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PAPER

An efficient approach to azirino and pyrrolo-fused dibenzazepines. Conformations of substituted dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepines†‡

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An effective approach to azepino-fused heterocycles is described. *trans*-1-Aryl-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepines were synthesised *via* a domino sequence: isomerization of *gem*-dichloroaziridine–intramolecular Friedel–Crafts acylation of the tethered benzene ring catalysed by $SnCl_4$ and subsequent hydride induced intramolecular cyclization. Cycloaddition of dibenzazepinium ylides, generated by heating these aziridines, to activated C═C, C≡C dipolarophiles and fullerene C_{60}, leads to derivatives of dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine. The reaction proceeds with complete stereoselectivity *via* cycloaddition of only W-ylide, which due to the high barrier does not undergo *E*,*Z*-isomerization under the reaction conditions. It was found that 2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine systems can exist in conformations of two types depending on the substituents at the pyrrolidine carbons in β-position with respect to nitrogen. Details of cycloaddition reactions and the conformational behavior of cycloadducts were studied by DFT calculations at the B3LYP/6-31G(d) level.

Introduction

Compounds with nitrogen heterocycles *ortho*-fused to dibenzo[*b*,*e*]azepine demonstrate various bioactivities: derivatives of dibenzo[*c*,*f*]imidazo[1,5-*a*]azepine have specific binding to histamine-1 and histamine-2 receptors[1] and can be used as antiallergics and antithrombotics,[2] sedative and antiulcer agents;[3] derivatives of dibenzo[*c*,*f*]pyrimido[1,6-*a*]azepine show antidepressive and anxiolytic activity;[4] derivatives of dibenzo[*c*,*f*]pyrido[1,2-*a*]azepine are highly specific for the glucocorticoid receptor,[5] partial agonists or antagonists of the progesterone receptor;[6] derivatives of dibenzo[*c*,*f*]pyrazino[1,2-*a*]azepine show anti-allergic and anti-asthmatic activities[7] and anxiolytic properties.[8] Derivatives of dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine were patented as having valuable antihistamine, sedative, and antidepressive properties,[9] but have been much less investigated than other *ortho*-fused dibenzo[*b*,*e*]azepines, probably because of the lack of simple methods for their preparation. The known methods of synthesis of tetrahydrodibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepines that involved formation of a pyrrole ring *via* cyclization of precursors with preformed dibenzo[*b*,*e*]azepine system[9] or formation of dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine moiety *via* cyclization of precursors with preformed pyrrole ring[10] or multistage transformation of pyrroloisoxazoles[11] did not provide a wide range of heterocycles of this type.

In the framework of our research concerning the synthesis of heterocycles *via* N-ylide reactions,[12] we have recently presented an effective approach to 1-aryl-1,11b-dihydroazirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines[13] which are excellent precursors of corresponding azomethine ylides. They easily undergo completely stereoselective 1,3-dipolar cycloaddition to C═C dipolarophiles with the formation of a great variety of derivatives of dibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepine. In this study we have extended our investigations to the replacement of the oxazepine moiety with azepine.

Results and discussion

Preparation of derivatives of 9*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine **1** *via* 7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepines **2** according to retrosynthetic Scheme 1 seemed to be an attractive idea. The synthesis of compounds **5a,b** was performed by reaction of imines **6a,b** with dichlorocarbene generated from $CHCl_3$ and solid KOH in the presence of TEBA as phase-transfer

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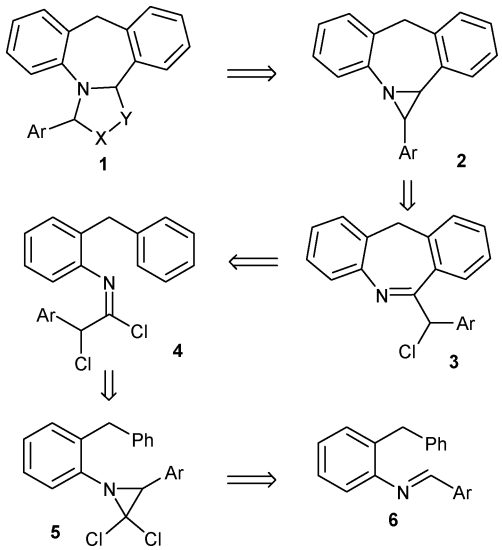
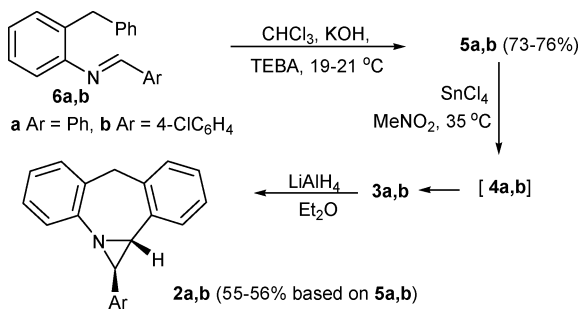
† Dedicated to Professor Oleg Nefedov on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: X-Ray diffraction data, refinement information and Cartesian coordinates. CCDC reference numbers 809443, 809444, 809445, 809446, and 809447 for **2b**, **13**, **16**, **18** & **20**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05081h



Scheme 1 Retrosynthetic approach to derivatives of dibenzo[*c*,*f*]-pyrrolo[1,2-*a*]azepine **1**.

catalyst at 19–21 °C (Scheme 2). However when we tried to synthesize compound **3** by making use of the domino sequence: isomerization of *gem*-dichloroaziridine **5**–intramolecular Friedel–Crafts acylation of the tethered benzene ring in **4** under the conditions used previously for preparation of the corresponding *O*-analogs[13a] ($AlCl_3/MeNO_2$/50 °C) the only isolated product from the complex reaction mixture was triphenylmethane. Probably, it is the product of disproportionation which is characteristic for alkylbenzenes in the presence of strong Lewis acids.[14] Therefore, we tested weaker Lewis acids ($SnCl_4$, $BF_3 \cdot Et_2O$, $TiCl_4$) as catalysts. It was found that with $BF_3 \cdot Et_2O$ or $TiCl_4$ as catalyst the reaction of aziridine **5b** proceeded very slowly at 35 °C, while long heating at this or higher temperature led to tarring and low yield of the target compound (less then 10%). The Lewis acid of choice for the realization of the target domino reaction proved to be $SnCl_4$, giving azepines **3a,b** in reasonable yields.



Scheme 2 Synthesis of azirinodibenzazepines **2a,b**.

Compounds **3a,b** are very unstable and therefore they were immediately introduced into the next step after workup of the reaction mixtures without further purification. The preparation of azirinodibenzazepines **2a,b** was performed by reduction of **3a,b** with $LiAlH_4$ in 55–56% yields based on the starting dichloroaziridines **5a,b**. The ^1H NMR spectra of compounds **2a,b** exhibited the characteristic coupling constant value for *trans*-aziridines of ~3 Hz (*J* for *cis*- and *trans*-aziridines are 6–7 and 2.5–3.5 Hz, respectively[15]).

The structure of compound **2b** was confirmed by X-ray analysis (Fig. 1). In the solid state aziridine **2b** is in the most stable conformation (*cf*. Fig. 3) with *anti*-oriented three-membered ring and the methylene group of the dibenzazepine fragment.

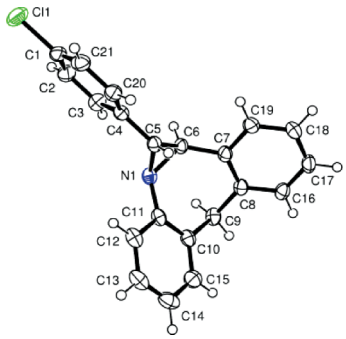


Fig. 1 X-Ray crystal structure of **2b**.

Heating aziridines **2a,b** in anhydrous toluene at 105 °C led to aziridine ring opening with formation of ylides **7** which in the presence of dipolarophiles **8–12** containing an activated C═C double bond gave rise to 1,3-dipolar adducts **13–20** in good yields (Table 1).

When the reactions were performed under solvent free conditions at 140 °C they proceeded much faster yielding the same products. The structures of compounds **13–20** were verified by ^1H, ^{13}C, ^1H 2D NOESY NMR, IR spectroscopy, and elemental analysis. Structures of **13**, **16**, **18** and **20** were confirmed by X-ray analysis (Fig. 2).

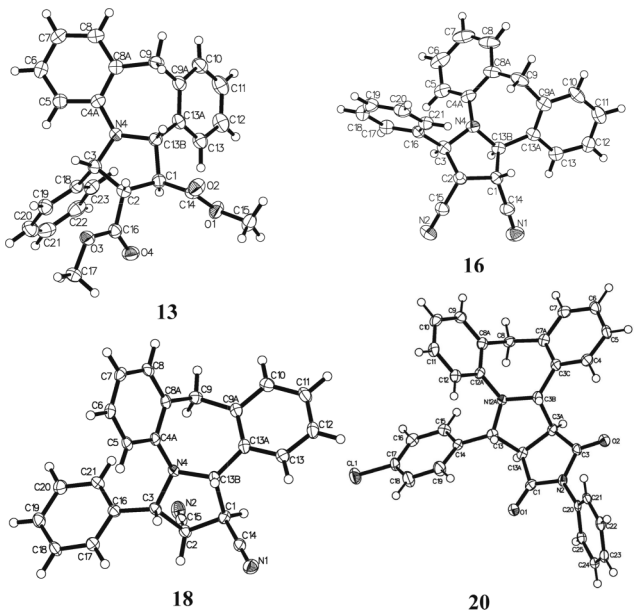
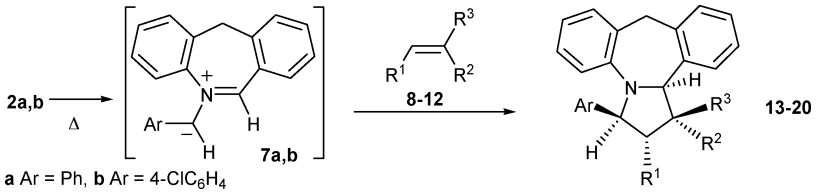


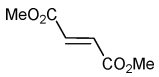
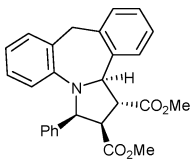
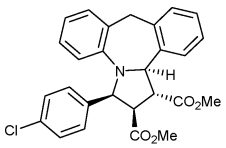
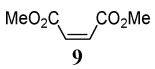
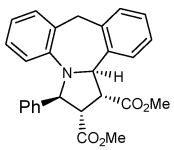
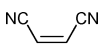
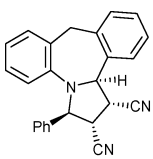
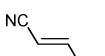
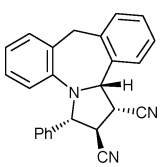
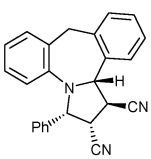
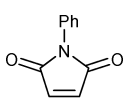
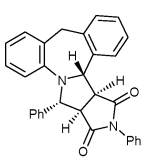
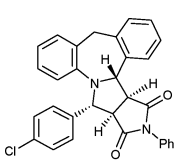
Fig. 2 X-Ray crystal structures of **13, 16, 18** and **20**.

The main feature of all the products of the cycloaddition is *cis*-configuration of pyrrolidine hydrogen at carbons in the α-position to the nitrogen. This means that the ylide which cycloadds to the C═C double bond of dipolarophiles has U- or W-configuration.[16] According to DFT B3LYP/6-31G(d) calculations (Fig. 3) the ring opening of aziridine *trans*-**2a** occurs conrotatory with the formation either of the W-ylide **21** or the U-ylide **22**. Formation of

Table 1 Reaction of aziridines **2a,b** with C═C dipolarophiles **8–12**



a Ar = Ph, **b** Ar = 4-ClC_6H_4

Entry	Aziridine **2**	Dipolarophile	Product	Method[a]	Time (h)	Yield (%)
1	**a**	 **8**	 **13**	A	16	70
2				B	4.5	70
3	**b**	**8**	 **14**	A	15	67
4	**a**	 **9**	 **15**	A	16	68
5	**a**	 **10**	 **16**	B	3.5	72
6	**a**	 **11**	 **17**  **18**	B	5	89
7	**a**	 **12**	 **19**	A	17	73
8	**b**	**12**	 **20**	A	18	78

[a] A: toluene, 105 °C; B: melt, 140 °C.

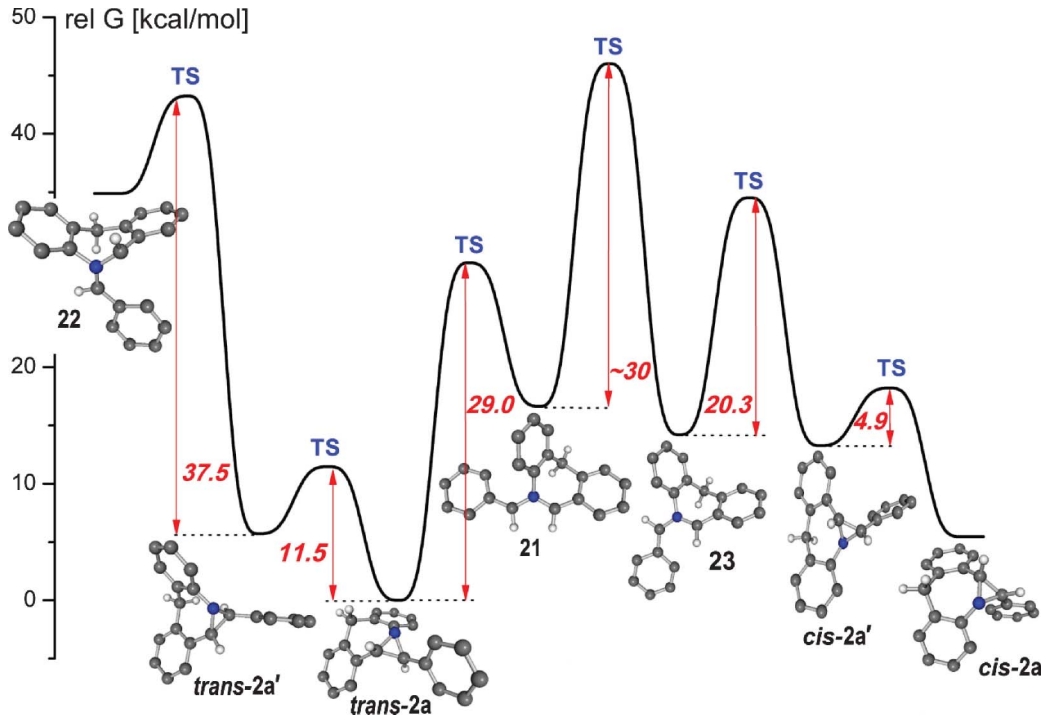


Fig. 3 Reaction profiles for transformations of aziridines and ylides. Relative free energies [kcal mol^{-1}] computed at the B3LYP/6-31G(d) level. Hydrogen atoms on aromatic rings are omitted for clarity.

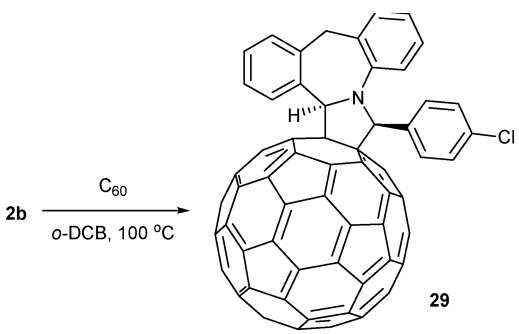
the latter involves transformation of the most stable conformation of aziridine *trans*-**2a** to the less stable conformation *trans*-**2a′** *via* inversion of azepine ring.

The W-ylide **21** is more stable than the U-ylide **22** by 18.3 kcal mol^{-1} and the barrier to formation of the former is 8.5 kcal mol^{-1} lower than that of the latter. Ylide **21** can be transformed to the even more stable S-ylide **23** by rotating the PhCH group around the C–N bond of the ylide. We were unable to find the transition state for the transformation of ylides **21**→**23** because of the extraordinary complexity of the potential energy surface. Evaluation of a barrier to isomerization of ylides **21**→**23** was based on the barriers to *Z*,*E*-isomerization of the iminium ylide: $^{-}CH_2$–$N^{+}H{=}CH_2$ (**24**), $^{-}CH_2$–$N^{+}Ph{=}CH_2$ (**25**), $^{-}CHPh$–$N^{+}H{=}CH_2$ (**26**), and 1,4-oxazepiniomethanide (**27**) which were calculated earlier[13b] and the corresponding barrier for azepiniomethanide **28** ($\Delta G^{\#}$ 29.6 kcal mol^{-1}) calculated in this work. By using both restricted and unrestricted B3LYP/6-31G(d) calculations, it was found that the barriers to *Z*,*E*-isomerization change only a little in the row of model ylidic structures **24**–**28**. Hence, the value of the barrier to transformation of ylides **21**→**23** is about 30 kcal mol^{-1}. The stereochemistry of cycloadducts **13**–**20** and calculated energy parameters testify to the participation of only W-ylide **21** in the cycloaddition.

One can also conclude from the results obtained that the observed stereoselectivity is due to the lower barrier to cycloaddition of ylide **21**, compared with the barrier to transformation of ylides **21**→**23**. The results of the calculations of transition states of cycloaddition of ylide **21** to fumaronitrile, maleonitrile, dimethyl maleate and *N*-phenylmaleimide do not contradict this conclusion. Four possible transition states were found (See Supporting Information) for each of these dipolarophiles. The lowest barriers to cycloaddition are 9.0, 9.5, 13.6 and 10.7 kcal mol^{-1}, respectively, that is much less then the estimated barrier to *Z*,*E*-isomerization of ylide **21**.

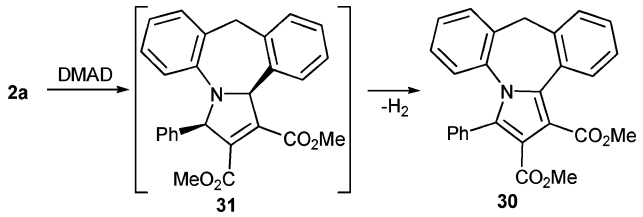
The cycloaddition of *cis*-dipolarophiles proceeds *via* the *exo*-transition state, which is in agreement with the results obtained by DFT B3LYP/6-31G(d) computations: the minimal barriers for *exo*-approach of maleonitrile, dimethyl maleate and *N*-phenymaleimide to ylide **21** are less than those for *endo*-approach by 2.2, 1.0, and 4.1 kcal mol^{-1}, respectively.

We also performed stereoselective cycloaddition of ylide **7b** to fullerene C_{60}. Heating aziridine **2b** and fullerene C_{60} in *o*-dichlorobenzene (o-DCB) at 100 °C led to the exclusive formation of fulleropyrrolidine **29** (Scheme 3), with *cis*-orientation of pyrrolidine hydrogens. The composition of the product **29** was confirmed by the exact mass experiments. The structure of the product is in agreement with ^{1}H-NMR and ^{13}C-NMR data. *cis*-Orientation of the pyrrolidine protons was confirmed by the presence of a through-space interaction between them (2D ^{1}H-NOESY).



Scheme 3 Synthesis of fulleropyrrolidine **29**.

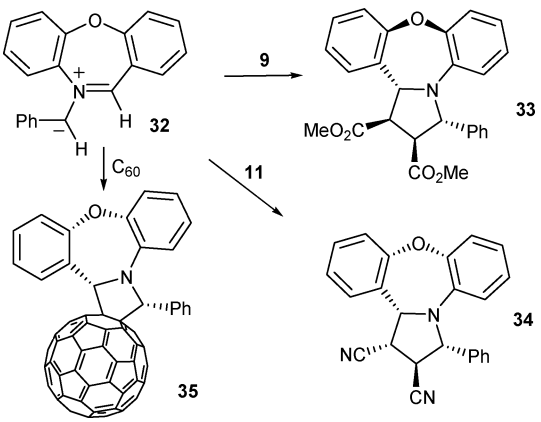
Heating aziridine **2a** and DMAD at 140 °C for 4.5 h gave rise to adduct **30** (Scheme 4) which was isolated in 76% yield. Obviously pyrrole **30** was formed *via* cycloaddition of ylide **7a** to the triple bond of DMAD and subsequent dehydrogenation of primarily pyrrolidine cycloadduct **31**.



Scheme 4 Synthesis of pyrrolodibenzazepine **30**.

The conformation and conformational dynamics of biologically relevant molecules is the key to understanding their functions.[17] Taking into account the bioactivity demonstrated by some derivatives, dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepines[9] and dibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepines,[9] we examined factors which have an influence on conformations of cycloadducts synthesised in this and previous works.[13]

Earlier it has been established[13a] by X-ray analysis that dibenzo[*c*,*f*]pyrrolo[1,2-*a*]oxazepines **33**, **34**, the adducts of ylide **32** (*O*-analog of ylide **7a**) to dimethyl maleate **9** and fumaronitrile **10**, have quite different conformations (Scheme 5). In compound **33** O-9 is *cis*-oriented to H-3 and H-13b and the pyrrolidine ring has a half-chair conformation in which H-3 is in the equatorial and H-13b is in the axial position (conformation **A** see Fig. 4). In contrast, in compound **34** O-9 is *trans*-oriented to H-3 and H-13b and pyrrolidine ring has an envelop conformation in which H-3 and H-13b are in axial positions (conformation **B**, see Fig. 4). According to calculations,[13b] the adduct **35** of ylide **32** to fullerene C_{60} has a conformation similar to conformation **B**. Experimentally the structure of this adduct was confirmed by the presence of a strong through-space interaction between the pyrrolidine protons in 2D ^{1}H-NOESY spectrum, taking into account that the distance between these protons in the conformation like **B** is 2.428 Å and in the conformation like **A** is 3.617 Å.[13b]



Scheme 5 Cycloaddition of ylide **32**.

There are two possible characteristic through-space interactions in 2D ^{1}H-NOESY spectra of compounds containing a dibenzazepine moiety that can be used for distinguishing between conformations of type **A** and **B** (See Fig. 4). Namely, in conformation **A** the interaction of H-9 and H-13b has to be present, while the interaction of H-3 and H-13b has to be absent; in conformation **B** the contrary has to be true, that is the interaction H-3 and H-13b has to be present, while the interaction H-9 and H-13b has to be absent. The analysis of X-ray data of compounds **13**, **16**, **18**, **20** and 2D ^{1}H-NOESY spectra of compounds **13, 15–18, 29** shows that compounds **13, 15** have conformation of type **A** and compounds **16–18**, **20** and **29** have conformation of type **B**. Thus, the adducts of the ylides with fullerene C_{60} and *N*-arylmaleimides have conformation of type **B** that can be determined by the rigidity of the fullerene and maleimide skeletons. But utterly unexpectedly the adducts with methoxycarbonyl-substituents have conformation of type **A**, while the adducts with cyano-substituents have conformation of type **B** irrespective of *cis*- or *trans*-arrangement of these substituents.

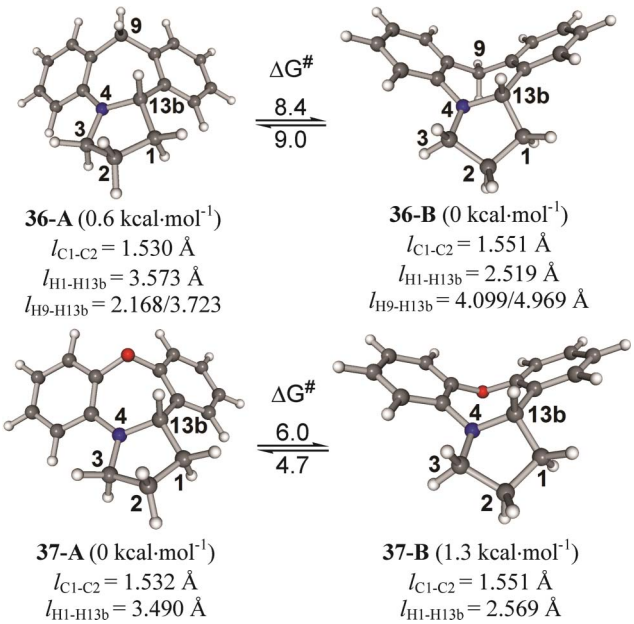


Fig. 4 Conformers of compounds **35**, **36**, the relative free energies, bond lengths, and H–H-distances computed at the B3LYP/6-31G(d) level.

To ascertain the reasons of the conformational preference of 2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine (**36**) and 1,2,3,13b-tetrahydrodibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepine (**37**) systems we performed DFT calculations of the conformations of parent compounds **36**, **37**. Two conformations of type **A** and **B** with close energy were found for each of compounds (Fig. 4). The barriers to transformations of conformations **A**, **B** *via* ring inversion according to computations are low (Fig. 4) and therefore the existence of compounds in one or the other of conformations is dependent on their relative free energies rather than on kinetic factors of their formation.

The results of these calculations are consistent with the suggestion that the conformational preference of adducts of fullerene and maleimides is due to the structural features of these fragments in compounds **20**, **29**, **35**. Namely, only in conformations **36B** and **37B** (Fig. 4) is there a possibility for fusion of bond C1–C2 with the practically planar maleimide pentagon and fullerene hexagons.

The characteristic feature of the conformations of compounds **36**, **37** is the difference of the C1–C2 bond lengths in the pyrrolidine

Table 2 The experimental and calculated bond lengths in methoxycarbonyl- and cyano-substituted molecules

Adduct	l_{C1-C2} [Å]	Compound	l_{C-C} [Å][a]	l_{C-C} [Å][b]
13-A	1.515(2)	CH_3CH_3	1.531	1.5351[18]
16-B	1.557(4)	EtCN	1.540	1.5479(15)[19]
18-B	1.551(4)	*ap*-Succinonitrile	1.551	1.561(6)[20]
33-A	1.543(3)	*sc*-Succinonitrile	1.550	—
34-B	1.562(3)	$EtCO_2Me$	1.527	—
		ap-Dimethyl succinate	1.527	1.509(5)[21]
		sc-Dimethyl succinate	1.526	—

[a] The CH_2–CH_2bond lengths computed at the B3LYP/6-31G(d) level. [b] The experimental CH_2–CH_2bond lengths.

ring: in conformations **A** it is much shorter than in conformations **B**.

The comparison of the C1–C2 bond lengths in compounds **13**, **16**, **18**, **33**, **34** determined by X-ray analysis (Table 2) disclose the same tendency. Therefore we have hypothesized that the influence of methoxycarbonyl- and cyano-substituents in the adducts on conformational preferences can be related to the influence of these substituents on single C–C bond length.

In fact, analysis of experimentally determined RH_2C–CH_2R' bond lengths in ethane, propanenitrile, dimethyl ester and dinitrile of butanedioic acid shows that introduction of methoxycarbonyl-substituents on the ethane C–C bond shortens this bond, while introduction of cyano-substituents lengthens it (Table 2). DFT B3LYP/6-31G(d) computations of the same molecules disclose the same tendency. In the case of disubstituted derivatives this influence weakly depends on the conformation (Table 2). These findings allow us to conclude that dependence of conformational preferences on methoxycarbonyl- and cyano-substituted adducts is at least partly related to the influence of these substituents on equilibrium bond lengths, as a deviation from these values destabilizes the corresponding conformation.

Conclusions

In summary, a novel effective approach to azepino-fused heterocycles is described. *trans*-1-Aryl-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepines were synthesised *via* domino sequence: isomerization of *gem*-dichloroaziridine–intramolecular Friedel–Crafts acylation of the tethered benzene ring catalysed by $SnCl_4$ and subsequent hydride induced intramolecular cyclization. These aziridines are excellent precursors of heterocyclic azomethine ylides which easily undergo completely stereospecific and stereoselective 1,3-dipolar cycloadditions to C═C dipolarophiles with the formation of dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine derivatives.[22] 1,3-Dipolar cycloaddition of the heterocyclic azomethine ylides was also easily performed with DMAD and fullerene C_{60} as dipolarophiles. Solvent free conditions allow the reactions to be performed much faster. The reaction proceeds *via* cycloaddition of W-ylide only, which does not undergo *E*,*Z*-isomerization under the reaction conditions due to the high activation barrier. This gives rise to cycloadducts with *cis*-configuration of pyrrolidine hydrogen at carbons in α-position with respect to nitrogen. The cycloaddition of *cis*-dipolarophiles proceeds *via* the *exo*-transition state that is in agreement with the results of DFT B3LYP/6-31G(d) computations. It was disclosed that 2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine systems can exist in conformations of two types: **A**, in which C-9 is *cis*-oriented to H-3 and H-13b and the pyrrolidine ring has a half-chair conformation with H-3 in the equatorial and H-13b in the axial position, and **B**, in which C-9 is *trans*-oriented to H-3 and H-13b and the pyrrolidine ring has an envelop conformation with H-3 and H-13b in axial positions. The conformation **B** is characteristic of compounds with the pyrrolidine ring fused with a planar ring (maleimide pentagon and fullerene hexagons) as well as cyano-substituted compounds, and the conformation **A** is characteristic of methoxycarbonyl-substituted compounds. It was suggested that the dependence on the substituents (CO_2Me/CN) is at least partly due to the influence of these substituents on simple bond lengths.

Experimental section

General experimental details

Melting points were determined on a hot stage microscope (Boetius) and are uncorrected. IR spectra were recorded on a Specord M80 spectrometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were determined in $CDCl_3$ or DMSO-d_6 with a Bruker DPX 300 spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Elemental analysis was performed on a Hewlett-Packard 185B CHN-analyser. The X-ray intensity data for **2b** were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System equipped with a two-circle goniometer and using Mo-Kα graphite monochromated radiation. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 for all data.[22] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL[23] default parameters. The single crystal X-ray data for the compounds **13** and **16** were collected at 120 K on a Bruker SMART CCD 6000 diffractometer equipped with a Cryostream (Oxford Cryosystems) open flow nitrogen cryostat and using graphite monochromated λMo-Kα radiation (λ = 0.71073 Å, ω-scan, –0.3°/frame). The data for compounds **18** and **20** were collected an a Bruker Microstar rotating anode diffractometer with APEXII CCD detector using mirror-focused λCu-Kα radiation (λ = 1.54188 Å, ω-scan, –0.3°/frame) and equipped with a Cobra (Oxford Cryosystems) cooling device at 120 and 100 K respectively. The structures were solved by a direct method and refined by full-matrix least squares on F^2 for all data using OLEX2 software.[24] Mass-spectrometry data were obtained using a micrOTOF 10223 equipped with an electrospray ion source or Accurate-Mass Q-TOF LC-MS G530. Flash chromatography was performed using Merck silica (0.040–0.063 mm). TLC analysis was performed on glass backed plates (Merck) coated with 0.2 mm silica layer with UV-indicator 60F254. Compound **6a** was prepared by the reported procedure.[25]

N-(4-Chlorobenzylidene)-2-benzylaniline (6b)

4-Chlorobenzaldehyde (2.21 g, 15.7 mmol) was added to a stirred solution of 2-benzylaniline (2.88 g, 15.7 mmol) in ethanol (15 mL) at 30–40 °C and then the reaction mixture was stirred for 4 h at rt. The formed precipitate was separated and recrystallized from ethanol to give 4.38 g (94%) of imine **6b** as a yellowish solid, mp 55–57 °C (from EtOH) (Found: C, 78.65; H, 5.25; N, 4.5. Calc.

for $C_{20}H_{16}ClN$: C, 78.55; H, 5.3; N, 4.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1632 (N═CH); δ_H (300 MHz; $CDCl_3$; Me_4Si) 4.16 (2H, s, CH_2), 6.99 (1 H, m, H_{arom}), 7.09–7.33 (8 H, m, H_{arom}), 7.47 (2 H, m, H_{arom}), 7.84 (2 H, m, H_{arom}), 8.29 (1 H, s, N═CH). δ_C (75 MHz; $CDCl_3$; Me_4Si) 37.5 (CH_2), 117.7, 125.7, 126.2, 127.3, 128.2, 128.9, 129.0, 129.9, 130.0, 134.9, 135.2, 137.2, 141.3, 150.2 (C_{arom}), 158.2 (N═CH).

1-(2-Benzylphenyl)-2,2-dichloro-3-phenylaziridine (5a)

Powdered KOH (3.35 g, 59.7 mmol) was added in small portions to a vigorously stirred solution of imine **6a** (2.70 g, 9.94 mmol) and benzyltriethylammonium chloride (TEBA) (0.451 g, 1.98 mmol) in chloroform (30 mL) at 19–21 °C, and then the reaction mixture was stirred for 3 h. After addition of hexane (100 mL) the reaction mixture was stirred for 0.5 h, then passed through a basic alumina plug, which was subsequently washed with hexane. The solvent was removed under reduced pressure, and the residue crystallized from hexane to give 2.62 g (74%) of aziridine **5a** as a colorless solid, mp 60–62 °C (from hexane) (Found: C, 71.1; H, 4.8; N, 4.1. Calc. for $C_{21}H_{17}Cl_2N$: C, 71.2; H, 4.8; N, 3.95%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1264, 1400, 1454, 1492, 1600, 3064; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.86 (1 H, s, CH), 4.17 (1 H, d, *J* 16, CH_2), 4.45 (1 H, d, *J* 16, CH_2), 6.88 (1 H, m, H_{arom}), 7.11–7.39 (13 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 37.6 (CH_2), 52.9 (CH), 76.5 (CCl_2), 118.3, 124.9, 126.2, 126.9, 127.9, 128.3, 128.4, 128.9, 129.4, 129.5, 130.3, 132.7, 135.2, 140.0, 143.0 (C_{arom}).

1-(2-Benzylphenyl)-2,2-dichloro-3-(4-chlorophenyl)aziridine (5b)

Compound **5b** was prepared, analogously to **5a** from imine **6b** (3.78 g, 12.36 mmol), KOH (4.16 g, 74.16 mmol), and benzyltriethylammonium chloride (TEBA) (0.563 g, 2.47 mmol) to afford 3.67 g (76%) of aziridine **5b** as a colorless solid, mp 49–51 °C (from hexane) (Found: C, 64.85; H, 4.3; N, 3.6. Calc. for $C_{21}H_{16}Cl_3N$: C, 64.9; H, 4.15; N, 3.6%); $\nu_{max}(CCl_4)/cm^{-1}$ 1016, 1454, 1494, 1600, 3068; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.80 (1 H, s, CH), 4.15 (1 H, d, *J* 16.2, CH_2), 4.41 (1 H, d, *J* 16.2, CH_2), 6.85 (1 H, m, H_{arom}), 7.10–7.45 (12 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 37.6 (CH_2), 52.2 (CH), 76.3 (CCl_2), 118.7, 125.5, 126.7, 127.4, 128.8, 129.0, 129.7, 129.9, 130.9, 131.7, 135.3, 135.4, 140.2, 143.0 (C_{arom}).

***trans*-1-Phenyl-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepine (2a)**

A solution of $SnCl_4$ (8.82 g, 33.87 mmol) in anhydrous nitromethane (10 mL) was added to a vigorously stirred solution of aziridine **5a** (4.0 g, 11.29 mmol) in nitromethane (25 mL) at r.t., and then the reaction mixture was stirred for 1.5 h at 35 °C. The reaction mixture was cooled, poured into cold water (100 mL) and extracted with dichloromethane (50 mL). The organic layer was separated and washed successively with water (2 × 25 mL), diluted solution of K_2CO_3, and then with water to neutral pH. The organic solution was dried (Na_2SO_4) and the solvents were removed on a rotary evaporator *in vacuo* (0.1 Torr/20 °C bath temperature) and the residue was immediately used for the next step without purification.

A suspension of $LiAlH_4$ (0.857 g, 22.58 mmol) in anhyd ether (25 mL) was slowly added to a stirred solution of the crude 6-[chloro(phenyl)methyl]-11*H*-dibenzo[*b*,*e*]azepine in anhydrous ether (70 mL), and then the reaction mixture was refluxed for 3 h. The mixture was cooled, treated with a saturated aq solution of Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was crystallized from hexane to give 1.82 g (56% based on starting **5a**) of compound **2a** as a colorless solid, mp 115–117 °C (from hexane) (Found: C, 89.1; H, 6.1; N, 5.0. Calc. for $C_{21}H_{17}N$: C, 89.0; H, 6.1; N, 4.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1232, 1452, 1488, 3068; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.28 (1 H, d, *J* 3.3, CH), 3.36 (1 H, d, *J* 13.2, CH_2), 3.86 (1 H, d, *J* 3.3, CH), 4.92 (1 H, d, *J* 13.2, CH_2), 6.82–6.84 (1 H, m, H_{arom}), 6.99–7.24 (12 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 38.4 (CH_2), 47.0 (CH), 48.9 (CH), 121.9, 122.0, 126.1, 127.1, 127.3, 127.5, 127.9, 127.9, 128.0, 128.6, 129.9, 133.1, 133.3, 139.3, 142.5, 148.4 (C_{arom}).

***trans*-1-(4-Chlorophenyl)-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepine (2b)**

Compound **2b** was prepared, analogously to **2a** from aziridine **5b** (1.50 g, 3.85 mmol), $SnCl_4$ (3.01 g, 11.55 mmol), and then $LiAlH_4$ (0.146 g, 3.85 mmol) to afford 0.67 g (55% based on starting **5a**) of compound **2b** as a colorless solid, mp 175–177 °C (from benzene) (Found: C, 79.5; H, 5.1; N, 4.4. Calc. for $C_{21}H_{16}ClN$: C, 79.4; H, 5.1; N, 4.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1312, 1454, 1490, 3068; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.23 (1 H, d, *J* 2.9, CH), 3.35 (1 H, d, *J* 14, CH_2), 3.79 (1 H, d, *J* 2.9, CH), 4.87 (1 H, d, *J* 14, CH_2), 6.79–6.83 (1 H, m, H_{arom}), 6.93–6.96(1 H, m, H_{arom}), 7.05–7.10 (2 H, m, H_{arom}), 7.13–7.31 (6 H, m, H_{arom}), 7.37–7.49 (3 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 38.3 (CH_2), 46.3 (CH), 49.1 (CH), 121.8, 122.0, 127.1, 127.3, 127.4, 127.9, 128.0, 128.05, 128.7, 129.8, 132.9, 133.0, 133.2, 137.8, 142.4, 148.1 (C_{arom}). Crystal data. $C_{21}H_{16}ClN$, $M = 317.80$, monoclinic, $a = 11.5596(6)$, $b = 9.9041(5)$, $c = 13.9757(7)$ Å, $\beta = 91.254(4)°$, $U = 1599.66(14)$ Å^3, $T = 173(2)$ K, space group $P\,2_1/n$ (no. 14), $Z = 4$, 7700 reflections measured, 3392 unique ($R_{int} = 0.0621$) which were used in all calculations. The final $wR(F^2)$ was 0.0957 (all data).

General procedures for cycloaddition of ylides from *trans*-1-aryl-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepines (2a,b) to dipolarophiles

A. A solution of compound **2a,b** (100 mg, 0.353/0.315 mmol) and dipolarophile in anhyd toluene (5 mL) was heated at 105 °C (reaction time is indicated in Table 1). The reaction was monitored by TLC. The solvent was removed *in vacuo* and the residue was purified by crystallisation or flash chromatography.

B. A mixture of compound **2a** (100 mg, 0.353 mmol) and dipolarophile was heated at 140 °C (reaction time is indicated in Table 1). After cooling the product was purified by crystallisation or flash chromatography.

Dimethyl (1*RS*,2*RS*,3*SR*,13b*RS*)-3-phenyl-2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarboxylate (13). Compound **13** (0.105 g, 70%) was obtained from **2a** (0.100 g, 0.353 mmol) and dimethyl fumarate **8** (0.101 g, 0.701 mmol) according to the procedure ***A*** and ***B***. A colorless solid, mp 178–180 °C (from CH_2Cl_2–MeOH) (Found: C, 75.5; H 5.9; N, 3.5. Calc. for $C_{27}H_{25}NO_4$: C, 75.9; H, 5.9; N, 3.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1008, 1172, 1304, 1492, 1596, 1736 (C═O), 3064; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.41 (3 H, s, CH_3), 3.72 (3 H, s, CH_3), 3.95 (1 H, dd, *J* 10.0, 8.6, CH), 4.00 (1 H, d, *J* 14, CH_2), 4.10 (1 H, dd, *J* 10.0, 10.6,

CH), 4.65 (1 H, d, *J* 14, CH_2), 5.19 (1 H, d, *J* 8.6, CH), 5.60 (1 H, d, *J* 10.6, CH), 6.32 (1 H, d, *J* 8, H_{arom}), 6.63–6.68 (1 H, m, H_{arom}), 6.84–6.89 (1 H, m, H_{arom}), 7.05–7.08 (1 H, m, H_{arom}), 7.17–7.34 (8 H, m, H_{arom}), 7.50–7.53 (1 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 40.3 (CH_2), 47.4 (CH), 51.7 (CH_3), 51.9 (CH_3), 52.4 (CH), 64.7 (CH), 66.5 (CH), 116.8, 119.5, 125.7, 126.9, 127.0, 127.5, 127.8, 128.0, 128.3, 128.4, 128.5, 129.4, 135.1, 138.7, 139.8, 144.0 (C_{arom}), 170.1 (C═O), 172.7 (C═O). Crystal data. $C_{27}H_{25}NO_4$, M = 427.48, monoclinic, a = 10.0710(2), b = 25.9843(5), c = 17.0032(3) Å, β = 104.46(1)°, U = 4308.58(14) Å^3, T = 120 K, space group $P\,2_1/n$ (no. 14), Z = 8, 52462 reflections measured, 11451 unique (R_{int} = 0.0702) were used in all calculations. The final $wR_2(F^2)$ was 0.0949 (all data).

Dimethyl (1*RS*,2*RS*,3*SR*,13b*RS*)-3-(4-chlorophenyl)-2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarboxylate (14). Compound **14** (0.097 g, 67%) was obtained from **2b** (0.100 g, 0.315 mmol) and dimethyl fumarate **8** (0.089 g, 0.617 mmol) according to the procedure ***A***. A colorless solid, mp 196–198 °C (from CH_2Cl_2–MeOH) (Found: C, 69.85; H, 5.35; N, 3.3. Calc. for $C_{27}H_{24}ClNO_4$: C, 70.2; H, 5.2; N 3.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1014, 1176, 1304, 1492, 1598, 1736 (C═O), 3068; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.44 (3 H, s, CH_3), 3.73 (3 H, s, CH_3), 3.94 (1 H, dd, *J* 10.0, 8.6, CH), 4.03 (1 H, d, *J* 14, CH_2), 4.10 (1 H, dd, *J* 10.0, 10.2, CH), 4.60 (1 H, d, *J* 14, CH_2), 5.19 (1 H, d, *J* 8.6, CH), 5.59 (1 H, d, *J* 10.2, CH), 6.29 (1 H, d, *J* 8.6, H_{arom}), 6.61–6.71 (1 H, m, H_{arom}), 6.86–6.91 (1 H, m, H_{arom}), 7.06–7.14 (3 H, m, H_{arom}), 7.16–7.33 (5 H, m, H_{arom}), 7.42–7.51 (1 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 40.2 (CH_2), 47.6 (CH), 51.7 (CH_3), 51.9 (CH_3), 52.5 (CH), 64.8 (CH), 65.8 (CH), 116.8, 119.9, 125.7, 127.0, 127.5, 124.8, 125.0, 125.9, 127.5, 128.4, 128.6, 129.5, 133.6, 135.0, 137.3, 143.6 (C_{arom}), 170.0 (C═O), 172.6 (C═O); *m*/*z* (ESI) 462.1465 (M + H^+. $C_{27}H_{25}ClNO_4^+$ requires 462.1467).

Dimethyl (1*RS*,2*SR*,3*SR*,13b*RS*)-3-phenyl-2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarboxylate (15). Compound **15** (0.100 g, 67%) was obtained from **2a** (0.100 g, 0.353 mmol) and dimethyl maleate **9** (0.101 g, 0.701 mmol) according to the procedure ***A***. A colorless solid, mp 198–200 °C (from CH_2Cl_2–MeOH) (Found: C, 75.5; H 6.0; N, 3.35. Calc. for $C_{27}H_{25}NO_4$: C, 75.9; H, 5.9; N, 3.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1028, 1176, 1292, 1492, 1596, 1744 (C═O), 3064; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.45 (1 H, dd, *J* 8.0, 4.1, CH), 3.73 (3 H, s, CH_3), 3.78 (3 H, s, CH_3), 3.84 (1 H, dd, *J* 8.0, 8.5, CH), 4.00 (1 H, d, *J* 14, CH_2), 4.74 (1 H, d, *J* 14, CH_2), 5.20 (1 H, d, *J* 4.1, CH), 5.85 (1 H, d, *J* 8.5, CH), 6.32 (1 H, d, *J* 8, H_{arom}), 6.63–6.67 (1 H, m, H_{arom}), 6.86–6.90 (1 H, m, H_{arom}), 7.06–7.09 (1 H, m, H_{arom}), 7.15–7.26 (8 H, m, H_{arom}), 7.50–7.53 (1 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 40.6 (CH_2), 47.7 (CH), 52.3 (CH_3), 52.34 (CH_3), 53.8 (CH), 62.7 (CH), 66.9 (CH), 116.8, 119.2, 124.3, 126.5, 126.9, 127.45, 127.5, 128.0, 128.7, 128.74, 129.5, 136.6, 139.4, 141.1, 144.3 (C_{arom}), 171.67 (C═O), 171.7 (C═O).

(1*RS*,2*SR*,3*SR*,13b*RS*)-3-Phenyl-2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarbonitrile (16). Compound **16** (0.091 g, 72%) was obtained from **2a** (0.100 g, 0.353 mmol) and maleonitrile **10** (0.055 g, 0.705 mmol) according to the procedure ***B***. A colorless solid, mp 189–191 °C (from CH_2Cl_2–MeOH); $\nu_{max}(CHCl_3)/cm^{-1}$ 1028, 1136, 1296, 1494, 1598, 2252 (CN), 3068; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.36 (1 H, dd, *J* 10.0, 7.7, CH), 3.63 (1 H, dd, *J* 10.0, 8.9, CH), 3.83 (1 H, d, *J* 13.8, CH_2), 4.68 (1 H, d, *J* 13.8, CH_2), 4.97 (1 H, d, *J* 8.9, CH), 4.99 (1 H, d, *J* 7.7, CH), 6.70 (1 H, d, *J* 7.3, H_{arom}), 6.89–6.93 (1 H, m, H_{arom}), 6.99–7.04 (1 H, m, H_{arom}), 7.19–7.21 (1 H, m, H_{arom}), 7.29–7.35 (8 H, m, H_{arom}), 7.42–7.45 (1 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 37.8 (CH_2), 39.4 (CH), 39.7 (CH), 68.0 (CH), 68.2 (CH), 116.6 (C≡N), 117.1 (C≡N), 119.7, 123.8, 126.6, 127.36, 127.42, 127.5, 128.4, 128.7, 129.0, 129.4, 129.9, 133.9, 135.6, 136.6, 137.3, 141.9 (C_{arom}); *m*/*z* (ESI) 362.168 (M + H^+. $C_{25}H_{20}N_3^+$ requires 362.165). Crystal data. $C_{25}H_{19}N_3 \times 0.125\ CH_2Cl_2$, M = 366.74, monoclinic, 36.9379(14), b = 28.7704(11), c = 15.8020(6) Å, β = 113.74(1)°, U = 15372.1(10) Å^3, T = 120 K, space group $C2/c$ (no. 15), Z = 32, 69184 reflections measured, 16751 unique (R_{int} = 0.1100) were used in all calculations. The final $wR_2(F^2)$ was 0.1546 (all data).

(1*RS*,2*RS*,3*RS*,13b*SR*)-3-Phenyl-2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarbonitrile (17) and (1*RS*,2*RS*,3*SR*,13b*RS*)-3-phenyl-2,3,9,13b-tetrahydro-1*H*-dibenzo[*c*,*f*]-pyrrolo[1,2-*a*]azepine-1,2-dicarbonitrile (18). A mixture of compounds **17** and **18** (0.112 g, 1.3 : 1, 89%) was obtained from **2a** (0.100 g, 0.353 mmol) and fumaronitrile **11** (0.082 g, 1.05 mmol) according to the procedure ***B***. A colorless solid, mp 204–207 °C (from ethyl ether) (Found: C, 82.7, H, 5.1; N, 11.6. Calc. for $C_{25}H_{19}N_3$: C, 83.0; H, 5.3; N 11.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1030, 1132, 1296, 1494, 1596, 2248 (CN), 3072; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.35 (1 H, dd *J* 7.4, 3.3, CH) (**18**), 3.55 (1 H, d, *J* 13.6, CH_2) (**18**), 3.63 (1.3 H, dd, *J* 8.7, 6.0, CH) (**17**), 3.74 (1 H, dd, *J* 5.8, 3.3, CH) (**18**), 3.80 (1.3 H, d, *J* 13.9, CH_2) (**17**), 3.84 (1.3 H, dd, *J* 7.2, 6.0, CH) (**17**), 4.68 (1 H, d, *J* 5.8, CH) (**18**), 4.73 (1.3 H, d, *J* 8.7, CH) (**17**), 4.83 (1.3 H, d, *J* 13.9, CH_2) (**17**), 4.86 (1 H, d, *J* 7.4, CH) (**18**), 5.03 (1.3 H, d, *J* 7.2, CH) (**17**), 5.12 (1 H, d, *J* 13.6, CH_2) (**18**), 6.65 (1.3 H, d, *J* 8.0, H_{arom}) (**17**), 6.83 (1 H, d, *J* 8.0, H_{arom}) (**18**), 6.91–7.07 (5.3 H, m, H_{arom}), 7.21–7.49 (22.3 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 38.8 (CH_2), 39.26 (CH_2), 39.3 (CH), 39.4 (CH), 40.0 (CH), 41.1 (CH), 65.6 (CH), 68.4 (CH), 68.5 (CH), 68.6 (CH), 116.9 (C≡N), 118.3 (C≡N), 119.8 (C≡N), 120.4 (C≡N), 124.0, 124.6, 126.8, 127.1, 127.2, 127.3, 127.4, 127.7, 128.0, 128.3, 128.6, 128.65, 128.7, 128.95, 129.0, 129.1, 129.4, 130.0, 130.1, 132.2, 133.9, 134.6, 136.2, 136.9, 138.6, 141.0, 142.0 (C_{arom}); *m*/*z* (ESI) 362.168 (M + H^+. $C_{25}H_{20}N_3^+$ requires 362.165). Crystal data. $C_{25}H_{19}N_3$, M = 361.43, monoclinic, a = 12.6196(2), b = 5.85170(10), c = 12.6336(2) Å, β = 99.290(1)°, U = 920.71(3) Å^3, T = 120 K, space group $P\,2_1$ (no. 4), Z = 2, 3871 reflections measured, 2041 unique (R_{int} = 0.0249) which were used in all calculations. The final $wR_2(F^2)$ was 0.0822 (all data).

(3a*RS*,3b*RS*,14*SR*,14a*SR*)-2,14-Diphenyl-3b,8,14,14a-tetrahydrodibenzo[*c*,*f*]pyrrolo[3′,4′:3,4]pyrrolo[1,2-*a*]azepine-1,3(2*H*,3a*H*)-dione (19). Compound **19** (0.118 g, 73%) was obtained from **2a** (0.100 g, 0.353 mmol) and *N*-phenylmaleimide **12** (0.121 g, 0.70 mmol) according to the procedure ***A***. A colorless solid, mp 214–217 °C (from CH_2Cl_2–MeOH) (Found: C, 81.6, H, 5.4, N, 5.9. Calc. for $C_{31}H_{24}N_2O_2$: C, 81.6, H 5.3, N 6.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 812, 1028, 1178, 1294, 1494, 1560, 1624, 1716, 3068; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.53 (1 H, dd, *J* 9.5, 8.0, CH), 3.70 (1 H, d, *J* 13.8, CH_2), 3.80 (1 H, dd, *J* 9.5, 6.7, CH), 4.78 (1 H, d, *J* 6.7, CH), 4.85 (1 H, d, *J* 8.0, CH), 4.98 (1 H, d, *J* 13.8, CH_2), 6.86–7.05 (3 H, m, H_{arom}), 7.21–7.59 (14 H, m, H_{arom}), 7.83 (1 H, d, *J* 7.3 Hz, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 40.4 (CH_2),

52.8 (CH), 53.0 (CH), 67.9 (CH), 68.5 (CH), 120.1, 124.3, 126.5, 126.9, 127.5, 127.6, 127.8, 128.45, 128.53, 129.17, 129.23, 129.57, 129.61, 129.94, 129.97, 132.1, 134.6, 136.8, 137.4, 138.0, 139.3, 144.0 (C_{arom}), 175.6 (C═O), 176.7 (C═O); *m/z* (ESI) 457.1901 (M + H^+. $C_{31}H_{25}N_2O_2^+$ requires 457.1911).

(3a*RS*,3b*RS*,14*SR*,14a*SR*)-14-(4-Chlorophenyl)-2-phenyl-3b,8,14,14a-tetrahydro-dibenzo[*c*,*f*]pyrrolo[3′,4′:3,4]pyrrolo[1,2-*a*]-azepine-1,3(2*H*,3a*H*)-dione (20). Compound **20** (0.121 g, 78%) was obtained from **2b** (0.100 g, 0.353 mmol) and *N*-phenylmaleimide **12** (0.107 g, 0.62 mmol) according to the procedure ***A***. A colorless solid, mp 220–223 °C (from CH_2Cl_2–MeOH); $\nu_{max}(CHCl_3)/cm^{-1}$ 1016, 1184, 1296, 1492, 1600, 1718, 3048; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.48 (1 H, dd, *J* 9.5, 7.9, CH), 3.69 (1 H, d, *J* 13.8, CH_2), 3.80 (1 H, dd, *J* 9.5, 6.7, CH), 4.77 (1 H, d, *J* 6.7, CH), 4.82 (1 H, d, *J* 7.9, CH), 4.95 (1 H, d, *J* 13.8, CH_2), 6.82–7.06 (3 H, m, H_{arom}), 7.22–7.61 (14 H, m, H_{arom}), 7.79–7.83 (1 H, m, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 39.9 (CH_2), 52.2 (CH), 52.5 (CH), 66.8 (CH), 68.0 (CH), 119.5, 124.1, 126.0, 126.4, 127.1, 127.2, 127.4, 128.2, 128.5, 128.8, 129.0, 129.1, 129.2, 129.5, 129.6, 131.5, 133.7, 136.2, 137.0, 137.4, 137.5, 143.2 (C_{arom}), 175.0 (C═O), 176.1 (C═O). *m/z* (ESI) 491.1541 (M + H^+. $C_{31}H_{24}N_2ClO_2^+$ requires 491.1521). Crystal data. $C_{31}H_{23}N_2ClO_2$, $M = 490.96$, monoclinic, = 10.6905(2), $b = 7.6706(1)$, $c = 29.1159(4)$ Å, $\beta = 90.142(1)°$, $U = 2387.57(6)$ Å^3, $T = 100$ K, space group $P2_1/n$ (no. 14), $Z = 4$, 8647 reflections measured, 2697 unique (R_{int} = 0.0909) which were used in all calculations. The final $wR_2(F^2)$ was 0.1178 (all data).

Compound 29. Solution of aziridine **2b** (11 mg, 0.035 mmol) in o-DCB (2 ml) was added dropwise to the stirred solution of C_{60} (72 mg, 0.1 mmol) in o-DCB (3 ml) at 100 °C over 30 min. The reaction mixture was stirred at 100 °C for additional 6 h. The solvent was evaporated *in vacuo* and the residue was dissolved in benzene and purified by column chromatography (silica gel, benzene – petroleum ether). The obtained crude product was washed with ether and dried under high vacuum to give 8 mg (22%) of the adduct **29** as brown solid. δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.74 d (1H, CH_2, *J* 12.9 Hz), 5.66 d (1H, CH_2, *J* 12.9 Hz), 6.05 (1H, CH), 6.28 (1H, C*H*–(C_6H_4Cl)), 7.02–7.10 m (2H, H_{arom}), 7.10–7.25 m (4H, H_{arom}), 7.35–7.42 m (3H, H_{arom}), 7.45–7.50 m (1H, H_{arom}), 7.60–7.65 m (1H, H_{arom}), 7.75–7.80 m (1H, H_{arom}); δ_C (75 MHz; C_6D_6; Me_4Si): 40.1 (CH_2), 75.5 (C_{sp3}), 76.5 (C_{sp3}), 76.6 (C_{sp3}), 79.2 (C_{sp3}), 123.2, 124.7, 126.6, 127.4, the region between 127.5 and 129.1 is shadowed with the signal of C_6D_5H, 129.5, 130.2, 130.90, 130.92, 131.1, 133.6, 134.4, 135.3, 136.6, 136.9, 137.2, 137.4, 139.6, 139.7, 139.87, 139.90, 140.4, 140.5, 141.8, 141.9, 142.0, 142.2, 142.3, 142.40, 142.45, 142.46, 142.5, 142.95, 142.99, 143.06, 143.14, 143.45, 143.46, 144.80, 144.83, 144.88, 145.0, 145.52, 145.56, 145.58, 145.59, 145.63, 145.64, 145.79, 145.82, 145.9, 146.0, 146.17, 146.21, 146.25, 146.50, 146.55, 146.63, 146.68, 146.72, 146.8, 146.9, 147.2, 147.6, 147.9, 152.7, 153.1, 153.8; *m/z* (ESI) 1037.0972 (M + e^-. $C_{81}H_{16}ClN^-$ requires 1037.0977).

Dimethyl 3-phenyl-9*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarboxylate (30). Compound **30** (0.113 g, 76%) was obtained from **2a** (0.100 g, 0.353 mmol) and DMAD (0.099 g, 0.70 mmol) according to the procedure ***B***. A colorless solid, mp 224–226 °C (from CH_2Cl_2–MeOH); $\nu_{max}(CHCl_3)/cm^{-1}$ 812, 1016, 1180, 1288, 1362, 1410, 1476, 1488, 1534, 1604, 1720, 3044; δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.71 (1H, d, *J* 13.2, CH_2), 3.77 (3H, s, CH_3), 3.85 (3H, s, CH_3), 4.16 (1H, d, *J* 13.2, CH_2), 6.60 (1H, d, *J* 8, H_{arom}), 6.80–6.85 (1H, m, H_{arom}), 7.08 (1H, m, H_{arom}), 7.11–7.34 (9H, m, H_{arom}), 7.60 (1H, d, *J* 8, H_{arom}); δ_C (75 MHz; $CDCl_3$; Me_4Si) 38.8 (CH_2), 51.7 (CH_3), 52.1 (CH_3), 115.4 (CH), 115.46 (CH), 126.4 (CH), 126.5 (CH), 126.7, 127.4, 127.7, 127.8, 127.9, 128.2, 129.1, 130.4, 130.7, 130.8, 134.4, 135.0, 136.4, 138.7, 141.3 (C_{arom}), 165.0 (C═O), 166.4 (C═O); *m/z* (ESI) 424.157 (M + H^+. $C_{27}H_{22}NO_4^+$ requires 424.154).

Computational Details

All calculations were performed with the B3LYP density functional method[26] by using the Gaussian suite of quantum chemical programs. Geometry optimizations of intermediates, transition states, reactants, and products in the gas phase were performed at the B3LYP/6-31G(d) level using Gaussian 03.[27] Stationary points on the respective potential-energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. Careful verification of the unique imaginary frequencies for transition states was carried out to check whether the frequency indeed pertains to the desired reaction coordinate. Intrinsic reaction coordinates (IRC) were calculated to authenticate all transition states.[28]

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