_f = 0.48 (AcOEt/hexane, 5:3). Yield: 70%; m.p. 256–258 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.44 (B of AB, $J_{8,7}$ = 16 Hz, 1 H, H8), 8.00–7.47 (various multiplets containing unassigned signals, 13 H), 8.10 (A of AB, $J_{7,8}$ = 16 Hz, 1 H, H7), 9.28 (s, 1 H, H5) ppm. MS: m/z = 281 [M^+], 280. $C_{21}H_{15}N$ (281.4): calcd. C 89.65, H 5.37, N 4.98; found C 89.87, H 5.37, N 4.98.

1,2-Di(6-quinolyl)ethene (4):[15] R_f = 0.20 (AcOEt/hexane, 5:1). Yield: 78%; m.p. 216–219 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.43 (dd, $J_{2,3/13,12}$ = 4.4, $J_{2,1/13,14}$ = 8.2 Hz, 2 H, H2 and H13), 7.45 (s, 2 H, H7 and H8), 7.90 (d, $J_{15,9/16,6}$ = 2 Hz, 2 H, H15 and H16), 8.03 (dd, $J_{6,16/9,15}$ = 2, $J_{6,5/9,10}$ = 8.8 Hz, 2 H, H6 and H9), 8.13 (d, $J_{5,6/10,9}$ = 8.8 Hz, 2 H, H5 and H10), 8.18 (d, $J_{1,2/14,13}$ = 8.2 Hz, 2 H, H1 and H14), 8.90 (dd, $J_{3,1/12,14}$ = 1.5, $J_{3,2/12,13}$ = 4.4 Hz, 2 H, H3 and H12) ppm. MS: m/z = 282 [M^+], 281. $C_{20}H_{14}N_2$ (282.3): calcd. C 85.08, H 5.00, N 9.92; found C 84.97, H 4.99, N 9.90.

1,2-Di(3-quinolyl)ethene (5): R_f = 0.30 (AcOEt/hexane, 5:1). Yield: 83%; m.p. 237–239 °C;^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.48 (s, 2 H, H7 and H8), 7.57 (ddd, $J_{2,4/13,11}$ = 1.3, $J_{2,3/13,12}$ = 6.8, $J_{2,1/13,14}$ = 8.1 Hz, 2 H, H2 and H13), 7.71 (ddd, $J_{3,1/12,14}$ = 1.5, $J_{3,2/12,13}$ = 6.8, $J_{3,4/12,11}$ = 8.4 Hz, 2 H, H3 and H12), 7.86 (dd, $J_{1,3/14,12}$ = 1.5, $J_{1,2/14,13}$ = 8.1 Hz, 2 H, H1 and H14), 8.12 (dd, $J_{4,2/11,13}$ = 1.3, $J_{4,3/11,12}$ = 8.4 Hz, 2 H, H4 and H11), 8.25 (d, $J_{15,9/16,6}$ = 2.3 Hz, 2 H, H15 and H16), 9.20 (d, $J_{6,16/9,15}$ = 2.3 Hz, 2 H, H6 and H9) ppm. MS: m/z = 282 [M^+], 281. $C_{20}H_{14}N_2$ (282.3): calcd. C 85.08, H 5.00, N 9.92; found C 85.27, H 5.01, N 9.94.

1,2-Di(3-isoquinolyl)ethene (6): R_f = 0.58 (AcOEt). Yield: 68%; m.p. 236–238 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56 (ddd, $J_{3,1/12,14}$ = 1.1, $J_{3,2/12,13}$ = 6.9, $J_{3,4/12,11}$ = 8.1 Hz, 2 H, H3 and H12), 7.67 (ddd, $J_{2,4/13,11}$ = 1.2, $J_{2,3/13,12}$ = 6.9, $J_{2,1/13,14}$ = 8.2 Hz, 2 H, H2 and H13), 7.70 (s, 2 H, H7 and H8), 7.82 (d, $J_{1,2/14,13}$ = 8.2 Hz, 2 H, H1 and H14), 7.96 (d, $J_{4,3/11,12}$ = 8.1 Hz, 2 H, H4 and H11), 8.01 (s, 2 H, H15 and H16), 9.28 (s, 2 H, H5 and H10) ppm. MS: m/z = 282 [M^+], 281. $C_{20}H_{14}N_2$ (282.3): calcd. C 85.08, H 5.00, N 9.92; found C 85.01, H 4.98, N 9.92.

2-(3-Isoquinolyl)-1-(6-quinolyl)ethene (7): R_f = 0.33 (AcOEt/hexane, 5:1). Yield: 78%; m.p. 129–130 °C. ^1H NMR(400 MHz, $CDCl_3$, 25 °C): δ = 7.40 (dd, $J_{2,3}$ = 4.4, $J_{2,1}$ = 8.13 Hz, 1 H, H2), 7.45 (d, $J_{7,8}$ = 15.8 Hz, 1 H, H7), 7.51 (s, 1 H, H15), 7.57 (ddd, $J_{12,14}$ = 1.2, $J_{12,13}$ = 6.8, $J_{12,11}$ = 8.0 Hz, 1 H, H12), 7.69 (ddd, $J_{13,11}$ = 1.2, $J_{13,12}$ = 6.8, $J_{13,14}$ = 8.2 Hz, 1 H, H13), 8.00 (d, $J_{8,7}$ = 15.8 Hz, 1 H, H8), 8.06 (dd, $J_{6,16}$ = 1.8, $J_{6,5}$ = 8.8 Hz, 1 H, H6), 8.12 (d, $J_{5,6}$ = 8.8 Hz, 1 H, H5), 8.17 (dd, $J_{1,3}$ = 1.8, $J_{1,2}$ = 8.13 Hz, 1 H, H1), 8.88 (dd, $J_{3,1}$ = 1.8, $J_{3,2}$ = 4.4 Hz, 1 H, H3], 9.30 (s, 1 H, H10) ppm. MS: m/z = 282 [M^+], 281. $C_{20}H_{14}N_2$ (282.3): calcd. C 85.08, H 5.00, N 9.92; found C 85.31, H 5.01, N 9.95.

1-(3-Quinolyl)-2-(6-quinolyl)ethene (8): R_f = 0.33 (AcOEt/hexane, 5:3). Yield: 72%; m.p. 220–224 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.25 (B of AB, $J_{7,8}$ = 16 Hz, 1 H, H7), 7.32 (dd, $J_{2,3}$ = 4.4, $J_{2,1}$ = 8.0 Hz, 1 H, H2), 7.36 (A of AB, $J_{8,7}$ = 16 Hz, 1 H, H8), 7.48 (dd, $J_{13,11}$ = 1.5, $J_{13,12}$ = 8.1 Hz, 1 H, H13), 7.63 (ddd, $J_{12,14}$ = 1.5 Hz, $J_{12,11}$ = 6.6 Hz, $J_{12,13}$ = 8.1 Hz, 1 H, H12), 8.11–7.72 (various multiplets containing unassigned signals, 7 H), 8.83 (dd, $J_{3,1}$ = 1.5, $J_{3,2}$ = 4.4 Hz, 1 H, H3), 9.09 (d, $J_{9,15}$ = 2.2 Hz, 1 H, H9) ppm. MS: m/z = 282 [M^+], 281. $C_{20}H_{14}N_2$ (282.3): calcd. C 85.08, H 5.00, N 9.92; found C 85.06, H 5.00, N 9.93.

2-(3-Isoquinolyl)-1-(3-quinolyl)ethene (9): R_f = 0.47 (AcOEt/hexane, 5:1). Yield: 89%; m.p. 211–212 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.54 (d, $J_{7,8}$ = 16 Hz, 1 H, H7), 8.14–7.46 (various multiplets containing unassigned signals, 9 H), 8.00 (d, $J_{8,7}$ = 16 Hz, 1 H, H8), 8.30 (d, $J_{16,6}$ = 2.3 Hz, 1 H, H16), 9.25 (d, $J_{6,16}$ = 2.3 Hz, 1 H, H6), 9.30 (s, 1 H, H10) ppm. MS: m/z = 282 [M^+], 281. $C_{20}H_{14}N_2$ (282.3): calcd. C 85.08, H 5.00, N 9.92; found C 84.84, H 5.01, N 9.88.

Photochemical Reactions. General Procedure: The appropriate ethene derivative (0.282 g, 1.0 mmol) was dissolved in ethyl acetate (150 mL) in a Pyrex vessel open to the air. The vessel was irradiated with visible light for a time ranging between 24 and 36 h. The irradiation was stopped when, and if, some tar had begun to form. The solvent was removed under vacuum, and the residue was chromatographed on silica gel. NMR data are given in Table 1.

4-Aza[5]helicene (10): R_f = 0.41 (AcOEt/hexane, 3:1). Yield: 47%; m.p. 170–172 °C. MS: m/z = 279 [M^+], 278. $C_{21}H_{13}N$ (279.3): calcd. C 90.30, H 4.69, N 5.01; found C 90.20, H 4.68, N 5.00.

5-Aza[5]helicene (11): R_f = 0.28 (AcOEt/hexane, 1:1). Yield: 82%; m.p. 198–200 °C. MS: m/z = 279 [M^+], 278. $C_{21}H_{13}N$ (279.3): calcd. C 90.30, H 4.69, N 5.01; found C 90.18, H 4.67, N 5.01.

6-Aza[5]helicene (12): R_f = 0.47 (AcOEt/hexane, 5:3). Yield: 40%; m.p. 223–225 °C. MS: m/z = 279 [M^+], 278. $C_{21}H_{13}N$ (279.3): calcd. C 90.30, H 4.69, N 5.01; found C 90.41, H 4.70, N 5.02.

4,11-Diaza[5]helicene (13): R_f = 0.50 (AcOEt/hexane, 5:1). Yield: 98%; m.p. 204–206 °C. MS: m/z = 280 [M^+], 279. $C_{20}H_{12}N_2$ (280.3): calcd. C 85.69, H 4.32, N 9.99; found C 85.34, H 4.30, N 9.96.

5,10-Diaza[5]helicene (14):[13] R_f = 0.33 (AcOEt/hexane, 5:1). Yield: 98%; m.p. 189–190 °C. MS: m/z = 280 [M^+], 279. $C_{20}H_{12}N_2$

(280.3): calcd. C 85.69, H 4.32, N 9.99; found C 85.52, H 4.31, N 9.96.

6,9-Diaza[5]helicene (15):[13] R_f = 0.27 (AcOEt: Hexane 5:1). Yield: 72%; m.p.155–156 °C. MS: m/z = 280 [M$^+$], 279. $C_{20}H_{12}N_2$ (280.3): calcd. C 85.69, H 4.32, N 9.99; found C 85.95, H 4.33, N 10.02.

4,9-Diaza[5]helicene (16): R_f = 0.22 (AcOEt/hexane, 5:1). Yield: 85%; m.p. 186–188 °C. MS (70 eV, EI): m/z = 280 [M$^+$], 279. $C_{20}H_{12}N_2$ (280.3): calcd. C 85.69, H 4.32, N 9.99; found C 85.61, H 4.31, N 9.98.

4,10-Diaza[5]helicene (17): R_f = 0.23 (AcOEt/hexane, 5:1). Yield: 98%; m.p. 162–164 °C. MS: m/z = 280 [M$^+$], 279. $C_{20}H_{12}N_2$ (280.3): calcd. C 85.69, H 4.32, N 9.99; found C 85.80, H 4.33, N 10.00.

5,9-Diaza[5]helicene (18): R_f = 0.35 (AcOEt/hexane, 5:1). Yield: 98%; m.p. 187–189 °C. MS: m/z = 280 [M$^+$], 279. $C_{20}H_{12}N_2$ (280.3): calcd. C 85.69, H 4.32, N 9.99; found C 85.55, H 4.30, N 9.97.

2-(7-Isoquinolyl)-1-(2-naphthyl)ethene (19): R_f = 0.53 (AcOEt/hexane, 5:1). Yield: 98%; m.p. 250–251. MS: m/z = 281 [M$^+$], 280. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.41 (B part of AB system, $J_{7,8}$ = 16.4 Hz, 1 H, H8 or H7), 7.45 (A part of AB system, $J_{7,8}$ = 16.4 Hz, 1 H, H7 or H8), 7.52–7.45 (ms, 2 H, H12 and H13), 7.64 (d, $J_{4,3}$ = 5.7 Hz, 1 H, H4), 7.79 (dd, J = 8.6 and 7.8 Hz, 1 H, H6), 7.88–7.81 (ms, 4 H, H5, H10, H11, H14), 7.93 (br. s, 1 H, H16), 8.00 (dd, $J_{9,10}$ = 8.6, $J_{9,15}$ = 1.8 Hz, 1 H, H9), 8.02 (br. s, 1 H, H15), 8.51 (d, $J_{3,4}$ = 5.7 Hz, 1 H, H3), 9.27 (s, 1 H, H1), $C_{21}H_{15}N$ (281.4): calcd. C 89.65, H 5.37, N 4.98; found C 89.95, H 5.36, N 5.00

7-Azabenzo[*ghi*]perylene (20): R_f = 0.61 (AcOEt/hexane, 3:1). Yield: 98%; m.p. 237–238 °C. MS: m/z = 277 [M$^+$], 138, 124. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.03 (d, $J_{4,3}$= 5.3 Hz, 1 H, H4), 8.08 (d, $J_{6,5}$ = 8.8 Hz, 1 H, H6), 8.18 (dd, $J_{12,11}$ = 7.8 and, $J_{12,13}$ = 7.8 Hz, 1 H, H12), 8.24–8.19 (AB system containing unassigned signals, 2 H), 8.37 (d, $J_{5,6}$ = 8.8 Hz, 1 H, H5), 8.39 (dd, $J_{11,12}$ = 7.8, $J_{11,13}$ = 1.3 Hz, 1 H, H11), 8.47–8.43 (AB system containing unassigned signals, 2 H), 9.22 (d, $J_{3,4}$ = 5.3 Hz, 1 H, H3), 9.72 (dd, $J_{13,12}$ = 7.8, $J_{13,11}$ = 1.3 Hz, 1 H, H13). $C_{21}H_{11}N$ (277.3): calcd. C 90.95, H 4.00, N 5.05; found C 90.84, H 4.02, N 5.06.

***N*-(2-Naphthalenemethylidene)-2-naphthaleneamine (21):** Yield: 98%; m.p. 173–176 °C (ref. 178 °C).[38]

X-ray Crystallographic Study: All crystals were mounted on a glass fiber in air and collected at room temperature on a Bruker SMART CCD (**10** and **11**) or a Bruker SMART-APEX CCD area-detector diffractometer (**12**). Crystal data are reported in Table 4.

Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used with the generator working at 45 kV and 40 mA (SMART) or 50 kV and 30 mA (SMART-APEX). Orientation matrixes were initially obtained from least-squares refinement on about 300 reflections measured in three different ω regions, in the range $0 < \theta < 23°$; cell parameters were optimized on the position, determined after integration, of all reflections above the 10σ(I) level. The intensity data were collected within the limits $0 < 2\theta < 50°$ in the full sphere (ω scan method), with sample–detector distances at 3.9, 3.4, and 4.7 cm for **10**, **11**, and **12**, respectively. 2400 Frames (at 60, 25, and 20 s per frame for **10**, **11**, and **12**, respectively; Δω = 0.3°) were collected; an empirical absorption correction was applied (SADABS).[39]

The structures were solved by direct methods (SIR-97)[40] and refined with full-matrix least-squares (SHELX-97)[41] on F^2 on the basis of independent reflections; anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogens were riding on their carbon atoms, though whenever possible (in **12**), they have been freely refined. Location of N atoms was assumed based on the absence of peaks at the expected position of a bonded H atom and by the reduced skeletal bond lengths. However, all the X-ray

Table 4. Crystal data and structure refinement details.

	10	11	12
Molecular formula	$C_{21}H_{13}N$	$C_{21}H_{13}N$	$C_{21}H_{13}N$
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $C2/c$	orthorhombic, $P2_1nb$	monoclinic, $P2_1/n$
Unit cell dimensions	a = 19.344(3) Å	a = 8.2496(4) Å	a = 13.7011(8) Å
	b = 8.828(1) Å	b = 9.9987(5) Å	b = 5.9854(3) Å
	c = 25.968(4) Å	c = 17.2243(8) Å	c = 17.7809(1) Å
	β = 100.773(5)°		β = 103.972(2)°
Volume	4298(1) Å^3	1420.75(1) Å^3	1415.0(1) Å^3
Z, calculated density	12, 1.295 Mg m^{-3}	4, 1.31 Mg m^{-3}	4, 1.31 Mg m^{-3}
Absorption coefficient	0.075 mm^{-1}	0.076 mm^{-1}	0.076 mm^{-1}
F(000)	1752	583.9	583.9
Crystal size	0.2×0.4×0.4 mm	0.2×0.2×0.3 mm	0.2×0.2×0.5 mm
θ range	2.6–23.3°	2.36–23.26°	1.69–29.8°
Limiting indices	$21 \leq h \leq 21$	$9 \leq h \leq 9$	$18 \leq h \leq 18$
	$9 \leq k \leq 9$	$11 \leq k \leq 11$	$8 \leq k \leq 7$
	$28 \leq l \leq 28$	$19 \leq l \leq 19$	$23 \leq l \leq 23$
Reflections collected/unique	18155/3098	13768/2040	20024/3792
R_{int}[a]	0.0494	0.0346	0.0303
Absorption correction	Sadabs	Sadabs	Sadabs
Data/restraints/parameters	3098/52/387	2040/1/200	3792/0/251
Goodness-of-fit on F^2	1.068	1.087	0.99
Final R indices [$I > 2\sigma(I)$][b]	$R1$ = 0.0596, $wR2$ = 0.1423	$R1$ = 0.0294, $wR2$ = 0.0773	$R1$ = 0.0455, $wR2$ = 0.1192
R indices (all data)[b]	$R1$ = 0.0816, $wR2$ = 0.1562	$R1$ = 0.0370, $wR2$ = 0.0839	$R1$ = 0.0678, $wR2$ = 0.1346
Largest diff. peak and hole	0.29 and –0.18 e Å^{-3}	0.089 and –0.097 e Å^{-3}	0.21 and –0.14 e Å^{-3}

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$; $R_\sigma = \Sigma\sigma(F_o^2)/\Sigma F_o^2$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$. GoF = $\{S/(n - p)\}^{0.5} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$.

geometries show smaller gaps between C–C and C–N pseudo-equivalent distances compared to DFT optimizations, thus suggesting the possible presence of some disorder about the molecular pseudo-twofold axis. No attempt to assign the correct absolute configuration was made for **11**.

The crystal structure of **10** is more problematic. In the isomorphous *C*2/*c* form of the parent helicene, one ordered molecule is lying on a twofold axis; at variance, **10** lacks the proper twofold symmetry and disorder would be implied. However, we were unable to refine this model satisfactorily. Instead, we refined a full molecule (with half occupancy) whose center of mass is lying somewhat apart from the twofold axis. This means that the observed disorder is not merely substitutional. Refinement was found to be quite difficult and became stable only after imposing a rigid conformation to the disordered molecule (identical to that of the ordered molecule in general position). Only in the last cycles were the rigid conformational constraints replaced by the softer restraints of the skeletal bond lengths. The thermal factors of some C atoms were refined only isotropically.

CCDC-232489–232491 (for **10**–**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We are indebted to MIUR for funding (PRIN 2002 no. 2002025473) and to Plataforma Solar de Almeria (Spain) for the use of their facilities.

---

[1] T. Verbiest, S. Van Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T. J. Katz, A. Persoons, *Science* **1998**, *282*, 913–915.

[2] K. E. S. Phillips, T. J. Katz, S. Jockusch, A. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11 899–11 907.

[3] M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770.

[4] a) R. H. Martin, *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660; b) T. J. Katz, *Angew. Chem. Int. Ed.* **2000**, *39*, 1921–1923; c) F. Vögtle, *Fascinating Molecules in Organic Chemistry*, Wiley, New York, **1992**, p. 156; d) K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1–76; e) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130; f) M. C. Carreno, S. Garcia-Cerrada, A. Urbano, *J. Am. Chem. Soc.* **2001**, *123*, 7929–7930; g) A. Urbano, *Angew. Chem. Int. Ed.* **2003**, *42*, 3986–3989; h) A. E. Rowan, J. M. Nolte, *Angew. Chem. Int. Ed.* **1998**, *37*, 63–68.

[5] a) H. Winberg, *Acc.Chem. Res.* **1971**, *4*, 65–73; b) Y. Dai, T. J. Katz, *J. Org. Chem.* **1997**, *62*, 1274–1285; c) C. Nuckolls, T. J. Katz, L. Castellanos, *J. Am. Chem. Soc.* **1996**, *118*, 3767–3768; d) S. Maiorana, A. Papagni, E. Licandro, R. Annunziata, P. Paravidino, D. Perdicchia, C. Giannini, M. Bencini, K. Clays, A. Persoons, *Tetrahedron* **2003**, *59*, 6481–6488.

[6] J. F. Field, T. J. Hill, D. Venkataraman, *J. Org. Chem.* **2003**, *68*, 6071–6078.

[7] a) H. Nakagawa, S. Ogashiwa, H. Tanaka, K. Yamada, H. Kawazura, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1903–1904; b) R. H. Martin, M. Flamming-Barbieux, J. P. Cosyn, M. Gelbke, *Tetrahedron Lett.* **1968**, 3507–3510; c) Ch. Goeditcke, H. Stegemeyer, *Tetrahedron Lett.* **1970**, *12*, 937–940; d) H. J. Bestmann, W. Both, *Chem. Ber.* **1974**, *107*, 2923–2925.

[8] T. Caronna, R. Sinisi, M. Catellani, S. Luzzati, S. Abbate, C. Longhi, *Synth. Met.* **2001**, *119*, 79–80.

[9] a) M. B. Groen, H. Wynberg, *J. Am. Chem. Soc.* **1971**, *93*, 2968–2974; b) D. A. Lightner, D. T. Hefelfinger, T. W. Powers, G. W. Frank, K. N. Trueblood, *J. Am. Chem. Soc.* **1972**, *94*, 3492–3497.

[10] a) J.-C. Rodriguez-Ubis, B. Alpha, D. Plancherel, J.-M. Lehn, *Helv. Chim. Acta* **1984**, *67*, 2264–2269; b) J.-M. Lehn, J.-B. Regnouf de Vains, *Helv. Chim. Acta* **1992**, *75*, 1221–1236.

[11] a) J.-M. Lehn, *Pure Appl. Chem.* **1978**, *50*, 871–892; b) V. Balzani, A. Credi, F. Scandola, in *Transition Metals in Supramolecular Chemistry* (Eds.: L. Fabbrizi, A. Poggi), Kluwer, Dordrecht, The Netherlands, **1994**; c) M. Grätzel, *Nature* **2001**, *414*, 338–344; d) M. Osawa, M. Hoshino, Y. Wakatsuki, *Angew. Chem. Int. Ed.* **2001**, *40*, 3472–3474; e) K. K. W. Lo, W. K. Hui, D. C. M. Ng, *J. Am. Chem. Soc.* **2002**, *124*, 9344–9345; f) W. J. Finkenzeller, H. Yersin, *Chem. Phys. Lett.* **2003**, *377*, 299–309.

[12] a) T. R. Govindachari, K. Nagarajan, B. R. Pai, V. N. Sundararajan, *Chem. Ber.* **1958**, *91*, 2053–2060; b) J. Meisenheimer, K. Witte, *Chem. Ber.* **1903**, *36*, 4153–4164; c) H. A. Staab, M. A. Zirnstein, C. Krieger, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 86–88; d) C. M. Thompson, S. Docter, *Tetrahedron Lett.* **1988**, *29*, 5213–5216; e) H. W. Galbraith, E. F. Degering, E. F. Hitch, *J. Am. Chem. Soc.* **1951**, *73*, 1323–1324; f) S. Kanoktanaporn, J. A. H. MacBride, *J. Chem. Soc., Perkin Trans. 1* **1978**, 1126–1131; g) J. W. Barton, R. B. Walker, *Tetrahedron Lett.* **1978**, *11*, 1005–1008; h) S. V. Kessar, Y. P. Gupta, P. Singh, V. Jain, P. S. Pahwa, *J. Chem. Soc. Pak.* **1979**, *1*, 129–130; i) K. Sato, S. Arai, *Cyclophane Chemistry for the 21st Century*, Research Signpost, Kerala, India, **2002**, 173–197.

[13] T. Caronna, S. Gabbiadini, A. Mele, F. Recupero, *Helv. Chim. Acta* **2002**, *85*, 1–7.

[14] a) F. Dietz, M. Scholz, *Tetrahedron* **1968**, *24*, 6845–6849; b) W. H. Laarhoven, Th. J. H. M. Cuppen, R. J. F. Nivard, *Tetrahedron* **1970**, *26*, 1069–1083; c) F. B. Mallory, C. W. Mallory, *J. Am. Chem. Soc.* **1972**, *94*, 6041–6048; d) D. D. Morgan, S. W. Organ, M. Orchin, *Tetrahedron Lett.* **1972**, 1789–1792.

[15] This compound was first reported in K. A. Muszkat, S. Sharafi-Ozeri, *Chem. Phys. Lett.* **1976**, *42*, 99–102, but without any characterization.

[16] M. Randić, N. Trinagistić, J. W. Knop, Z. Jericêvić, *J. Am. Chem. Soc.* **1985**, *107*, 849–859.

[17] a) M. Gorsane, R. H. Martin, *Bull. Chem. Soc. Belg.* **1985**, *94*, 205–214; b) C. Puls, A. Stolle, A. de Meijere, *Chem. Ber.* **1993**, *126*, 1635–1641.

[18] a) R. H. Martin, M. Baes, *Tetrahedron* **1975**, *31*, 2135–2137; b) R. H. Martin, V. Libert, *J. Chem. Res. (M)* **1980**, *4*,1937–1945.

[19] a) C. E. Loader, M. V. Sargent, C. J. Timmons, *J. Chem. Soc., Chem. Commun.* **1965**, 127–128; b) P. Bortolus, G. Gauzzo, G. Galiazzo, *Tetrahedron Lett.* **1966**, *2*, 239–242; c) C. E. Loader, C. J. Timmons, *J. Chem. Soc. (C)* **1966**, 1078–1081.

[20] C. M. Thompson, S. Docter, *Tetrahedron Lett.* **1988**, *29*, 5213–5216.

[21] V. N. Gogte, G. B. Mullick, B. D. Tilak, *Indian J. Chem.* **1974**, *12*, 1227–1229.

[22] a) A. O. McIntosh, J. Monteath Robertson, V. Vand, *J. Chem. Soc.* **1954**, 1661–1668; b) R. Kuorda, *J. Chem. Soc., Perkin Trans. 2* **1982**, 789–794.

[23] a) J. D. Dunitz, V. Schomaker, K. N. Trueblood, *J. Phys. Chem.* **1988**, *92*, 856–867; b) J. D. Dunitz, E. F. Maverick, K. N. Trueblood, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 880–895; c) E. F. Maverik, K. N. Trueblood, THMA14c, University of California, Los Angeles, USA, **1999**.

[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. J. Zakrzewski, A. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. D. Morokuma, K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gon-

zalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Revision A.7, Gaussian Inc., Pittsburgh, PA, **1998**.

[25] a) J. Trotter, *Acta Crystallogr.* **1963**, *16*, 605–608; b) R. Mason, *Mol. Phys.* **1961**, *4*, 413–415; c) D. W. Jones, J. Yerkess, *J. Cryst. Mol. Struct.* **1971**, *1*, 17–23; d) M. I. Kay, Y. Okaya, D. E. Cox, *Acta Crystallogr., Sect B* **1971**, *27*, 26–33; e) V. Petricek, I. Cisarova, L. Hummel, J. Kroupa, B. Brezina, *Acta Crystallogr., Sect. B* **1990**, *46*, 830–832.

[26] F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. Rodgers, D. G. Watson, *Acta Crystallogr., Sect. B* **1979**, *35*, 2331–2339.

[27] J. B. Birks, *Photophysics of Organic Molecules*, Wiley-Interscience, London, **1970**.

[28] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024.

[29] a) N. B. Chapman, J. F. A. Williams, *J. Chem. Soc.* **1952**, 5044–5046; b) A. H. A. Tinnemans, W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2* **1976**, 1104–1111.

[30] S. Rodionov, V. M. Schemjakin, *Zh. Obshch. Khim.* **1946**, *16*, 2072–2075; *Chem. Abstr.* **1948**, 881.

[31] F. Gialdi, R. Ponci, *Il Farmaco* **1951**, *6*, 327–330.

[32] G. Guanti, R. Riva, *Tetrahedron: Asymmetry* **2001**, *12*, 1185–1200.

[33] A. Boutros, J.-Y. Legros, J.-C. Fiaud, *Tetrahedron* **2000**, *56*, 2239–2246.

[34] C. Kaslow, *J. Org. Chem.* **1935**, *18*, 55–56.

[35] B. R. Brown, D. L. Hammick, B. H. Thewlis, *J. Chem. Soc.* **1951**, 1145–1147.

[36] C. M. Kaslow, J. M. Schlatter, *J. Am. Chem. Soc.* **1955**, *77*, 1054–1055.

[37] G. Bartocci, A. Spalletti, F. Masetti, G. Cruciani, *J. Mol. Struct.* **1993**, *298*, 165–176.

[38] M. P. Cava, R. H. Schlessinger, *Tetrahedron Lett*. **1964**, 2109–2111.

[39] G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, **1996**.

[40] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[41] G. M. Sheldrick, *SHELX-97 Programs for Crystal Structure Analysis*, Release 97-2, University of Göttingen, Germany, **1997**.

Received: September 15, 2004