Experimental and theoretical studies of a chiral azulenophane: synthesis, structure and circular dichroism spectra of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane

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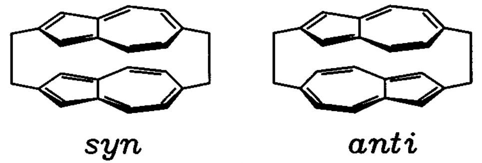
The synthesis of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane **2c** was achieved by dithia[3.3]phane cyclisation and photodesulfurization. The enantiomeric separation of the planar chiral (±**2c**) was performed by HPLC on cellulose carbamate and the circular dichroism (CD) spectrum is reported. The results of theoretical density functional calculations combined with a random phase approximation (DFT/RPA) approach for the CD spectrum compare well with the experimental data in the recorded energy range (1.5–6.5 eV). A good agreement between the X-ray structure and the theoretically optimized ground state geometry could only be achieved at the correlated *ab initio* MP2 level. The character of the excited states could be assigned and qualitatively analyzed with data obtained for azulene and dimethyl[7]paracyclophane as model chromophores. It is found that most of the seven experimentally resolved bands can be interpreted as perturbed locally excited transitions in the two chromophoric units. Charge transfer $\pi\rightarrow\pi$ states between the benzene and azulene fragments are found at relatively low energies (>3.2 eV) but they have low rotatory strengths. Furthermore, the CD intensities of the locally excited benzene type $\pi\rightarrow\pi(E_{1u})$ states are amplified in the phane by a factor of about ten due to the presence of the azulene chromophore. By comparison of theoretical and experimental CD data the absolute configuration of **2c** could be assigned as [CD(−)638, CD(+)218] = (*S*).

I. Introduction

Investigations on strain in organic compounds with special consideration of excited electronic states have been carried out by organic chemists for the last decades (for reviews see *e.g.* ref. 1). In the course of our investigations on structure–chiroptic relationships[2–6] we have become interested in the synthesis, structures and chiroptical properties of strained chiral molecules. Examples of such systems are 4,5-disubstituted phenanthrenes,[7] [*n*]helicenes[8,9] or substituted [2.2]paracyclophanes and [2.2]metacyclophanes.[10] However, especially in the latter systems, the (mainly through-space) interactions of two (nearly) identical chromophores (benzenes in this case) result in complicated spectra with a high density of states in a small energy region. Although in general good results from theoretical calculations have been obtained for the CD spectra,[6] even a qualitative analysis of the excited states involved and their interactions is relatively difficult.

In order to circumvent this problem and to learn more about structure–chiroptic relationships in cyclophanes, we have decided to couple two different chromophores. Our choice was to connect an azulene molecule with a [*n*]paracyclophane unit (see Scheme 2). Assuming that azulene itself has a minimum structure with C_{2v} symmetry (*cf.* the theoretical work in ref. 11) the resulting structure has C_s symmetry which becomes chiral by *e.g.* substitution of the benzene ring in appropriate positions. To minimize electronic substituent effects two methyl groups have been introduced.

The chemistry of azulenophanes started with the synthesis of [2.2](2,6)azulenophane (see Scheme 1) reported in 1976 by two groups.[12,13]



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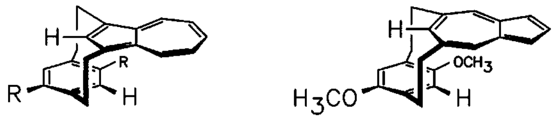
Scheme 1

Several unsubstituted and achiral [2.2]azulenophanes have been synthesized in the last two decades and their geometries and transannular interactions have been studied (for reviews see *e.g.* ref. 10). The first planar-chiral [2.2]azulenophanes with methoxy substituents (**2b** and **3** in Scheme 2) have been mentioned by Itô[14] but no chiroptical properties were reported.



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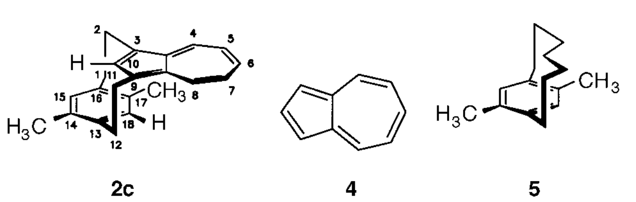
2a: R = H
b: R = OCH_3
c: R = CH_3

Scheme 2

Numerous experimental and theoretical investigations of the singlet excited states of azulene and simple derivatives have been published (see *e.g.* refs. 15 and 16). From that, the existence of six excited singlet states with up to 5.5 eV excitation energy has been established. Because the energy gaps between the first two and the intense fourth state of azulene are quite large (the excitation energies ΔE are about 2.1, 3.6 and 4.5 eV[17]) and they are well separated from the first excited state of the benzene chromophore ($\Delta E \approx 4.9$ eV) we expect less overlapping bands than in other para- or metacyclophanes and thus a simplified analysis of the interactions between the two chromophoric groups. This is of particular importance because it was deduced from the UV spectra of the unsubstituted [2.2]azulenoparacyclophane **2a** that 'no appreciable transannular interactions' could be detected.[18] It will be shown in this work that these interactions are still present in these compounds and can be observed in the CD spectra.

In this paper we describe i) the synthesis and enantiomeric separation of the 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane **2c** and ii) a detailed analysis of the chiroptical properties using CD spectroscopy in combination with theoretical calculations of the structures and electronic spectra. The origin of the CD in the azulenoparacyclophane is analyzed by dividing the molecule into two model chromophores: the achiral azulene system (**4**) and the chiral dimethyl[7]paracyclophane (**5**) chromophoric unit (see Scheme 3).



Scheme 3

To assign experimental CD bands to molecular states and to predict the absolute configuration, high level theoretical calculations of the first few singlet excited states and rotatory strengths of the corresponding transitions from the ground state are needed. Due to the importance of differential dynamic electron correlation effects in the case of aromatic chromophores[19] standard *ab initio* techniques cannot be employed in the case of such large systems lacking any symmetry element. Recently, a new scheme for the theoretical description of excited states based on a combination of density functional theory (DFT) and the single excitation configuration interaction method (DFT/SCI) has been proposed by one of us.[20] The new method is clearly superior to the standard *ab initio* HF/SCI approach due to the implicit accounting for dynamic electron correlation effects. Especially for the prediction of CD spectra very good results have been obtained.[6,20,21] Here we employ the DFT/RPA (random phase approximation) variant of this approach[6,22] which gives a further improved description of electronic transition moments (see *e.g.* ref. 23).

II. Theoretical methods

All DFT and *ab initio* SCF and MP2 (second order perturbation theory to account for electron correlation) calculations have been performed with the TURBOMOLE suite of programs.[24,25] Valence double-ζ Gaussian AO basis sets ([3s2p]/[2s][26]) augmented with d-polarisation functions $a_d(\mathrm{C}) = 0.75$, VDZd) at the carbon atoms and Becke's hybrid exchange-correlation functional[27,28] (B3LYP) have been used throughout. The MP2 calculations were performed with an approximate resolution of the identity (RI) for the two-electron integrals.[29] The auxiliary basis sets used were the same as in ref. 29. All computed excitation energies represent vertical transitions, *i.e.* employing fully optimized ground state geometries only, which represents an approximation to the experimental transition energy at the band maximum. In the DFT/RPA approach[6] all singlet single hole-particle functions resulting from the distribution of all valence electrons in all virtual MOs were included (15125 for **2c**). The inclusion of all valence electrons is of particular importance for a reliable description of the CD in large low-symmetry species, especially when an inherently achiral chromophore (azulene in this case) is slightly perturbed by a large 'molecular rest'. In order to reduce the computation times in the RPA calculations of the phane, the RI approximation has been employed as in the MP2 calculations. According to prior experience the errors introduced by the RI method are less than 0.01 eV for the excitation energies and also the calculated properties are influenced very little. All transition moments were calculated in the dipole lengths form which are, however, in most cases very similar to those from the dipole velocity form. The theoretical simulations of the CD spectra were obtained by summing Gaussian curves with constant half-widths of 0.4 eV for each electronic transition.

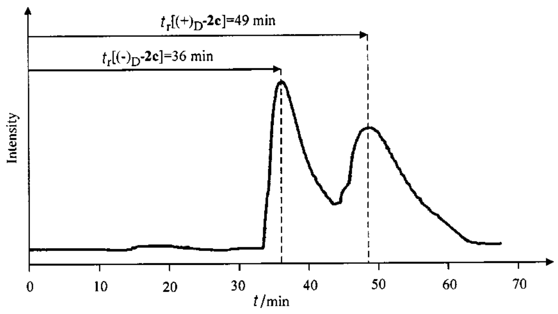
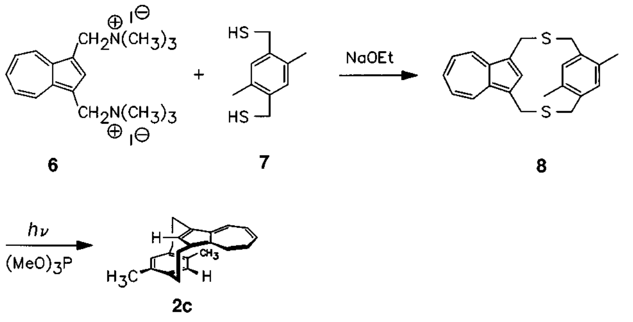


Fig. 1 HPLC trace for the enantiomeric separation of racemic **2c**.

III. Synthesis and structures

Following the preparation pathway of the unsubstituted, achiral [2](1,3)azuleno[2]paracyclophane[18] the chiral compound **2c** was obtained by dithia[3.3]phane cyclisation and photodesulfurization (see Scheme 4).



Scheme 4

The coupling of azulene-1,3-bis[(trimethylammonium)-methyl] diiodide[30] **6** and 1,4-bis(mercaptomethyl)-2,5-dimethylbenzene[5] **7** under high dilution conditions[31] leads in a cyclization reaction to the dithiaphane **8** (yield 27%). Irradiation with a high pressure mercury lamp in the presence of trimethyl phosphite as thiophilic reagent gives [2]azuleno[2]paracyclophane **2c** (yield 40%), which is obtained as a racemic mixture. The planar chiral [2]azuleno[2]paracyclophane **2c** was enantiomerically enriched by enantioselective chromatographic techniques with a cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC)[32] HPLC column as chiral stationary phase. A HPLC trace from a typical run is shown in Fig. 1. Although the maxima corresponding to the two enantiomers are separated by 13 min, complete resolution could not be achieved (estimated enrichment: 80%) due to the broadness of the peaks.

The X-ray structure of **2c** is shown in Fig. 2. Important structural data are compared with theoretical results at the DFT/B3LYP and RI-MP2 level of theory in Table 1. In general, our

Table 1 Comparison of theoretical and experimental structural data of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane. Bond lengths and non-bonded distances are given in Å, deformation angles α, β and γ (for a definition see Fig. 2) in degrees

	DFT/B3LYP	RI-MP2	Exp.
Alkyl bridges			
r_{1-2}	1.601	1.589	1.584
r_{11-12}	1.596	1.585	1.579
r_{2-3}	1.515	1.507	1.516
r_{9-11}	1.513	1.506	1.508
r_{1-16}	1.517	1.510	1.504
r_{12-13}	1.517	1.510	1.516
Azulene rings			
r_{3-10}	1.413	1.416	1.398
r_{9-10}	1.411	1.416	1.395
$r_{3'-4}$	1.417	1.418	1.408
$r_{8-9'}$	1.418	1.418	1.406
$r_{3'-8'}$	1.510	1.510	1.507
$r_{3'-4}$	1.395	1.397	1.391
$r_{8'-8}$	1.395	1.397	1.389
r_{4-5}	1.405	1.410	1.394
r_{7-8}	1.407	1.409	1.390
r_{5-6}	1.405	1.408	1.391
r_{6-7}	1.404	1.409	1.393
Benzene ring			
r_{16-17}	1.414	1.417	1.413
r_{13-18}	1.405	1.408	1.395
r_{15-16}	1.404	1.407	1.391
r_{13-14}	1.412	1.413	1.399
r_{17-18}	1.403	1.405	1.389
r_{14-15}	1.407	1.411	1.397
Azulene–benzene non-bonded distances			
r_1	2.946	2.849	2.884
r_2	2.722	2.655	2.667
r_3	2.796	2.678	2.733
r_4	3.101	2.966	3.006
r_5	3.337	3.055	3.187
Deformation angles			
α_1	15.0	13.1	14.1
α_2	14.4	12.0	12.3
β_1	14.0	14.8	15.6
β_2	13.8	14.0	14.4
γ	7.5	4.8	5.7

experimental structure of **2c** is quite similar to that of the unsubstituted parent **2a** reported by Itô *et al.*[18]

Inspection of the structure in Fig. 2 and the data in Table 1 shows clearly, that the geometry of **2c** is quite symmetric. The azulene moiety has essentially local C_s symmetry (xz plane) with bond lengths differences between both sides not exceeding 0.004 Å. The deviation of the azulene substructure from planarity is also small, *i.e.* the deformation angle γ (see Fig. 2) is only 5.7 degrees and the mean absolute deviation of the ten ring atoms from the 'best' plane is 0.024 Å. The situation for the benzene unit is a little bit more difficult. Here, we have to distinguish between the aromatic ring itself (which has locally C_2 symmetry due to the two methyl groups) and the bridging group which destroys this symmetry element. The investigations in ref. 21 have shown that the inherent chirality of the dimethyl[7]paracyclophane moiety (which is an element of the azulenophane structure) is substantial. Thus we conclude from these geometrical considerations that **2c** is made from an inherently achiral azulene chromophore coupled with a distorted and chiral paracyclophane ring system. Of particular importance for the spectral properties of the chromophore are the inter-ring distances and the deformation of the benzene unit. The deformation angles α and β range from 12.3 to 15.6 degrees which are very similar to the corresponding values of *e.g.* dimethyl[7]paracyclophane.[21] A very short non-bonded distance of about 2.67 Å between C10 and the midpoint of the C14–C15 bond is found, indicating strong ring–ring interactions.

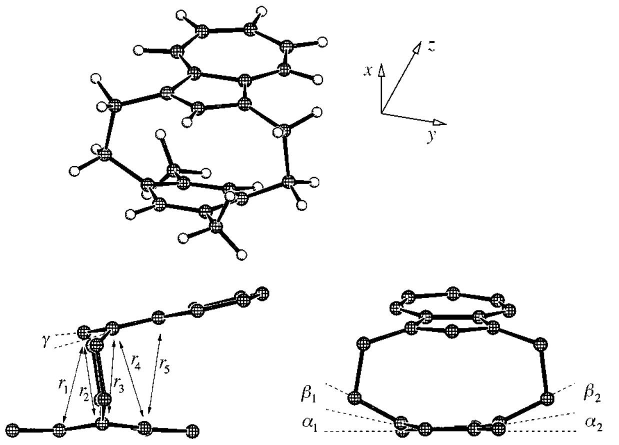


Fig. 2 X-Ray structure of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane. In the side views (bottom) the deformation angles α, β and γ and the non-bonded distances r_1–r_5 are defined. The values for r_1–r_5 refer to projective distances as shown in the figure and were determined between the midpoints of bonds or the benzene ring center.

Experimentally, the findings of the X-ray measurements can be confirmed qualitatively by inspection of NMR data. The short distance of the five-membered ring in the azulene part to the benzene moiety reveals itself by a high-field shift of the H10 resonance down to 6.22 ppm. For the unsubstituted **2a** a value of 6.08 ppm has been reported.[18] The shift of about 1.7 ppm relative to the corresponding proton resonance in azulene itself could be corroborated by *ab initio* GIAO/SCF calculations in which a value of 1.5 ppm was found. This seems to be lower than expected from the short distance of H10 to the midpoint of the ring but inspection of the molecular structure shows that this atom is displaced away from the midpoint of the benzene ring into less shielded regions above the C14–C15 bond. The chemical shift differences between the carbon atoms symmetrically disposed with respect to the C_2 axis of the azulene moiety are too small to be resolved in the NMR spectra which confirms the local C_s symmetry of the azulene part found in the solid state.

In general, the theoretical geometries predicted by DFT/B3LYP and RI-MP2 methods are in good agreement with the experimental data. The aromatic bond lengths are systematically overestimated by ≈0.01–0.02 Å in both approaches. The deformation angles α and β are within 1–2 degrees of the experimental values and the trends ($\alpha_1/\beta_1 > \alpha_2/\beta_2$) are also reproduced. In the RI-MP2 method, the elongated sp^3–sp^3 bond lengths in the alkyl bridge (≈1.58 Å) and the inter-ring distances r_1–r_5 are predicted with higher accuracy compared to the DFT treatment in which these distances are systematically overestimated. The overestimation of the trans-annular interactions in the DFT treatment furthermore results in a too strong out-of-plane bending of the azulene five-membered ring ($\gamma = 7.5$ (DFT) *vs.* 4.8 (MP2) or 5.7 (exp.) degrees). The failure of DFT to account for the attractive (dispersive) part of π–π interactions has recently been found also for other cyclophanes.[33] Test calculations for the CD spectrum (see below) with the DFT/B3LYP optimized geometry gave similar, but slightly inferior results compared to those obtained with the RI-MP2 geometry. Hence, only results obtained with the RI-MP2 structure will be discussed in the following section concerned with the electronic spectra.

IV. Excited states of the model chromophores

In this section we want to discuss the excited state properties of

Table 2 Theoretical (DFT/RPA) excitation energies (ΔE, in eV), oscillator strengths (f), magnetic dipole transition moments (m, in atomic units) and rotatory strengths[a] (R, in 10^{-40} cgs units) for some low-lying excited singlet states of the model chromophores azulene, 1,3-dimethylazulene and (S)-dimethyl[7]paracyclophane

	Excited state			
	S_1	S_2	S_3	S_4
Azulene, calc.				
	$1B_2$	$2A_1$	$2B_2$	$3A_1$
ΔE	2.07	3.37	4.19	5.10
f^b	0.003	0.002	0.042	1.163
m^c	0.791	0	0.920	0
Azulene, exp.[d]				
ΔE	2.1	3.6	4.3	4.5
f	0.009	0.06	0.03	≈1
1,3-Dimethylazulene, calc.				
ΔE	1.90	3.18	4.11	4.88
f^b	0.003	0.020	0.056	1.086
m^c	0.668	0	0.302	0
1,3-Dimethylazulene, exp.[d]				
ΔE	1.9	3.5	4.1	4.3
Dimethyl[7]paracyclophane, calc.				
ΔE	4.23	5.05	5.80	6.14
f	0.001	0.103	0.376	0.367
R	−1.3	−34.2	15.3	39.4

[a] In cgs, R has units of 3.336×10^{-15} C^2 m^3 s^{-1}. The R values are zero for azulene due to symmetry. [b] Transitions to the $B_2(A_1)$ states are short(long)-axis polarized. [c] The values for transitions to A_1 states are zero due to symmetry. [d] The values refer to band maxima in UV and MCD spectra.[15,16]

the model chromophores on the basis of experimental and theoretical data (see Table 2). The assignment of the first four excited states of azulene as L_b ($1B_2$), L_a ($2A_1$), B_b ($2B_2$) and B_a ($3A_1$) is without problems and in accordance with previous (semiempirical) calculations. The excitation energies (ΔE) and oscillator strengths of the first three states are accurately predicted at the DFT/RPA level while the ΔE value of the B_a ($3A_1$) state is too high by ≈0.6 eV.† In agreement with the results of Thulstrup *et al.*[15] we assign the band seen in the MCD spectrum at 4.2 eV to the $3B_2$ state. The first four $\pi\pi^*$ states are all of charge transfer (CT) character, *i.e.* the orientation of the dipole moment is inverted with respect to the ground state (CT from the five- to the seven-membered ring). Due to symmetry, only transitions to the B_2 states have non-zero magnetic dipole moments (m) aligned perpendicular to the molecular plane. Thus, a rotatory strength for these transitions may be induced by borrowing small amounts of electric dipole transition probability from other states. Possible mechanisms are slight geometric distortions or through-space (exciton) couplings. For the A_1 states with a zero magnetic dipole transition moment and low oscillator strengths (f) we therefore expect very weak CD intensities. The $3A_1$ state, however, with a f value of about unity may be different because a small amount of borrowed magnetic moment is amplified by the large electric dipole transition moment.

Of particular importance for the assignment of electronic states in **2c** is the shift of the excitation energies introduced by the alkyl substituents relative to the parent azulene. We compare theoretical results for 1,3-dimethylazulene as an unstrained reference system with experimental data in Table 2. In agreement with experimental data it is found that the first four excitation energies are red-shifted with respect to azulene by 0.1–0.2 eV due to the inductive and hyperconjugative effects of the two alkyl groups.

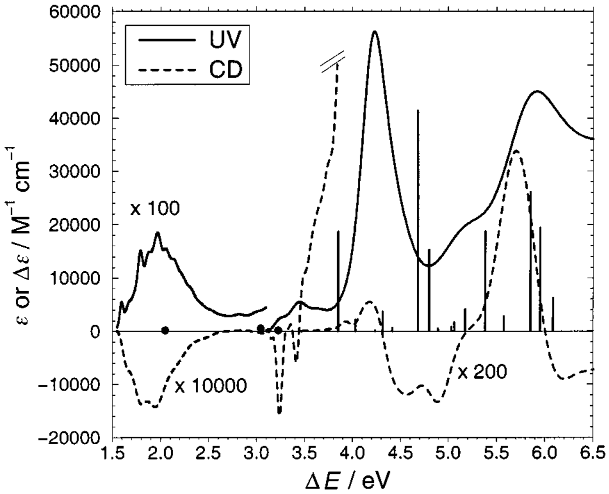


Fig. 3 Comparison of experimental (in *n*-hexane) UV and CD spectra of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane. The solid lines and filled circles indicate the positions of the calculated states (DFT/RPA).

The low-lying excited states of the dimethyl[7]paracyclophane (**5**) have been already discussed in the literature in connection with the interpretation of the CD spectrum of 9,12-dimethyl[7]oxaparacyclophane.[21] Because of the boat-type deformation of the benzene ring, the first four $\pi\pi^*$ states L_b, L_a and perturbed $B_{a/b}$ (E_{1u}) are red-shifted by about 0.6–1.0 eV compared to those of the parent benzene. Due to the dimethyl substitution pattern, this compound is already chiral and non-zero rotatory strengths are computed. The R values for the first two states are negative while the two $B_{a/b}$ transitions (S_3 and S_4) show positive values. Although no experimental data are available for this molecule, the calculated results seem to be correct because of the close similarity of the calculated dimethyl[7]paracyclophane and 9,12-dimethyl[7]oxaparacyclophane CD spectra,[21] the latter being in good agreement with experiment.

V. Excited states and chiroptical properties of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane

First, we want to discuss the experimental UV spectrum of **2c** in *n*-hexane which is shown in Fig. 3 together with the experimental CD spectrum. The solid lines indicate the positions and oscillator strengths for the calculated transitions. The UV spectrum is quite similar to that of azulene itself, *i.e.* a weak structured band at about 2.0 eV ($1B_2$ of azulene), a stronger absorption at about 3.5 eV ($2A_1$) and an intense transition with a maximum at 4.2 eV ($3A_1$) are observed. These findings are in agreement with those of Itô,[14] *i.e.* UV spectroscopy is not sensitive enough to detect ring–ring interactions between the benzene and azulene moieties. The comparison with the theoretical data reveals in general a quite good agreement for the band positions and intensities. As discussed in the previous section, however, the excitation energy of the intense $3A_1$ transition in the azulene part is also overestimated in the phane (by 0.4 eV). The comparison of the UV and CD spectra shows a clear correspondence between UV and CD transitions only for bands A, B and D.

Because the enantiomers of **2c** could only be enriched, absolute CD intensities could not be determined. Hence, the

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† Preliminary results from a DFT/CI treatment including double and triple excitations (S. Grimme, to be published) show that the $3A_1$ state has significant contributions from multiple excitations (the error is reduced from 0.6 to 0.2 eV) which are neither implicitly nor explicitly accounted for by the DFT/RPA method.

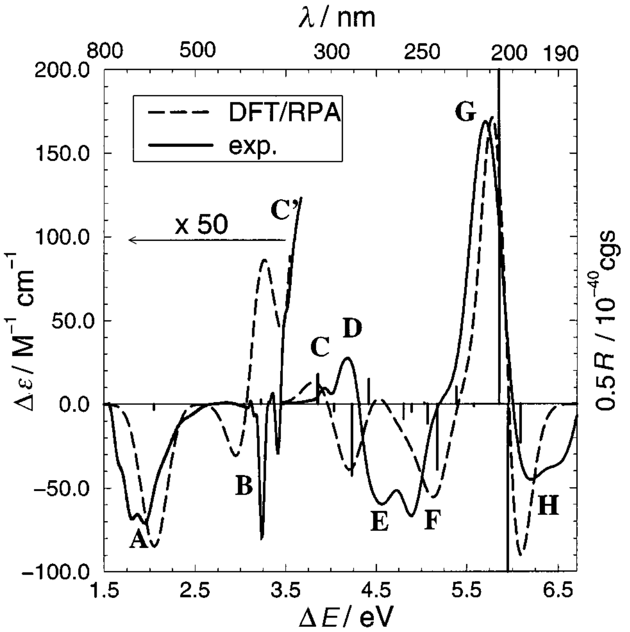

Fig. 4 Comparison of theoretical (DFT/RPA) and experimental (in *n*-hexane) CD spectra of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane. The solid lines indicate the positions of the calculated states. The simulation (dashed curve) has been performed by summing rotatory strength weighted Gaussian curves with constant half-widths of 0.4 eV for each electronic transition.

experimental data are scaled to the maximum theoretical intensity of band G. The experimental CD spectrum obtained in *n*-hexane exhibits eight resolved CD bands A–H and is shown in comparison with the theoretical simulation in Fig. 4. The solid lines indicate the positions and rotatory strengths for the calculated transitions. In Table 3 we give an assignment of the electronic states involved which is based on the states of the two model chromophores.

The comparison of the experimental and theoretical CD data is good, *i.e.* with the exception of bands D and E, all bands are predicted with the correct CD sign and reliable relative intensities. This quantitative agreement allows the assignment of the absolute configuration of **2c**: the (−)-enantiomer with the strong positive CD band at 5.7 eV has the (*S*)-configuration.

In the long-wavelength part of the CD spectrum we observed two weak negative bands which are attributed to the two lowest locally excited states of the azulene chromophore. Although vibronic progressions are clearly visible, the sign of the CD could be predicted correctly in the theoretical treatment using the same geometries for the ground and excited states. Thus we conclude that static perturbations due to the attached benzene ring are responsible for the CD. Next follows the positive band C which exhibits a shoulder on the long-wavelength side of the band. The two states calculated in this energy region are of charge-transfer character, *i.e.* the excitation takes place between the highest filled benzene ring π orbitals and the virtual π* orbitals of the azulene ring. The lowest of these MOs are located mainly in the seven-membered ring of the azulene moiety which corresponds to the resonance picture of azulene (the highest(lowest) lying (un)occupied orbitals are mainly located in the negatively(positively) charged five(seven)-membered ring). In the region of band D we find beside the benzene L_b and azulene $3A_1$ states a transition with reversed CT character, *i.e.* the excitation takes place between occupied azulene π and benzene π* MOs. Because of the nearly exact coincidence of the maximum of the band D in the CD and the intense maximum in the UV spectrum at 4.2 eV, we attribute this CD band to the azulene $3A_1$ state. As noted before, the theoretical description for this transition is not good enough. The error for the excitation energy is about 0.45 eV (the theoretical value has been corrected by this amount) and also the calculated rotatory strength has the wrong sign. In the experimental spectrum the close-lying bands E and F follow for which a detailed assignment is quite difficult. Theoretically, we find several states with CT character, the benzene L_a state and the azulene $3B_2$ and $4A_1$ states in this region. The high energy part of the spectrum between 5.7 and 6.2 eV is dominated by a +/− CD couplet (bands G and H) made from two individual transitions. Both correspond to the split 'E_{1u}' components localized in the benzene moiety. Compared to the dimethyl[7]paracyclophane reference system the rotatory strengths are increased by a factor of about 10–20 and furthermore, the CD sign for the second component is reversed. These dramatic changes must be attributed to the presence of the geometrically close-lying five-membered azulene ring.

VI. Conclusions

In summary we conclude that the comparison of experimental and accurate theoretical CD spectra provides not only an assignment of the absolute configuration of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane and other azulenocyclophanes synthesized in the future but also a more detailed picture of the interactions between the azulene and benzene chromophoric groups. Transannular interactions between the two aromatic parts in the phane not only give rise to additional states with charge-transfer character but also result in an amplification of the CD intensity for locally excited states. Future studies with azulenophanes where the methyl groups are replaced by other substituents, thereby changing the donor or acceptor capabilities of the benzene ring, should provide more experimental information about the nature of the intramolecular charge-transfer states in cyclophanes with different aromatic units.

VII. Experimental

16,19-Dimethyl-2,13-dithia[3](1,3)azuleno[3]paracyclophane (8)

Solution 1: azulene-1,3-bis[(trimethylammonium)methyl] diiodide **6** (4.21 g, 8 mmol) was dissolved in 50 mL of absolute and degassed methanol. Solution 2: sodium ethoxide (0.86 g, 16 mmol) and 1,4-bis(mercaptomethyl)-2,5-dimethylbenzene **7** (1.57 g, 8 mmol) was dissolved in 50 mL of absolute and degassed ethanol. Solutions 1 and 2 were simultaneously and separately dropped over 25 h into 1.8 L of boiling ethanol under argon atmosphere. A medical perfusor with two 50 mL syringes was used as a two-component high-dilution apparatus. After the reaction mixture had been refluxed for an additional 24 h, the solvent was evaporated and the residue purified by flash chromatography (Al_2O_3; light petroleum (bp 40–60 °C)–CH_2Cl_2, 5:1, $R_f = 0.33$). Recrystallization from *n*-hexane gave 0.76 g (27%) of **8** as a blue crystalline solid; mp 127 °C (decomp.). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ_H 1.97 (s, 6H, CH_3), 3.75 (d, $J = 13.5$ Hz, 2H, CH_2), 3.93 (d, $J = 13.5$ Hz, 2H, CH_2), 4.04 (d, $J = 15.8$ Hz, 2H, CH_2), 4.10 (d, $J = 15.8$ Hz, 2H, CH_2), 6.48 (s, 1H, ArH), 6.53 (s, 2H, ArH), 7.03 (m, $J = 9.8$ Hz, 2H, ArH), 7.49 (m, $J = 9.8$ Hz, 1H, ArH), 8.28 (d, $J = 9.3$ Hz, 2H, ArH); ^{13}C-NMR (100.6 MHz, $CDCl_3$, 25 °C): δ_C 18.74 (CH_3), 29.61 (CH_2), 35.71 (CH_2), 121.27 (CH), 125.19 (Cq), 132.05 (CH), 133.79 (Cq), 134.13 (CH), 135.47 (Cq), 135.83 (Cq), 136.73 (CH), 137.43 (CH). HRMS (EI) calcd. for $C_{22}H_{22}S_2$ 350.1163, found 350.1157.

14,17-Dimethyl[2](1,3)azuleno[2]paracyclophane (2c)

8 (0.76 g, 2.17 mmol) was dissolved in trimethyl phosphite (220 mL) and irradiated with a 250 W high pressure mercury lamp for 8 h at 0 °C under argon atmosphere. The solvent was evaporated and the residue chromatographed (Al_2O_3; light petroleum (bp 40–60 °C)–CH_2Cl_2, 10:1, $R_f = 0.59$) to give 0.25 g

Table 3 Comparison of theoretical (DFT/RPA) and experimental excitation energies (ΔE, in eV), oscillator strengths (f), rotatory strengths[a] (R, in 10^{-40} cgs units) and CD/UV intensities (ε and $\Delta\varepsilon$, in M^{-1} cm^{-1}) for the excited singlet states of 14,17-dimethyl[2](1,3)azuleno[2]paracyclophane

	DFT/SCI			Exp.[a]			
State	ΔE	f	R	ΔE	ε[c]	$\Delta\varepsilon$	Assignment[b]
				band A			
2A	2.05	0.002	−6.7	2.0	185	−1.5	$1B_2$(Az)
				band B			
3A	3.04	0.006	−3.1	3.3		−1.6	$2A_1$(Az)
				shoulder C′			
4A	3.23	0.002	5.4			⊕	CT(Bz→Az(7))
				band C			
5A	3.85	0.187	36.0	3.9		+9.4	CT(Bz→Az(7))
				band D			
6A	4.03	0.022	−8.3				$2B_2$(Az) + CT
10A	4.23[d]	0.414	−85.3	4.2	56000	+27.5	$3A_1$(Az)
7A	4.23	0.002	−4.3				L_b(Bz)
8A	4.32	0.037	−1.5				CT(Bz→Az(7))
9A	4.41	0.006	29.8				CT(Az(5)→Bz)
				band E			
				4.6		−59.7	
				band F			
11A	4.80	0.153	−17.3				CT(Az(5)→Bz)
12A	4.89	0.006	−9.0				L_a(Bz)
13A	5.03	0.008	−20.3				CT(Az→Bz)
14A	5.06	0.017	1.5				CT(Az→Bz)
15A	5.17	0.041	−78.1	4.9		−66.6	CT(Az→Bz)
16A	5.38	0.187	20.5				$3B_2$(Az)
17A	5.58	0.028	−2.4				$4A_1$(Az)
				band G			
18A	5.85	0.260	494.5	5.7	45000	+169.0	E_{1u}(Bz)
				band H			
19A	5.95	0.193	−341.4	6.2	45000	−45.0	E_{1u}(Bz)

[a] In cgs, R has units of 3.336×10^{-15} C^2 m^3 s^{-1}. The values given refer to CD band maxima in *n*-hexane solution. [b] The acronyms given in parentheses refer to the active chromophore, *i.e.* Az for azulene and Bz for the benzene moiety. (5) and (7), respectively, refer to MOs localized mainly in the five- or seven-membered rings of the azulene moiety. [c] Data are given only if the UV band maximum corresponds to a resolved band in the CD spectrum. [d] The theoretical value of 4.68 eV has been shifted by 0.45 eV (see text).

(40%) of **2c** as a blue crystalline solid; mp 153 °C. ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C): δ_H 1.20 (s, 3H, CH_3), 2.45 (m, 2H, CH_2), 2.49 (s, 3H, CH_3), 2.90 (m, 2H, CH_2), 3.26 (m, 2H, CH_2), 5.07 (s, 1H, ArH), 6.22 (s, 1H, ArH), 6.80 (s, 1H, ArH), 6.93 (m, $J = 9.7$, 9.4 Hz, 1H, ArH), 6.95 (m, $J = 9.5$, 9.6 Hz, 1H, ArH), 7.40 (m, $J = 9.9$, 9.8 Hz, 1H, ArH), 7.98 (d, $J = 9.8$ Hz, 1H, ArH), 8.01 (d, $J = 9.7$ Hz, 1H, ArH); ^{13}C-NMR (100.6 MHz, CDCl$_3$, 25 °C): δ_C 18.16 (CH_3), 18.63 (CH_3), 24.35 (CH_2), 26.19 (CH_2), 31.98 (CH_2), 33.34 (CH_2), 120.36 (CH), 120.50 (CH), 127.77 (Cq), 128.33 (Cq), 131.55 (Cq), 131.99 (CH), 132.02 (CH), 132.63 (CH), 133.12 (CH), 134.43 (Cq), 135.75 (CH), 136.28 (Cq), 137.13 (Cq), 137.56 (Cq), 141.68 (CH). HRMS (EI) calcd. for $C_{22}H_{22}$ 286.1721, found 286.1719.

Enantiomeric separation and CD measurement of 2c

Column: cellulose tris(3,5-dimethylphenyl)carbamate (CDMPC),[32] 4.6 × 250 mm, eluent *n*-hexane–isopropanol (99.2 : 0.8), 1.5 ml min^{-1}, pressure 16 bar, temperature 298 K, detection: UV, $\lambda = 254$ nm, $t_r[(-)_D$-**2c**$] = 36$ min, $t_r[(+)_D$-**2c**$] = 49$ min. A complete enantiomeric separation could not be accomplished, but enantiomers were enriched. CD measurement: JASCO-spectropolarimeter J 720, 0.0065 mol l^{-1} solution in *n*-hexane, 0.02 mm cell, temperature 25 °C.

X-Ray structure of 2c ‡

Crystal data: $C_{22}H_{22}$; 286.40; blue crystals; 0.30 × 0.18 × 0.08 mm; monoclinic; space group: $P2_1$ (no. 4); $a = 7.9870(2)$ Å, $b = 12.6805(4)$ Å, $c = 8.1337(3)$ Å, $\alpha = 90°$, $\beta = 105.788(2)°$, $\gamma = 90°$; $V = 792.70(4)$ Å^3; $Z = 2$; $d_{calc} = 1.200$ Mg m^{-3}; absorption coefficient: 0.067 mm^{-1}; $F(000) = 308$; Nonius KappaCCD diffractometer; wavelength: 0.71073 Å (Mo-K$_\alpha$); temperature: 123(2) K; monochromator: graphite; θ range for data collection 3.06 to 28.29°; index ranges: $-10 \leq h \leq 9$, $-16 \leq k \leq 16$, $-10 \leq l \leq 10$; reflections collected: 11472; independent reflections: 3718($R_{int} = 0.0370$); refinement method: full-matrix least-squares on F^2; data/restraints/parameters: 3718/1/202; goodness-of-fit on F^2: 1.044; final R indices $[I > 2\sigma(i)]$: $R1 = 0.0413$, $wR2 = 0.0965$; R indices (all data): $R1 = 0.0470$, $wR2 = 0.0981$; largest diff. peak and hole: 0.286 and −0.183

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‡ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/154. See http://www.rsc.org/suppdata/p2/1999/521/ for crystallographic files in .cif format.

Å^{-3}. An extinction correction was applied. The absolute structure cannot be determined reliably [Flock's x-parameter $-2(7)$].

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