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Enantiomer Resolution, Absolute Configuration, and Attempted Thermal Racemization of Two Tetrabenzocyclooctatetraene (*o*-Tetraphenylene) Derivatives. An Exceptionally High Barrier to Ring Inversion

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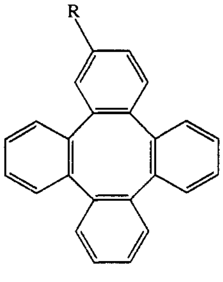
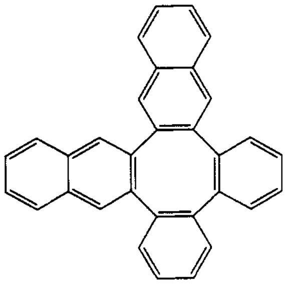
2-Acetyltetrabenzo[*a*,*c*,*e*,*g*]cyclooctatetraene (**1c**) and dibenzo[*a*,*c*]dinaphtho[2,3-*e*;2,3-*g*]cyclooctatetraene (**2**) have been resolved to high enantiomeric purity by repeated chromatography on microcrystalline, swollen triacetylcellulose. The circular dichroism spectra have been recorded, and the absolute configurations of the enantiomers of **1c** and **2** have been assigned on the basis of calculations of the rotational strengths of the dominant transitions by the coupled oscillator technique. Thermal racemization of **1c** could not be achieved because of complete decomposition already at +250 °C, but **2** could be partly racemized with only partial decomposition at +600 °C, with a rate corresponding to a free energy barrier to ring inversion of 67.2 ± 0.8 kcal/mol.

Several years ago[3-7] attempts were made to determine the barrier to ring inversion in tetrabenzo[*a*,*c*,*e*,*g*]cyclooctatetraene (*o*-tetraphenylene, **1a**). In spite of claims to the opposite,[3] it was evident that this barrier is quite high. A CNDO/2 calculation predicted 222 kcal/mol,[5] while a lower limit of 45 kcal/mol was established by the observation that a partially resolved monocarboxylic acid (**1b**) showed no racemization after long heating in biphenyl at 251 °C.[7]



1a, R = H
b, R = CO_2H
c, R = COMe



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Inspired by the ready access to optically active forms of many chiral organic compounds lacking functional groups through chromatography on swollen microcrystalline triacetylcellulose (TAC),[8-11] we have attempted to resolve the chiral tetrabenzocyclooctatetraene derivatives **1c**[3] and **2**[12] to determine their absolute configurations and to study their possible thermal racemization.

Table I. CD Spectra in Ethanol

compd	λ_{max}/nm ($\Delta\epsilon$)
(+)-1c	342.5 (+0.10), 317.5 (−0.19), 267.5 (+28.3), 243.0 (−54.7), 223.5 (+26.2), 209.0 (−22.0)
(−)-2	327 (+0.24), 320 (−0.20), 298.5 (−14.5), 287 (−17.4), 275 (−17.4), 256 (−81.1), 234 (+196.0), 216.5 (−132.0), 197 (+101.0)
(+)-3	277 (+0.57), 265.5 (+0.83), 232 (+36.7), 217 (+77.3), 200 (−96.1), 192.5 (−142.1)

Table II. UV Spectra in Ethanol

compd	λ_{max}/nm (ϵ)
1c	340 S[a] (61), 352 S (89), 260 S (15 300), 243 S (28 000), 211 (68 000)
2	297 S (5600), 282 S (14 200), 272 S (21 600), 237.5 (90 900), 214.5 (62 200)
3	273 S (520), 263 S (1040), 234.5 (11 200), 208.5 (44 300)

[a] S = shoulder.

The chromatogram for **1c** showed strongly overlapping bands in the UV detector trace,[9] but recycling six times, each time with rejection of the intermediate fraction, eventually gave (+) and (−) fractions for which the UV and polarimeter traces were congruent, indicating high optical purity.[13] The first eluted enantiomer (E_1), (+)-**1c**, gave a CD spectrum (Figure 1a and Table I) with strong bands at 209 (−), 223.5 (+), 243 (−), and 267.5 (+) nm and weak bands at 317.5 (−) and 342.5 (+). The latter are assigned to n → π* transitions in the acetyl group, possibly in two different conformations. The UV spectrum of **1c** (Table II) shows only one maximum (210 nm) but several shoulders at longer wavelengths.

We have attempted to analyze and reproduce the CD spectrum of the enantiomer of **1c** that has *R* configuration of rings 1 and 2 (see Table III) in the coupled oscillator model[14] by using a semiempirical program for calculation of rotational strengths devised by Schellman and coworkers.[15] This permits interactions between all transitions included by using a matrix formalism, and it requires as input the strengths and directions of the transition

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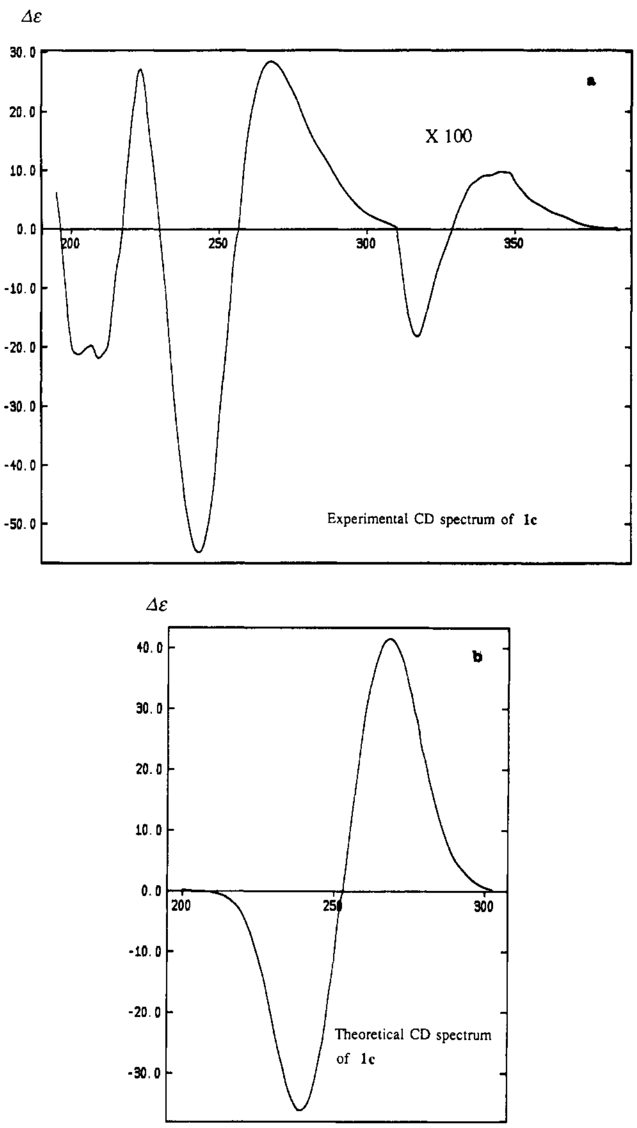
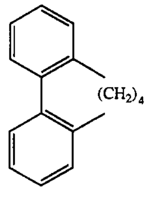


Figure 1. (a) Experimental CD spectrum of the E_1 (+) enantiomer of **1c** in ethanol. (b) Calculated CD spectrum of **1c** with *R* configuration of rings 1 and 2 (Table III).

moments and the corresponding transition charge densities. The program also permits the calculation of the rotational strengths of the n → π* transitions by using the one-electron[16] and m-μ[17] models, but since the orientation of the acetyl group in **1c** is unknown, these contributions have not been considered.

We have confined our calculations to the ^1L_b and ^1L_a[18] transitions in the benzene and acetylbenzene chromophores in **1c**. An X-ray crystallographic study of **1a**[19] shows that the average of the dihedral angles between the benzene rings is 66°, indicating only moderate conjugative interactions between the rings. The benzene rings in **1c** are therefore treated as isolated chromophores. The moments for the ^1L_b transitions have been derived by the spectroscopic moment technique[20] using UV and CD spectra of 9,10,11,12-tetrahydrodibenzo[*a*,*c*]cyclooctene[11] (**3**, Tables I and II) to derive the spectroscopic moment of a phenyl substituent (+0.36 D). According to MMP2 calculations, the twist angle in the biphenyl unit of **3** is 59°.



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The moment for a bridge CH_2 was assumed to be the same as that for an ethyl group (0.21 D),[20b] and that for an acetyl group the same as that for a formyl group (−0.97 D).[20b] The UV spectra of acetophenone and benzaldehyde are very similar.[21]

The ^1L_a transitions pose a particular problem since they are oriented along the pivot bonds and interact in each biphenyl unit to give an allowed low energy and a forbidden high energy combination.[22] Only the former (the "A" transition)[23] needs to be considered. A further complication is that these transitions are inherently chiral and give contributions to the rotational strengths, which are not included in the coupled oscillator treatment. However, these contributions cancel, that from rings 2 + 3 with that from rings 3 + 4, and that from rings 1 + 4 largely with that from rings 1 + 2. The residue from the latter contributions should be positive[24] and add to the positive band calculated at ca. 260 nm. The transition moments involving rings 2, 3, and 4 were derived from the UV spectrum of **3** (2.42 D). The 1–4 combination was also treated as a simple biphenyl unit, since a *m*-acetyl substituent can be expected to have little influence. The 1–2 biphenyl unit, with a *p*-acetyl substituent, will have a large A-transition moment. This transition gives a band at 276 nm in the spectrum of *p*-phenylacetophenone (ϵ = 20 700)[21] but must have higher energy in **1c** with the larger twist angle. A shoulder at 243 nm (ϵ = 28 000) in the spectrum of **1c** has been tentatively assigned to this transition, corresponding to a transition moment (μ_A) of 7.3 D. The A-transition moments were split into equal parts (μ_{ring}) by using eq 1

$$\mu_{ring} = [0.5\mu_A{}^2]^{1/2} \qquad (1)$$

and centered in the individual rings, to conform with the requirements of the program.[15] The transition charge densities were obtained from a CNDO/S calculation on a 60° twisted biphenyl and scaled to conform with the μ_{ring} values. The input data are found in Table III. The agreement between the experimental and calculated CD spectra for **1c** (Figure 1) is quite good with respect both to the signs of the dominant components and to the intensities. Since the sign of the strong couplet must depend on the spatial relation between the strong transition moment more than on their absolute magnitudes, it seems safe to assume that the (+) (E_1) enantiomer of **1c** has an *R* configuration of the 1–2 and 3–4 biphenyl units (Figure 2).

Attempts to observe thermal racemization of (+)-**1c** failed. The compound underwent complete decomposition when kept at +250 °C for 30 min in an evacuated ampoule.

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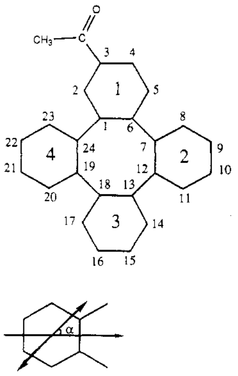
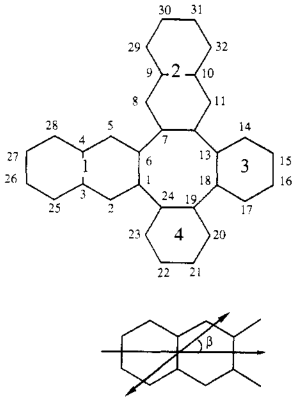
Table III. Input Data for Calculation of CD Spectra of 1c and 2

compound	ring(s)	transition and direction	energy/ 10^{-3} cm^{-1}	Δ^a/nm	transn moment/ D	transn monopoles^b
	1	$^{1}\mathrm{L}_{\mathrm{b}}$, α: 88.8°	35.87	15	0.85	1;4: ∓ 0.0532 2;5: ∓ 0.0836 3;6: ∓ 0.0306
	2, 3, 4	$^{1}\mathrm{L}_{\mathrm{b}}$, α: 0°	37.24	15	0.36	(7,12);(9,10):^{c,d} ± 0.0306
	1, 2	$^{1}\mathrm{L}_{\mathrm{a}}$, α: 30°	41.15	15	5.16	(1,5);(9,11): −0.2630 (2,4);(8,12): +0.1768 3;7: −0.4650 6;10: +0.4432
	1, 4 2, 3 3, 4	$^{1}\mathrm{L}_{\mathrm{a}}$, α: 30°	42.64	15	1.92	7: −0.1650^d 8;12: +0.0982 9;11: −0.0660 10: +0.1734
	1, 2	$^{1}\mathrm{L}_{\mathrm{b}}$, β: 0°	31.78	10	0.36	(1,6);(26,27):^{c,d} ± 0.0070 (2,5);(25,28):^{c,d} ± 0.0018
	1, 2	$^{1}\mathrm{L}_{\mathrm{a}}$, β: 90°	35.00	10	2.49	(1,26);(6,27):^{c,d} ± 0.0119 (2,25);(5,28):^{d,e} ± 0.0475
	1, 2	$^{1}\mathrm{B}_{\mathrm{b}}$, β: 0°	45.45	10	6.85	(1,6);(26,27):^{d,e} ± 0.1307 (2,5);(25,28):^{d,e} ± 0.0327
	3, 4	$^{1}\mathrm{L}_{\mathrm{b}}$ and $^{1}\mathrm{L}_{\mathrm{a}}$, as for 1c				

[a] Half-width at $1/e$ of maximum intensity, assuming Gaussian band shape. [b] In units of electronic charge. [c] First group +, second −. [d] And corresponding positions in the other ring(s).

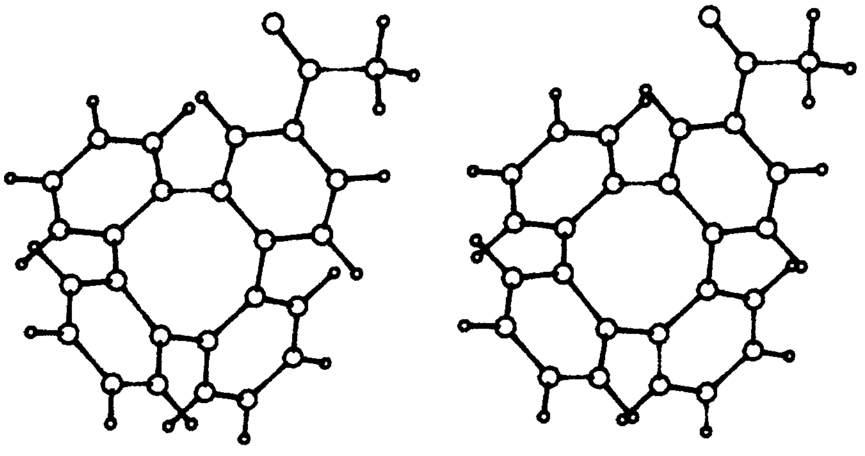


Figure 2. Stereoview of 1c with *R* configuration of rings 1 and 2 (and 3 and 4).

The resolution of the dibenzodinaphthocyclooctatetraene **2** by chromatography on TAC was superior to that of **1c**, and enantiomerically pure forms (ee > 0.95) were obtained after recycling twice. The CD spectrum of the E_1 (−) enantiomer (Figure 3a, Table I) shows strong bands at 197 (+), 216.5 (−), 234 (+), and 256 (−) nm with a succession of weaker negative bands at 275, 287, and 298.5 nm and with a weak positive couplet centered at 323 nm. The UV spectrum (Table II) shows maxima at 215 and 237 nm with shoulders at 275, 285, and 296 nm. The CD and UV bands in the range 275–300 nm are assigned to the $^{1}\mathrm{L}_{\mathrm{b}}$ transition in the naphthalene chromophore,[25,26] and the CD band at 256 nm to the $^{1}\mathrm{L}_{\mathrm{a}}$ transition. The positive CD couplet centered at 225 nm is assigned to an interaction between the $^{1}\mathrm{B}_{\mathrm{b}}$ transitions in the two naphthalene chromophores.

The absolute configurations of several 1,1′-binaphthyls have been determined by Akimoto and co-workers[27] by using the anomalous scattering technique in X-ray crystallography[27a] and by chemical correlations,[27b] and Mason and co-workers[28] have shown that the CD spectra of

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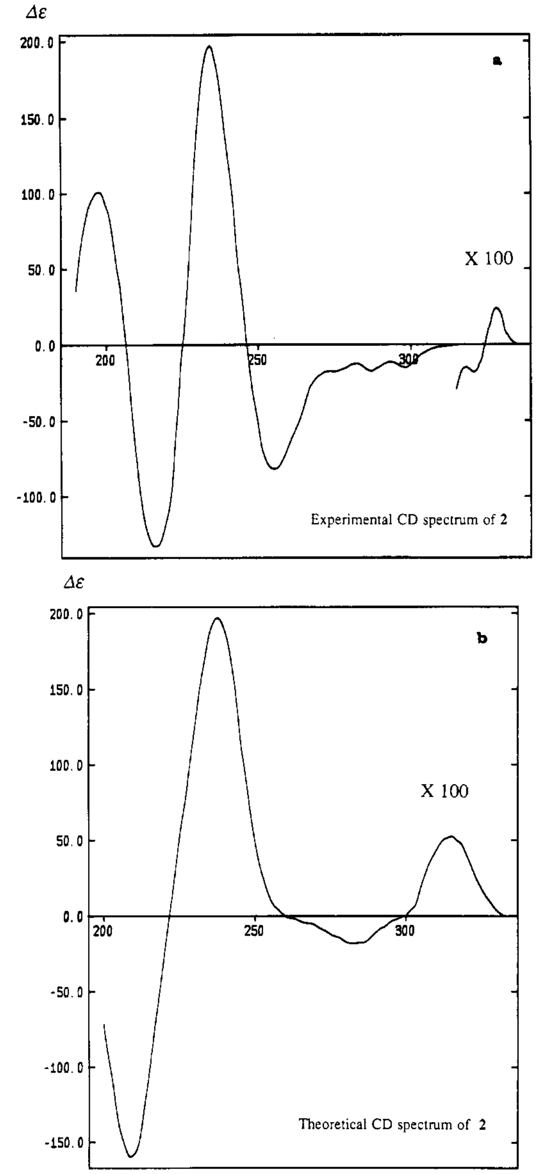
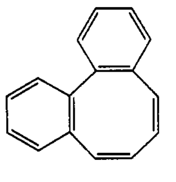


Figure 3. (a) Experimental CD spectrum of the E_1 (–) enantiomer of **2** in ethanol. (b) Calculated CD spectrum of **2** with (*S*)-2,2′-binaphthyl unit.

(*S*)-1,1′-binaphthyls display positive $^{1}B_b$ couplets around 225 nm and negative $^{1}L_a$ bands at longer wavelength. No similar study seems to have been reported for 2,2′-binaphthyls. A calculation on a 66° twisted (*S*)-2,2′-binaphthyl with the matrix program described in ref 15a and with input based on the data for the $^{1}L_b$, $^{1}L_a$, and $^{1}B_b$ transitions in naphthalene in ref 25 and on a CNDO/S calculation of transition charge densities gave rotational strengths for the $^{1}B_b$ (positive couplet) and $^{1}L_a$ (negative band) transitions similar to those predicted by Mason et al.[28a] for the 1,1′ analogues. A calculation for the entire **2** with a (*S*)-2,2′-binaphthyl unit gave good agreement with the experimental curve (Figure 3) and shows that the CD spectrum of **2** is dominated by the contribution from the binaphthyl unit. The signs and orders of magnitude of the rotational strengths of the benzene and naphthalene $^{1}L_b$ transitions and the naphthalene $^{1}L_a$ transition are well reproduced. The main shortcoming is the failure to reproduce the negative band at 256 nm. This may be due to inherently chiral transitions occurring in the 2-phenylnaphthalene units. However, the general agreement is so good that the (*S*)-2,2-binaphthyl configuration (Figure 4) with confidence is assigned to the E_1 (–) enantiomer of **2**.

Thermal racemization of pure (+)-**2** was more successful than with **1**. Up to +500 °C no racemization and only little decomposition was observed, but after 17 min at +550 °C some carbonization had occurred. The purified sample on chromatography on TAC showed 2–3% of (–)-**2**. After 5 min at +600 °C, 7–10% of (–)-**2** was observed, and at +650 °C, complete decomposition occurred within 5 minutes. The racemization rates observed at +550 and +600 °C correspond to a free activation energy for ring inversion of 67.2 ± 0.8 kcal/mol. To our knowledge, this is the highest barrier to conformational change ever reported. This barrier should be approximately valid also for **1a**.

We have earlier found the free energy barrier to ring inversion in dibenzo[*a*,*c*]cyclooctatetraene (**4**) to be 30.0 kcal/mol[11] by a racemization experiment. It may be worthwhile to compare the inversion barriers of **2** and **4**. The barrier for **4** has a contribution from the resistance of the cyclooctatetraene ring to approach planarity of ca. 15 kcal/mol.[29] The annelated benzene rings in **4** con-



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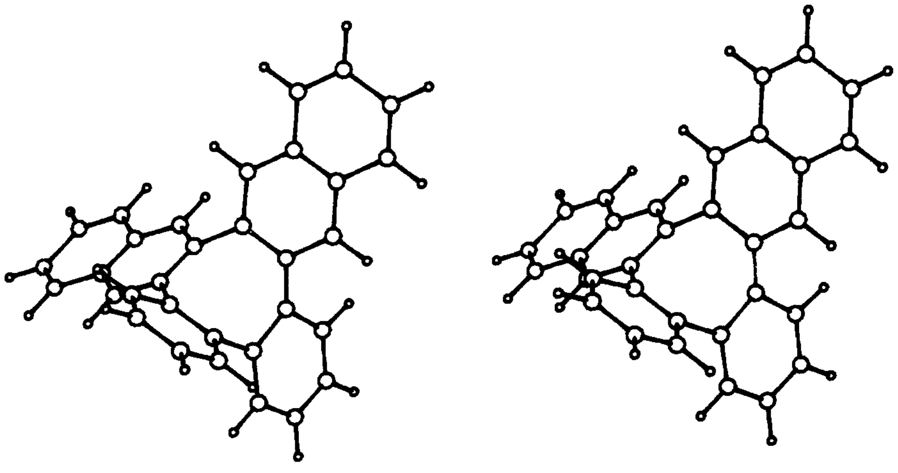

Figure 4. Stereoview of **2** with (*S*)-2,2′-binaphthyl unit.

tribute to the barrier mainly by inter-ring and notably the H-4⋯H-5 repulsion and possibly also by stiffening the carbon skeleton. The latter effect is probably insignificant since the inversion barrier in benzocyclooctatetraene is 13.4 kcal/mol[30] and in dibenzo[*a*,*e*]cyclooctatetraene 12.3 kcal/mol.[6] Considering that **1** and **2** have four repulsive H⋯H interactions along the reaction coordinate to inversion, a simplistic calculation assuming a nearly planar transition state leads to the prediction of an inversion barrier of the order of 75 kcal/mol. The deviation from the observed value is small enough to allow a nearly planar transition state to appear as a fairly realistic model. This conclusion is supported by the observation by Müllen and co-workers[31] that 6-methyltribenzo[*a*,*c*,*e*]cyclooctatetraene has a free energy barrier to racemization of 41 kcal/mol, corresponding to a barrier to ring inversion of 41.7 kcal/mol.

It could be argued that the racemization occurs by a ring opening–ring closure mechanism involving free radicals. Friedman and Lindow[32] have shown that biphenylene on pyrolysis at 330–350 °C forms tetraphenylene in high yield. At higher temperatures biphenyl, *o*-terphenyl, and triphenylene are formed (but no tetraphenylene), and experiments with deuterium-labeled aromatic substrates showed that the radicals initially formed react by hydrogen abstraction. To effect ring inversion, a diradical would have to undergo 180° rotations about all three remaining inter-ring bonds before recyclization. It seems likely that, if the radicals formed were sufficiently long-lived to perform this process, they would also have time to abstract hydrogen atoms from other molecules and form quaterphenyl derivatives. If two bonds should break with formation of biradicals related to biphenyl, analogues of the other products found by Friedman and Lindow should be observed. However, a 300-MHz ^1H NMR spectrum of a sample kept for 5 min at +580 °C showed strong resonances of **2** and no other resonances. We therefore believe that all radicals formed immediately react to insoluble polymeric material and that the racemization of **2** occurs by ring inversion.

Experimental Section

Materials. 2-Acetyltetrabenzo[*a*,*c*,*e*,*g*]cyclooctatetraene (**1c**) was prepared as described by Figeys and Dralants,[3] mp 201 °C after recrystallization from ethanol. The preparation of dibenzo[*a*,*c*]dinaphtho[2,3-*e*;2,3-*g*]cyclooctatetraene (**2**) will be described elsewhere,[12] and the preparation of 9,10,11,12-tetrahydrodibenzo[*a*,*c*]cyclooctatetraene (**3**) has recently been described.[11]

The enantiomer resolution was performed with the equipment and technique described in ref 9 with ethanol as the mobile phase. The eluted fractions were directly subjected to CD spectroscopy, and their concentrations were monitored by UV spectroscopy after suitable dilution.

CD spectra were recorded by a JASCO Model J-500A spectropolarimeter, and **UV spectra** with a Cary Model 2290 spectrometer.

Racemization Experiments. Small samples (0.5 mg) of pure (+)-**2** were sealed in thick-walled Pyrex ampules (6.2 × 15 mm) under vacuum and placed in a Carbolite oven at preset temperatures. The oven temperature is precise to ±5 °C, and the sample comes to the set temperature within 30 s. After the finished experiment, the ampule was rapidly cooled and opened, and the black residue ($t > 500$ °C) was extracted with $CHCl_3$, which was filtered and evaporated. The colorless residue consisted of pure **2** according to NMR and chromatography on TAC, but in the experiments at +550 and +600 °C, small peaks with negative rotation could be observed at the place of (−)-**2**. The (+) enantiomer was chosen for the racemization experiments since the (−) form has a sharper band in the chromatogram, and small amounts of it can be observed with greater certainty. At 550 °C, 2–3% of the (−) form (p) was observed after 1020 s (t, corrected value). By use of the expression $k_{\mathrm{inv}} = (t)^{-1} \ln (100/(100 - p))$ and the Eyring equation,[33] free activation energies, $\Delta G^{\ddagger}$, were found in the range 67.5–66.9 kcal/mol. The corresponding values obtained at 600 °C are $p = 7$–10% and $t = 300$ s, corresponding to $\Delta G^{\ddagger} = 67.4$–66.8 kcal/mol. The uncertainty in temperature and heating time adds ca. 0.5 kcal mol^{-1} to the total uncertainty, and the free energy barrier to inversion is 67.2 ± 0.8 kcal/mol. The retention times for (+)-**2** and (−)-**2** after the racemization experiment were exactly the same as those observed before.

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