Table I. Spectroscopic and Analytical Data for Oligonuclear Ruthenocenes

						UV/vis spectra[d]					
						band system V		band system IV		band system II	
			anal. found[c]								
compd	mp, °C[a]	P+,[b] m/e	C	H		λ_{max}, nm	ε, M^{-1} cm^{-1}	λ_{max}, nm	ε, M^{-1} cm^{-1}	λ_{max} nm	ε, M^{-1} cm^{-1}
biruthenocene (3, n = 2)	238-239	462	51.98	4.04	a	249	6400	261	5300	322	670
					b	247	6300	262	4500	320	620
1,1′-terruthenocene (3, n = 3)	276	692	52.11	3.99	a	252	9400	265	8600	322	1050
					b	250	e	266	e	322	e
1,1′-quaterruthenocene (3, n = 4)	269-271	922	52.07	3.80	a	253	9400	265	8500	323	1300
					b[e]						

[a] Capillary sealed under N_2. [b] Mass spectral parent ion peak for ^{102}Ru (70 eV; 200-400 °C inlet temp). [c] Anal. Calcd for 3 (n = 2): C, 52.16; H, 3.94. Calcd for 3 (n = 3): C, 52.24; H, 3.80. Calcd for 3 (n = 4): C, 52.28; H, 3.73. [d] Band-system designation in Gray's notation.[7] Line a was determined in 1,2-dichloroethane and line b in hexane. The molar extinction coefficient, ε, was calculated per metallocene unit. For comparison, λ_{max}, nm (ε, M^{-1} cm^{-1}), of ruthenocene is given for band systems V, IV, and II in hexane solution as 218 (4800), 238 (2300), and 320 (230) and for band systems IV and II in 1,2-dichloroethane solution as 237 (3800) and 322 (235). [e] Not determined in hexane because of insufficient solubility.

crystalline compounds. The electronic absorption spectra, taken on hexane and 1,2-dichloroethane solutions, show significant batho- and hyperchromic shifts of the characteristic charge-transfer bands in the UV region (band systems IV and V in Gray's notation;[7] Table I) as one goes from ruthenocene to the dimer. In the latter, one may expect an essentially parallel alignment of the two directly interconnected cyclopentadienyl rings and, hence, a moderate extent of conjugation between the two metallocene units. Only minor further shifts are apparent in the trimer spectrum, and the differences between the spectra of the trimer and the tetramer are negligible. This trend, reflecting the lack of substantial electronic charge delocalization across the metal center in the ruthenium complex, is comparable to the situation in the analogous oligoferrocene series, where both λ_{max} and ε were found to reach their highest values in the trimer/tetramer region, with no additional shifts occurring on further chain extension.[4]

It is of interest to note that, contrasting with the UV band systems IV and V, the ligand-field absorption maximum near 320 nm (band system II;[7] Table I) remains invariant with the degree of polymerization. This invariance, however, is a fortuitous result of the interplay of the two transitions[7] contributing to this composite band. Careful inspection of the dichloroethane solution spectra reveals the existence of two submaxima, viz., a predominant one near 310 nm in ruthenocene (315-322 nm in the dimer and trimer) and a second somewhat less intense maximum at about 335 nm in ruthenocene (345-350 nm in the dimer and trimer).[8] As a consequence of vibrational distortion in the oligomers,[9] both component bands increase in intensity in the sequence ruthenocene, biruthenocene, terruthenocene, quaterruthenocene, the greatest enhancement being noticeable in the dimer relative to the monomer. Our spectra indicate the 310-nm component band to be enhanced in intensity more rapidly with growing degree of polymerization than that near 335 nm, which explains the observed failure of the composite maximum (Table I) to follow the bathochromic shift trend shown by the band systems IV and V.

Experimental Section

The preparative procedure was as follows. 1,1′-Dilithioruthenocene (chelated with TMEDA, 2, 16.0 mmol), prepared from ruthenocene (20 mmol), n-butyllithium (40 mmol, 1.5 M in hexane), and TMEDA (40 mmol) in hexane medium and isolated in the solid state[10] as described,[2] was suspended in di-n-butyl ether (DBE; 100 mL) at 25 °C under Ar. To the stirred suspension was slowly added a solution of 1 (10.3 mmol) in DBE (200 mL), and stirring of the mixture was continued for 7 h at about 25 °C and for 35 h at 65 °C. The glassware used was flamed and argon purged, and all solvents and reagents were dried and deoxygenated as in previous work.[1-5] The solid reaction products obtained after hydrolysis (1 M aqueous HCl, 40 mL; 0 °C) from the organic phase were dried at 50 °C in vacuo (24 h) and treated with $NiCl_2$ (10 mmol) and $LiAlH_4$ (10 mmol) in THF as described by Ashby and Lin.[11] Admixed ruthenocene (20%) was removed from the recovered product mixture by sublimation (50 °C, 0.1 torr), and the sublimation residue (24%, based on total 1 and 2 employed) was chromatographed on alumina (activity grade II). Benzene/hexane (1:4) eluted traces of ruthenocene, followed by a band containing biruthenocene (crude yield 7%). Further elution with benzene/hexane (1:1) and neat benzene produced a trimer-containing (3.5%) band and a zone containing tetramer (2.2%). The three crude oligomers were recrystallized several times from heptane, heptane/benzene, and toluene, respectively. The material remaining on the column was extracted with boiling toluene, and from the strongly concentrated extracts a grayish polymeric fraction of 3 (5.5%) was obtained by precipitation with excess hexane.

Registry No. 1, 70210-63-8; 2, 70210-60-5; 3 (n = 2), 67126-04-9; 3 (n = 3), 73178-90-2; 3 (n = 4), 73178-91-3.

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(7) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).

(8) The two maxima, associated with the $a_{1g} \rightarrow e_{1g}$ and $e_{2g} \rightarrow e_{1g}$ one-electron d-d transitions (in D_{5d} symmetry), were first observed[7] at 339 and 308 nm in a frozen EPA solution of ruthenocene at 77 K.

(9) Ring tilt, known to contribute to the relaxation of the selection rules in tilted ferocenes [T. H. Barr and W. E. Watts, *J. Organomet. Chem.*, **15**, 177 (1968); H. L. Lentzner and W. E. Watts, *Chem. Commun.*, 26 (1970)], does not appear to be a contributing factor in the present oligoruthenocene case, no unusual splitting or shifts of the characteristic absorptions in the CC stretching (1350-1420 cm^{-1}) and CH out-of-plane deformation (800-850 cm^{-1}) regions manifesting themselves in the IR spectra of the oligomeric compounds. A more detailed presentation of spectral data (including NMR) will be given in a future paper.

(10) This isolation, brought about by removing the lithiation mother liquor through filtration and washing the residual, insoluble 2 with hexane, ensured that contamination with monolithioruthenocene (chelated with TMEDA), more soluble than 2, was minimized.

(11) E. C. Ashby and J. J. Lin, *J. Org. Chem.*, **43**, 1263 (1978).

Thermal Cis-Trans Isomerization in 1,2-Dibenzoyl-1,2-dihydroacenaphthylene[1]

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Considerable interest has recently been shown in the properties of biradicaloid intermediates based on 1,8-

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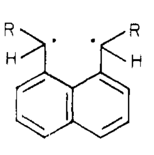
(1) Part of this work was done at The Weizmann Institute of Science, Rehovot, Israel, while F.G. was on sabbatical leave.

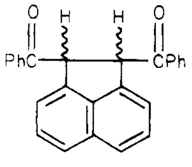
Table I. Some Spectral Properties of the Isomers of 2

	trans-2[a]	*cis*-2[b]
mp, °C	199-201	205-206
NMR (CDCl$_3$), δ	8.20-6.86 (arom m, 16 H) 6.21 (H$_{1,2}$ s, 2 H)	7.80-7.17 (arom m, 16 H) 5.70 (H$_{1,2}$ s, 2 H)
IR (CHCl$_3$), cm^{-1}	1675 (C=O)	1680 (C=O)
UV (EtOH), nm	242 (π,π*)	238 (π,π*)

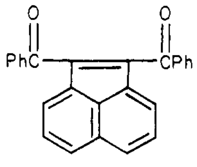
[a] From 3 + Na$_2$S$_2$O$_4$ + K$_2$CO$_3$. [b] From 3 + Na$_2$S$_2$O$_4$.



1a, R = H
b, R = PhCO



2



3

naphthoquinodimethane[2] (**1a**). A source of these species, other than the usual azo precursors, may be substituted dihydroacenaphthylenes when subjected to conditions favoring homolytic carbon–carbon bond cleavage. This process and the resulting diradical intermediates offer fundamental mechanistic insights and have received much attention in cyclopropanes[3] but have been seldom explored in the acenaphthylene series. Having obtained the geometric isomers of 1,2-dibenzoyl-1,2-dihydroacenaphthylene (*cis*-**2**, *trans*-**2**) in connection with another study, we began to examine conditions that might product the dibenzoyl intermediate **1b**. We have found that thermolysis of *cis*-**2** results in isomerization to *trans*-**2**,[4] which is the subject of this note along with the synthesis of the title compounds.

The preparation of one isomer of **2** by reduction of 1,2-dibenzoylacenaphthylene (**3**) with zinc in acetic acid was reported in 1938.[5] No effort was made to investigate the stereochemistry. We have repeated the earlier work and obtained the same substance, shown below to be *trans*-**2**. We have found that reduction of **3** with sodium dithionite in aqueous sulfolane at 60 °C, in contrast to the action of zinc in acetic acid, affords only an isomeric product, whose spectral properties (Table I) and chemical behavior lead to the assignment of the cis configuration for this compound.

The conclusion is based, in part, on the assumption that the absorption spectra will reflect the higher energy of the cis isomer. This is exactly the situation with the 1,2-dibenzoylcyclopropanes.[6] In the case of **2**, the spectral characteristics of the less stable isomer, i.e., the higher frequency carbonyl stretching (by 5 cm^{-1}), the higher field α-hydrogen chemical shift (by δ 0.51), and the shorter wavelength π,π* transition (by 4 nm), are seen in the 205–206 °C compound, which is therefore cis.

This assignment is also supported by the mass spectra, in which the molecular peak of the 199–201 °C (*trans*-**2**) isomer is 1.5 times more intense than that of the 205–206 °C (*cis*-**2**) isomer, thus mirroring the greater energy requirement for ionization of the more stable species.

Finally, treatment of *cis*-**2** with hot alcoholic sodium carbonate under argon leads to *trans*-**2**.[7] This isomerization presumably occurs via an enolate ion that, on protonation, yields the more stable configuration. Utilizing this result, we were able to obtain *trans*-**2** in one operation by subjecting **3** to the action of dithionite in the presence of potassium carbonate.

Heating *cis*-**2** at 200–220 °C (1 torr) for 30 min resulted in predominate conversion to *trans*-**2**. Applying the same conditions to *trans*-**2** afforded only unreacted *trans*-**2**. That the reaction is not glass catalyzed is shown by observing the same transformation in a tube made of Teflon.

The thermal *cis*-**2** to *trans*-**2** isomerization was also effected in sulfolane and diethyl oxalate at 170 °C. The course of the reaction was monitored by NMR spectroscopy, and the half-times in these solvents were 1 and 3 h, respectively. In Me$_2$SO-d_6 at 150 °C, the isomerization was complete in 5 min, presumably due to the basic character of this solvent.[8]

While the diradical **1b** serves as an attractive rationale for the thermal isomerization, evidence for a nonhomolytic pathway was obtained. Heating *cis*-**2** (10^{-2} M) at 70 °C for 1 h in sulfolane–CH$_3$OD resulted in exchange (>90%) of the α hydrogens for deuterium. After 24 h at 70 °C in sulfolane–CH$_3$OH, a 1:1 *cis*-**2**/*trans*-**2** mixture was obtained. Repeating the above experiments at 55 °C for 2 h gave H–D exchange (84%) while maintaining stereochemical configuration.

These observations are most easily accommodated by assuming the isomerization and exchange occur via an enol or enolate that yields *trans*-**2** at higher temperatures but at 55 °C affords *cis*-**2**. The lower barrier to *cis*-**2** presumably arises through the solvent donating deuterium from the less hindered side, furthest from the benzoyl group.[9] Ketonization of the same intermediate would also account for the stereoselective reduction of **3** with dithionite to give *cis*-**2** as the kinetically controlled product. In accord with the lower energy of *trans*-**2**, treatment of *trans*-**2** with sulfolane–CH$_3$OD at 55 °C for 18 h produced no more than 20% exchange.

Although **1b** cannot be dismissed as an intermediate in the neat isomerization, melted *cis*-**2** itself may provide a medium that is sufficiently polar to promote enolization as the major pathway. We hope to test the possibility of thermal C–C cleavage by examining the behavior of 1,1,2,2-tetrasubstituted acenaphthylene derivatives where the absence of 1,2-hydrogens excludes enolization.

Experimental Section

Melting points were taken on a Thomas-Hoover or Fisher-Johns apparatus and are uncorrected. NMR spectra (Table I) were recorded in CDCl$_3$ on a Varian T-60 or Perkin-Elmer Hitachi R20 spectrometer with Me$_4$Si as an internal standard. Mass spectra were obtained on a MAT 731 spectrometer. Ultraviolet spectra were recorded on a Perkin-Elmer 202 spectrophotometer. Infrared spectra were determined in 5–10% chloroform solutions on a Perkin-Elmer 457 grating spectrometer. The elemental analysis was performed by Mr. Raoul Heller of The Weizmann Institute of Science, Microanalytical Laboratory. TLC was done on Merck Kieselgel 60-F254 precoated aluminum plates or Baker-flex silica gel 1B precoated polyester sheets. Sulfolane and diethyl oxalate

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(2) M. Gisin, E. Rommel, J. Wirz, M. N. Burnett, and R. M. Pagni, *J. Am. Chem. Soc.*, **101**, 2216 (1979), and references therein.

(3) (a) J. A. Berson, *Annu. Rev. Phys. Chem.*, **28**, 111 (1977); (b) R. G. Bergman in "Free Radicals", Vol. 1, J. Kochi, Ed. Wiley, New York, 1973, Chapter 5.

(4) We have also observed and are currently investigating the photoisomerization of *cis*-2 to *trans*-2.

(5) W. Dilthey, S. Henkels, and M. Leonhard, *J. Prakt. Chem.*, **151**, 97 (1938).

(6) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963).

(7) Bases such as sodium methoxide and potassium acetate in methanol as well as neutral alumina converted *cis*-2 to 3. This sensitivity to air oxidation in basic solution was noted in ref 5, where the same heterocycle was obtained from reaction of hydrazine with both 3 and *trans*-2.

(8) "Dimethyl Sulfoxide Technical Bulletin", Crown Zellerbach Corp., Chemical Products Division, Camas, WA, 1966, p 9.

(9) A somewhat analogous case is the Birch reduction of 1-hydroxy-1,2-diarylacenaphthylene derivatives to give *cis*-1,2-diaryl-1,2-dihydroacenaphthylenes: A. R. Miller and D. Y. Curtin, *J. Am. Chem. Soc.*, **98**, 1860 (1976).

Table II

2	solvent[a]	$10^2[2]$, M	t, °C	time, h	% exchange	% isomerization
cis	B	5.72	55	2	78	nd[b]
cis	B	5.00	55	2	91	nd
cis	A	6.00	55	3		nd
trans	B	3.72	55	18	18	nd
cis and trans	B	2.92, 2.88	56	3	c	
cis	A	5.59	55	27		16
cis	A	5.59	70	24		50
cis	B	5.32	70	1	>90	detectable

[a] Solvent A = sulfolane + CH_3OH; solvent B = sulfolane + CH_3OD. [b] nd = none detected. [c] 66% cis. The trans isomer was not detected.

were British Drug House reagent grade and were distilled before use.

1,2-Dibenzoylacenaphthylene (3). The method employed was essentially that of Dilthey, Henkels, and Leonhard.[5]

***cis*-1,2-Dibenzoyl-1,2-dihydroacenaphthylene (*cis*-2).** To a stirred solution of 3 (0.416 g, 1.15 mmol) in 5 mL of sulfolane at 60 °C was added in one portion sodium dithionite (0.400 g, 2.3 mmol) dissolved in 3 mL of water. The mixture developed a red color that became lighter, and in 1–2 min, a yellow-white precipitate emerged. After the mixture was stirred for 5 min, 40 mL of water was added and the mixture was chilled in an ice bath. The solid was filtered with vacuum, washed with 100 mL of distilled water in small portions, and dried by applying a vacuum. Purification was effected by dissolving the solid in 15 mL of CH_2Cl_2, adding 20 mL of cyclohexane, concentrating to about 25 mL, and allowing the solution to stand overnight. After the mixture was cooled, the solid was filtered with vacuum and washed with cold cyclohexane, affording 0.326 g (78%) of a mostly white solid. The melting point in an evacuated and sealed capillary, introduced into an oil bath at 194 °C, was 205–206 °C: mass spectrum, m/e 362 (M^+); UV (EtOH) λ_{max} (ϵ) 225 (59 600), 238 (27 100), 283 (7690), 342 (3680) nm. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01. Found: C, 86.34; H, 5.28.

***trans*-2. A. Base-Catalyzed Isomerization of *cis*-2.** A mixture of *cis*-2 (75 mg, 0.21 mmol), sodium carbonate (150 mg, 1.42 mmol), and 25 mL of ethanol was heated at 80 °C under argon. A yellow color developed in 10 min and progressively became more intense. After 3 h the mixture was cooled, affording a crop of small needles that were pipetted from the solid sodium carbonate and collected by vacuum filtration. The residual sodium carbonate was washed with ethanol to obtain additional product. The latter was washed with cold ethanol and dried. Recrystallization from CH_2Cl_2–cyclohexane gave 39 mg (52%) of a white solid: mp 199–201 °C (lit.[5] mp 176 °C); mass spectrum, m/e 362 (M^+); UV (EtOH) λ_{max} (ϵ) 224 (74 900), 242 (31 500), 283 (9200), 325 sh (1700) nm.

Evaporation of the filtrate to dryness yielded a yellow oil and solid. This was taken up in CH_2Cl_2 and thereby freed of Na_2CO_3. Removal of the CH_2Cl_2 left 28 mg of a yellow oil whose NMR spectrum showed *trans*-2 and peaks characteristic of 3. TLC also showed the presence of 3.[7]

B. Zinc-Dust Reduction of 3. To a refluxing, rapidly stirred mixture of 3 (0.200 g, 0.556 mmol) and 30 mL of glacial acetic acid was added zinc dust periodically in 0.1-g portions over 40 min until the originally orange mixture was a constant light yellow. After the mixture had cooled, crystals of zinc acetate were removed by filtration and water was added to the filtrate giving a yellow-white precipitate. The latter was collected by vacuum filtration, washed with water, and dried, affording 0.101 g (50%), mp 170–180 °C. The NMR spectrum was identical with that obtained in A.

C. Dithionite Reduction of 1 in the Presence of Potassium Carbonate. A mixture of 3 (366 mg, 1.02 mmol), sodium dithionite (1.80 g, 10.4 mmol), and potassium carbonate (360 mg, 2.62 mmol) in 20 mL of ethanol and 1 mL of water was heated at reflux with stirring for 16 h. After the ethanol was evaporated at reduced pressure, 50 mL of water was added to the yellow residue. The resulting precipitate was vacuum filtered, washed with water, and dried, giving 347 mg (94%) of a drab yellow solid whose NMR spectrum was identical with that of *trans*-2. Recrystallization from CH_2Cl_2–cyclohexane and then from ethanol yielded 210 mg (57%) of white needles, mp 199–201 °C. The melting point of a mixture of *cis*-2 and *trans*-2 was 175–195 °C.

Thermal Isomerization. A. Neat. An open NMR tube containing 18 mg of *cis*-2 was placed in a side arm test tube filled to a depth of 2 cm with silicone oil. The stoppered test tube was evacuated (1 torr) and then placed in a bath at 200 °C. The solid gave a yellow melt at 210 °C and some sublimate. After 35 min the bath temperature reached 220 °C, and most of the material had distilled and/or sublimed onto the cooler, upper portion of the tube. After the sample cooled and the vacuum was disconnected, $CDCl_3$ was added and the NMR spectrum recorded. This showed a mixture of *trans*-2 and *cis*-2; multiple integration of the 1,2-hydrogens revealed 83% conversion to *trans*-2.

TLC also indicated the predominance of *trans*-2 and did not detect 3. Repeptition of this treatment in a Teflon tube gave a *trans*-2/*cis*-2 mixture in a 3:1 ratio. Identical treatment of *trans*-2 did not give detectable amounts of *cis*-2.

B. In Solution. Argon gas was passed through Fieser's solution[10] and then through a mixture of 9.2 mg of *cis*-2 in 0.55 mL of sulfolane in an NMR tube for 20 min. After the sample tube was degassed, it was capped and placed in a bath at 170 ± 1 °C for 60 min. The NMR spectrum was then recorded with multiple integrations over $H_{1,2}$ showing a 50:50 mixture of *cis*-2 and *trans*-2 ($\Delta\delta_{H_{1,2}}$[*cis*-2–*trans*-2] = 5 Hz). Following addition of $CDCl_3$, integration indicated a 56:44 *cis*-2/*trans*-2 mixture ($\Delta\delta_{H_{1,2}}$[*cis*-2–*trans*-2] = 10 Hz). Repetition of the above trial without degassing gave similar results: 46:54 *cis*-2/*trans*-2 ratio.

Isomerizations in ethyl oxalate were conducted as above at comparable concentrations without deoxygenating. In two trials, after 180 and 200 min, respectively, the corresponding *cis*-2/*trans*-2 NMR integrals were in the ratio 59:41 and 48:52 ($\Delta\delta_{H_{1,2}}$[*cis*-2–*trans*-2] = 12 Hz).

An NMR tube containing *cis*-2 and Me_2SO-d_6 was placed in the probe of a Bruker 90 (90 MHz) spectrometer. The temperature was raised from ambient temperature to 150 °C during a period of 5 min, after which time the spectrum was that of *trans*-2.

Attempts to monitor the isomerization in ethylene carbonate and γ-butyrolactone were not reproducible and were abandoned.

Hydrogen–Deuterium Exchange. General Procedure. A mixture of 0.20 mL of CH_3OD, 0.20 mL of sulfolane, and 7.0–9.0 mg of *cis*-2 or *trans*-2 in a capped NMR tube was placed in a constant-temperature bath at 55 ± 0.1 or 70 ± 0.1 °C. With *cis*-2 a yellow color was seen in a few minutes, while with *trans*-2 no color change was perceptible. Solution of all or most of the substrate occurred in a few minutes. The tube was removed periodically and the NMR spectrum was recorded.

Acknowledgment. This work was supported, in part, by funds from the Sponsored Programs Grant Awards Program, the State University College at Buffalo. We thank Dr. Edward M. Schulman for helpful discussions and Dr. Yehiel Gaoni for the opportunity to work in his laboratory.

Registry No. *cis*-2, 73199-06-1; *trans*-2, 73199-07-2; 3, 38458-29-6.

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[10] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 393.