pionic anhydride for acetic anhydride in the reduction of 3,4-hexanedione and found that the reaction is equally facile, yielding 4-oxo-3-hexyl propanoate in 98% yield.

Summary

We have examined the reduction of α-diketones and α-keto esters in HI–acetic anhydride mixtures and found that the reaction gives good-to-excellent yields of α-acetoxy ketones and esters.

Experimental Section

All the starting α-diketones and α-keto esters were available from Aldrich Chemical Co., Milwaukee WI. Acetylated biacetyl (3-acetoxy-3-buten-2-one) used for GC comparison was obtained by the method of Ardecky et al.[14]

General Procedure for the Reduction of α-Diketones and α-Keto Esters. A 30-mL sample of acetic anhydride was chilled on ice, and then 8.2 g of 47% aqueous HI (30 mmol of HI) was added slowly to the magnetically stirred solution. **Caution**: The reaction of aqueous HI and acetic anhydride is very exothermic and can be deceptive as there is a variable induction period of several seconds to a couple of minutes. Therefore it is imperative that the addition be performed cautiously. After addition was complete, the reaction was allowed to stir an additional 5–10 min. During the course of the reaction the stabilizer (H_3PO_2, an oxidation inhibitor) usually added to HI precipitates, and the solid impurity is removed by filtration through a fine fritted-glass filter. The resultant solution, which can be colored anywhere from grey to orange–red depending on the source of the HI, is added to a 100-mL round-bottomed flask, and 10 mmol of the α-keto carbonyl compound added. In the case of α-diketones the reduction was performed at room temperature with stirring at room temperature for 15–20 min, while α-keto esters were reduced at elevated temperatures (at either 50–55 or 70–75 °C as indicated in Table I) for 30 min.

The product was isolated[15] by adding 10% aqueous sodium bisulfite, cautiously at first, to the reaction mixture until the orange color of iodine is completely dissipated.[16] The reaction mixture was then added to a 250-mL separatory funnel, and 100 mL of distilled water added. The aqueous layer was extracted three times with diethyl ether. The ether layers were combined and back extracted twice with 50-mL washes of distilled water, with a wash of 50 mL of 10% NaOH, and finally with an additional 50 mL of distilled water. The ether layer was dried over K_2CO_3 (except in example 9, where Na_2SO_4 was used instead) and then filtered. The ether was then removed in vacuo. In most cases no further refinement was necessary, but further purification could be accomplished by simple distillation in a Kugelrohr oven when desired with little loss in yield. With the exception of 4-acetoxy-3-hexanone and 4-oxo-3-hexyl propanoate (examples 3 and 10, respectively) all the products were known in the literature and were identified on the basis of their spectroscopic properties. The appropriate literature references appear in Table I. These literature references are not exhaustive as some of these compounds have many citations.

4-Acetoxy-3-hexanone. Following the general procedure, 3,4-hexanedione was converted to 4-acetoxy-3-hexanone in 88% yield: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.08 (t, 3 H), 1.68–1.92 (m, 2 H), 2.17 (s, 3 H), 2.35–2.62 (m, 2 H), 4.98 (dd, 1 H, J = 5, 8 Hz); 75-MHz ^{13}C NMR ($CDCl_3$) 7.3, 9.7, 20.8, 24.1, 32.2, 79.8, 171.4, 208.9; IR (CH_2Cl_2) 1730 m^{-1} (vs, br); MS (50 eV) m/e = 43, 57, 101, 115, 129, 158; exact mass calcd for $C_8H_{14}O_3$ 158.0943, found 158.0952.

4-Oxo-3-hexyl Propanoate. Following the general procedure, 3,4-hexanedione was converted to 4-oxo-3-hexyl propanoate in 98% yield: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.08 (t, 3 H), 1.20 (t, 3 H), 1.68–1.92 (m, 2 H), 2.30–2.65 (m, 4 H), 4.98 (dd, 1 H, J = 5, 8 Hz); 75-MHz ^{13}C NMR ($CDCl_3$) δ 7.3, 9.1, 9.7, 24.2, 27.5, 32.2, 79.6, 174.9, 209.1; IR (CH_2Cl_2) 1730 cm^{-1} (vs, br); Ms (50 eV) m/e = 57, 114, 115, 143, 172; exact mass calcd for $C_9H_{16}O_3$ 172.1100, found 172.1109.

Acetyl Acetoin. Acetyl acetoin used in GC analyses could be generated by the literature reference,[10a] but a more convenient method was to add an 85% aqueous solution of acetoin (3-hydroxy-2-butanone, obtained from Aldrich Chemical Co.) in several small portions to a mixture of 60 mL of acetic anhydride and 0.9 g of Amberlyst-15. The reaction predictably undergoes an exothermic reaction. Gradually, over the 1.5-h reaction period, the reaction turns orange–brown. The solution is filtered to remove the Amberlyst-15 resin and distilled at 12 mmHg to give 24.25 g of acetyl acetoin boiling between 62–65 °C (yield based on 85% acetoin: 69%).

Acknowledgment. We would like to thank Onzie Woods for his assistance in performing the GC analyses for biacetyl and its reduction products.

Registry No. MeC(=O)C(=O)Me, 431-03-8; PhC(=O)C(=O)Ph, 134-81-6; EtC(=O)C(=O)Et, 4437-51-8; PhC(=O)C(=O)Me, 579-07-7; PhC(=O)C(=O)OMe, 15206-55-0; MeC(=O)C(=O)OEt, 617-35-6; *i*-PrC(=O)C(=O)OEt, 20201-24-5; $\mathrm{\overline{C(CH_3)_2CH_2OC({=}O)C}({=}O)}$, 13031-04-4; EtCO$_2$C(=O)C(=O)CO$_2$Et, 59743-08-7; MeCH(OAc)C(=O)Me, 4906-24-5; PhCH(OAc)C(=O)Ph, 574-06-1; EtCH(OAc)C(=O)Et, 99768-38-4; PhCH(OAc)C(=O)Me, 19275-80-0; MeCH(OAc)C(=O)Ph, 19347-08-1; PhCH(OAc)C(=O)OMe, 947-94-4; MeCH(OAc)C(=O)OEt, 2985-28-6; *i*-PrCH(OAc)C(=O)OEt, 74108-96-6; (CH$_3$)$_2$C=C(OAc)CO$_2$Et, 85801-14-5; $\mathrm{\overline{C(CH_3)_2CH_2OCH(OAc)C}({=}O)}$, 123241-21-4; EtCO$_2$CH(OAc)C(=O)CO$_2$Et, 99173-90-7; EtCO$_2$CH(Et)C(=O)Et, 117090-85-4; HI, 10034-85-2; CH$_2$C(=O)CH(OH)CH$_3$, 513-86-0.

Structure and Reactivity in 9,10-Bridged Anthracenes

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Interest in [*n*]paracyclophanes (1) has continued unabated.[1] Synthetic success has been hard won, beginning with Allinger's prediction of the feasibility of [7]paracyclophane synthesis[2] and his much later accomplishment of that goal.[3] Since then, [6]paracyclophane targets[4] have fallen and [5]paracyclophane, initially invoked as a transient intermediate in the pyrolysis of the corresponding Dewar isomer, has been prepared and observed at low temperature.[5] Recently, [4]paracyclophane has been

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[14] Ardecky, R. J.; Dominguez, D.; Cara, M. P. *J. Org. Chem.* **1982**, *47*, 409.

[15] All the yields listed in Table I are for compounds that were isolated by the described procedure with the exception of the reduction of biacetyl described in example 1, which could not be readily isolated by this procedure and was determined by GC and verified by comparison of its GC–MS with genuine material.

[16] We verified that the reduction was not caused by bisulfite by examining a biacetyl reduction with and without the addition of bisulfite at the end of the reaction. There was no discernible difference between the two reactions.

(1) Rosenfeld, S. M.; Choe, K. A. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. 1, pp 311–357.

(2) Allinger, N. L.; Freibert, L. A.; Hermann, R. B.; Miller, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 1171.

(3) Allinger, N. L.; Walter, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 9267.

(4) (a) Kane, V. V.; Wolf, A. D.; Jones, M. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Yoshito, T.; Ueda, K.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1983**, 1645. (c) Liebe, J.; Wolff, C.; Kreiger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985**, *118*, 4144. (d) Yoshito, T.; Ueda, K.; Kakiuchi, K.; Odaira, Y. *Angew. Chem.* **1986**, *98*, 364.

(5) (a) van Straten, J. W.; Landheer, I. O.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 4499. (b) Weinges, K.; Klessing, K. *Chem. Ber.* **1976**, *109*, 793. (c) Jenneskens, L. W.; de Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; de Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716.

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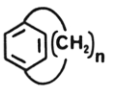
Table I. MMX Calculated Heats of Formation and Strain Energies for 3–8

compd	symmetry	ΔH_f, kcal/mol	strain energy, kcal/mol
3	C_2	68.36	44.87
4	C_2	56.46	39.98
4	C_s	59.14	42.21
5	C_2	50.37	39.40
6	C_2	44.18	39.57
6	C_s	43.08	38.28
7	C_2	40.13	41.06
8	–	34.92	34.04

shown to have a finite lifetime, and a similar scenario has begun to unfold.[6] Of course, much of the excitement surrounding these systems derives from the question of how severe distortion of benzene rings affects their aromaticity, and accordingly, [*n*]paracyclophanes continue to be an important vehicle for refining the concept of aromaticity.[7] Surprisingly, progress in the synthesis of benzologous systems has been remarkably slow. The smallest saturated aliphatic-bridge member of the [*n*]-(9,10)anthracenophane series has $n = 10$.[1,8] However, 3,6-diketo[8](9,10)anthracenophane (2) has been reported,[9] and its conformational behavior has been described.[10] Cyclophane 2 undergoes air oxidation in solution on a time scale of hours. Similarly, the dithia[8](9,10)-anthracenophane 3 undergoes easy air oxidation in solution and even (over several weeks) in the solid state.[11] The enhanced reactivity observed for both of these compounds is almost certainly a result of distortion of the central ring of the anthracene subunit, and yet, on the basis of the [*n*]paracyclophane experience, bending of that ring is expected to be slight at these bridge lengths.



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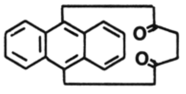


2

Our interest in the feasibility of isolating smaller [*n*]-(9,10)anthracenophanes and in their potential utility in the synthesis of [2.2.2.*n*]paddlanes via Diels–Alder methodology (despite earlier mixed results in this area[12]) has led us to examine this situation. We hoped, for example, to learn how the degree of distortion of the anthracene ring compares to that observed in [*n*]paracyclophanes and how this alters the ionization potential of these compounds. Our approach includes a combination of molecular mechanics evaluation of probable geometries and energies, MNDO calculation of ionization potentials, and measurement of charge-transfer transitions for the tetracyanoethylene (TCNE) π-complexes of a series of dithia-[*n*](9,10)anthracenophanes.

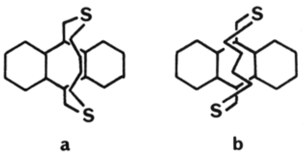


Figure 1. Stylized representation of the conformers of 3 with (a) C_s and (b) C_2 symmetry.

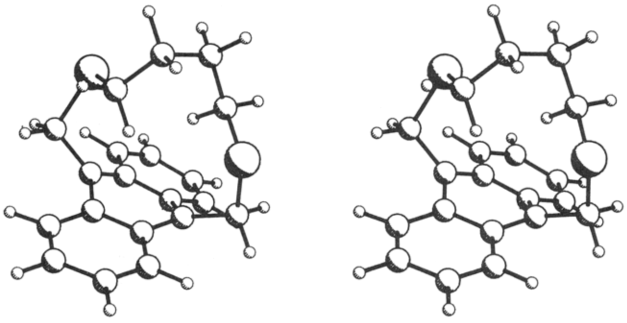


Figure 2. PLUTO plot of a stereopair showing the optimized C_2 geometry of 3.

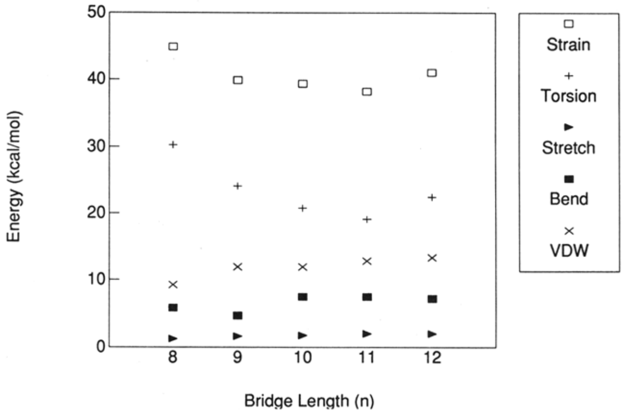


Figure 3. Strain energy and selected individual components of the molecular mechanics steric energy for the lowest energy conformers of 3–7.

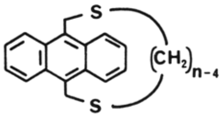
Table II. Bridge Bond Angles in 3–7

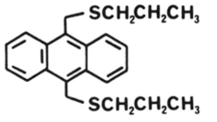
compd	av bridge carbon bond angle,[a] deg	largest single bridge carbon bond angle, deg	C–S–C bond angle, deg
3	112.7	117.7	99.1
4	112.0	113.8	100.1
5	113.8	115.6	102.8
6(C_s)	113.2	115.4	102.3
7	113.2	115.4	101.8
8	(111.4)		(100.4)

[a] Bridge carbon bond angles are the angles between bonds to carbon or sulfur for each methylene carbon in the bridge.

Results and Discussion

We have located conformational minima for dithiaanthracenophanes 3–7 and model compound 8 via molecular mechanics energy minimization procedures using the MMX force field.[13] For the even-bridged cyclophanes,





3 n = 8
4 n = 9
5 n = 10
6 n = 11
7 n = 12

8

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(6) (a) Kostermans, G. B. M.; Bobeldijk, M.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987**, *109*, 2471. (b) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1988**, *110*, 2157.

(7) Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo, D. A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 2902.

(8) Bender, V. D.; Unterberg, H.; Müllen, K. *Angew. Chem.* **1986**, *98*, 446.

(9) (a) Wynberg, H.; Helder, R. *Tetrahedron Lett.* **1971**, 4317. (b) Helder, R. Ph.D. Thesis, Rijksuniversiteit te Groningen, 1974.

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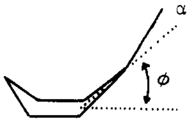
Table III. Structural Parameters for the Molecular Mechanics Geometries of 3–8



compd	β,[a] deg	ϕ, deg	α, deg
3	5.90	23.67	6.19
4(C_2)	2.25	12.22	–0.19
4(C_s)	0.50	17.42	1.14
5	0.48	12.80	0.03
6(C_s)	2.12	2.89	–1.06
6(C_2)	0.26	8.01	0.83
7	4.79	2.18	–0.35

[a] Angle β is defined in footnote 18.

we have located energy minima corresponding to geometries with approximate C_2 symmetry, and for the odd-bridged cyclophanes, both C_s and C_2 conformations were found (Figures 1 and 2). Calculated heats of formation and strain energies for these conformers are summarized in Table I. The strain energy and some of the individual components of the steric energy are plotted in Figure 3. Clearly, none of these compounds are highly strained; the most strained member of the series (**3**) has a strain energy only ca. 11 kcal/mol greater than that for model compound **8**. Bond stretching and bond angle distortion (Table II[14]) are not major contributors to the steric energy, which is determined largely by van der Waals interactions and torsional strain. Since torsional strain encompasses both aliphatic and aromatic bonds, this term grows steadily with decreasing n due to the onset of significant bending of the central ring of the anthracene subunit.

The molecular mechanics derived geometries of **3–7** are qualitatively similar to those described by Allinger et al.[15] for the [n]paracyclophanes using the MM1 force field and to those reported by Carballeira et al.[16] using a force field developed by Boyd. Allinger found a preference for the C_2 geometry in compounds with even values of n and in the n = 9 member of the series, with C_s geometry favored at n = 5 and 7. In compounds **3–7**, C_s geometry is favored at n = 11 only.

Of course, compounds **3–7** cannot necessarily be compared with the [n]paracyclophanes of corresponding bridge length since sulfur bond angles and longer C–S bonds presumably have a significant (though opposing[17]) effect on interactions within the bridge. A comparison of ring bending angle ϕ[18] (Table III) serves as a calibration for the two families of compounds. Surprisingly, the ring bending angles for the molecular mechanics calculated optimum geometries for **3–5** are *larger* than those determined by Allinger for the [n]paracyclophanes having the same value of n. In **3**, our value is about 11° higher than the value for the corresponding [n]paracyclophane while the values for **4**(C_2) and **5** are about 4° higher and roughly equal to each other as is also true for the [n]paracyclophanes. The associated strain energy, corrected for the strain in model compound **8**, is lower than Allinger's value for the corresponding [n]paracyclophane by about 5 kcal/mol, some of which is certainly due to the reduction in peri interactions when the center ring of **3** is bent. The rise in strain energy at n = 12 (compound **7**), due to increasing torsional strain in the bridge, is analogous to the effect observed by Allinger with onset at n = 10. Also, the puckering of the benzyl carbon in the direction opposite the ring bending (negative value for α) for the larger anthracenophanes has precedent in the [n]paracyclophane result. The nature of the aryl ring distortion in **3** and **4** (C_s conformation) is significantly different in that the four central carbons in **4** lie essentially in a single plane while **3** exhibits a twist[18] (represented by angle β in Table III) that may be induced by the torque inherent at the 9,10-positions in the C_2 conformations of the shortest bridged compounds.

Table IV. MNDO Ionization Potentials for 3–8

compd	ionizatn energy, eV	HOMO–LUMO gap, eV
3	8.06	6.75
4(C_2)	8.18	6.91
4(C_s)	8.14	6.85
5	8.08	6.91
6(C_s)	8.15	6.95
6(C_2)	–	–
7	8.20	6.96
8	8.18	6.96

Table V. CT Absorption Bands of Solutions of 3–5, 7, and 8 (0.006 M) and TCNE (0.04 M) in $CHCl_3/CH_2Cl_2$ (4:3)

compd	λ_{max}, nm	$h\nu_{CT}$, eV	calcd first ionizatn energy, eV
3	802	1.54	7.10
4	783	1.58	7.16
5	760	1.62	7.22
7	760	1.62	7.22
8	753	1.64	7.25

The preferred geometries for **3–8** were used to calculate ionization potentials by the MNDO method (assuming the validity of Koopmans' theorem) without further geometry optimization, and these are recorded in Table IV.[19] In the even-bridged cyclophanes, calculated ionization potentials drop from **7** to **6** to **5** to **3**. Compound **4** deviates

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(13) We used the MMX87 force field in the computer programs MMX and PCMODEL purchased from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076. MMX is a derivative of Allinger's MM2 with π VESCF subroutines. The PLUTO plot in Figure 2 was produced with the program PCDISPLAY, also available from Serena Software.

(14) No symmetry constraints were applied in the molecular mechanics calculations, and therefore, angles that would be symmetry equivalent in structures with perfect C_2 or C_s symmetry are not necessarily equal. In practice, the difference are generally small, and average angles have been recorded in Tables II and III. The greatest differences in symmetry-equivalent bridge-carbon bond angles are 0.4°, 0.1°, 0.04°, 2.5°, and 2.9° for **3**, **4**, **5**, **6**, and **7**, respectively. For ϕ, the complementary bending angles differ by 0.17°, 1.41°, 0.18°, 0.04°, and 1.55° in **3**, **4**(C_2), **5**, **6**(C_s), and **7**, respectively.

(15) These authors describe an additional C_2 conformer (for odd values of n) with the hydrogens of the central bridge methylene group pointing into the aromatic ring, but this geometry had significantly higher strain energy than the others. Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.

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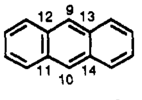
(17) Case, D. A. In *Conformational Analysis of Medium Size Heterocycles*; Glass, R. S., Ed.; VCH Publishers: Weinheim, 1988; pp 1–34.

(18) This angle, despite regular use in descriptions of paracyclophane ring bending, is not characterized clearly in the literature. Schaefer[6] has commented briefly on the fact that the four ring carbons that define the horizontal plane in Table III do not always lie in the same plane! In our own work, the deviation from planarity (β in Table III) is the angle defined by a normal to the plane occupied by center ring atoms C_{11}–C_{12}–C_{13} and a second normal to the C_{11}–C_{13}–C_{14} plane. (This type of distortion breaks C_s symmetry but not C_2). The angle between the average of these two normals and the normal to the C_9–C_{12}–C_{13} plane and the analogous angle using the C_{10}–C_{11}–C_{14} normal were averaged to give ϕ.



(19) Our MNDO calculations were performed by using MOPAC, version 4.00 (Quantum Chemistry Program Exchange). Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, *99*, 4899.

from this trend, and its HOMO–LUMO gap is also inconsistent with the series trend that is otherwise in qualitative agreement with the reported position of the longest wavelength UV transitions for these compounds.[11] Presumably, the structure for **4** is inaccurate.

Freshly mixed chloroform/methylene chloride solutions of TCNE and compounds **3–5**, **7**, and **8** exhibit broad, featureless charge-transfer (CT) absorption bands in the visible region of the spectrum (Table V) as well as an additional CT band that is not fully resolved from the absorption of the parent anthracene. The increase in λ_{max} from **8**, **7**, and **5** to **4** and **3** reflects increasing π-base strength of the donor, the result of increasing distortion of the anthracene ring.[20] For simpler (nonbridged) anthracenes, the energy of the CT transition has been shown by Kochi to correlate with standard oxidation potentials and first ionization energies (from a π-molecular orbital with maximum electron density at the 9,10-positions) of the donor anthracene.[21] Table IV lists ionization energies calculated from the CT transition energies by using Kochi's relations. The ionization energies are uniformly ca. 1 kcal/mol lower than the MNDO calculated values, but this is a result of the well-known tendency of MNDO to overestimate ionization potentials.[22] The trend within this limited data set suggests that **5** and **7** have anthracene rings that are equally bent and more so than model compound **8**, that **4** is more distorted than these, and that **3** is even more so.

Since the anthracene–TCNE π-complex is a true intermediate in the Diels–Alder reaction, a correlation between reaction rate and the donor properties of the anthracene would not be surprising, particularly in the case of an "early transition state" that resembles the complex.[23] However, any such correlation for compounds **3–5** and **7** will almost certainly be confounded by an increase in strain energy in the Diels–Alder adduct.[24] In this regard, the CT bands that we observed were quite persistent. For example, the longer wavelength CT band from a solution of TCNE and **4** retained 80% of its initial absorbance 48 h after mixing. For all of the anthracenophanes **3–5** and **7**, the decrease in absorbance for this CT transition was less than 6% from t = 0.5 min (first spectrum after mixing) to t = 5 min. However, solutions of **8** and TCNE in $CDCl_3$ (initial concentrations ca. 0.1 M) exhibit ^1H NMR spectra in which the peaks of **8** are nearly completely replaced on a time scale of 10 min with a spectrum that is entirely consistent with formation of the expected 9,10-Diels–Alder adduct.[25] Spectra of solutions of lower concentration consist of peaks assignable to **8** and this adduct only and afford an equilibrium constant of ca. 10^3 L mol^{-1}. Solutions of TCNE and **3–5** and **7** in $CDCl_3$ have somewhat more complicated spectra, consisting of starting compound peaks, peaks assignable to 9,10-adducts, and smaller peaks due to at least one (and probably more than one) additional reaction product. For all of these, the time scale for reaching equilibrium is days rather than minutes. Clearly, incorporation of a 9,10-bridge of any length has the effect of reducing the rate of the Diels–Alder addition of TCNE.

In summary, of the known dithia[*n*](9,10)-anthracenophanes, those with the shortest bridges have a significantly distorted anthracene ring. Molecular mechanics calculations and CT transition energies of the TCNE complexes of these compounds are generally in qualitative agreement in reflecting this situation. The distortion of the anthracene ring in these compounds is, surprisingly, greater than that of the benzene ring in [*n*]paracyclophanes of the same value of *n*, perhaps due to easier bending of the anthracene ring compared to benzene. Strain energy for **3**, the most reactive (toward O_2) known member of the series, though calculated to be ca. 5 kcal/mol less than that of the corresponding [*n*]-paracyclophane, is approximately equal to the resonance energy lost upon addition to the 9,10-positions of anthracenes. Finally, it is at this value of *n* (8) that strain energy rises significantly in the dithia[*n*](9,10)-anthracenophanes.

Experimental Section

General Procedures. NMR spectra ($CDCl_3$, TMS) were recorded on an IBM WP 100 SY spectrometer, and visible absorption spectra were recorded on a Varian DMS 100 spectrophotometer. Compounds **3–5** and **7** were prepared by previously reported procedures[11,12b] and were purified by preparative plate chromatography (Analtech silica plates/CH_2Cl_2).

9,10-Bis(2-thiapentyl)anthracene (8). This compound was prepared by the method used for **3–5**[11] except that high-dilution conditions were not required: 85% yield after recrystallization from benzene; mp 172.5–173.5 °C; ^1H NMR δ 1.05 (ppm) (t, 3 H), 1.8 (m, 2 H), 2.7 (t, 2 H), 4.75 (s, 2 H), 7.6 (m, 2 H), 8.2 (m, 2 H); high-resolution MS[26] calcd for $C_{22}H_{26}S_2$ 354.1476, obsd 354.1475 (M^+).

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Registry No. **3**, 84050-71-5; **3**·TCNE, 124443-18-1; **4**, 84050-70-4; **4**·TCNE, 124443-19-2; **5**, 84050-69-1; **5**·TCNE, 124443-20-5; **6**, 124443-17-0; **7**, 65121-51-9; **7**·TCNE, 124443-21-6; **8**, 124461-04-7; **8**·TCNE, 124443-22-7; **8** TCNE adduct, 124633-36-9; TCNE, 670-54-2.

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(24) In this regard, it is of interest that the retro-Diels–Alder reaction of ethyl acrylate adducts of **7** and one larger homologue is not significantly faster than that of an appropriate nonbridged model compound. Chung, Y.; Duerr, B. F.; McKelvey, T. A.; Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.* **1989**, *54*, 1018.

(25) NMR: δ 1.15 (ppm) (t, 3 H), 1.9 (m, 2 H), 2.95 (t, 2 H), 3.95 (s, 2 H), 7.6 (m, 2 H), 8.0 (m, 2 H).

(26) The high-resolution mass spectrum was supplied by the MIT Mass Spectrometry Facility, supported by NIH Research Grant No. RR00317.

Stereochemical Assignments via Cyclic Derivatives: A Cautionary Note

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As part of a project on catalyzed hydroborations of allylic amine derivatives,[1] we needed to determine the stereo-

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