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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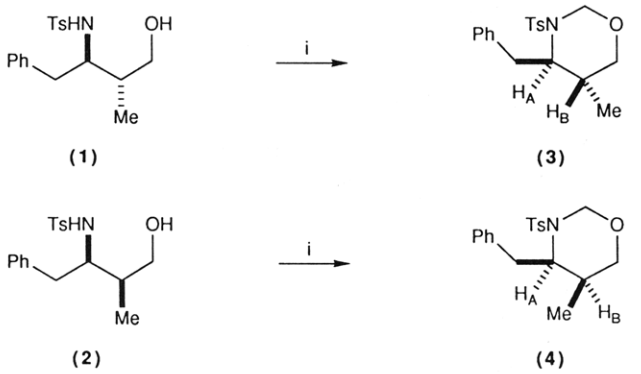
Scheme I[a]



[a] (i) 3NaH, cat. Bu_4NI, THF, 20 °C; $3CH_2BrCl$; then 60 °C, 4 h.

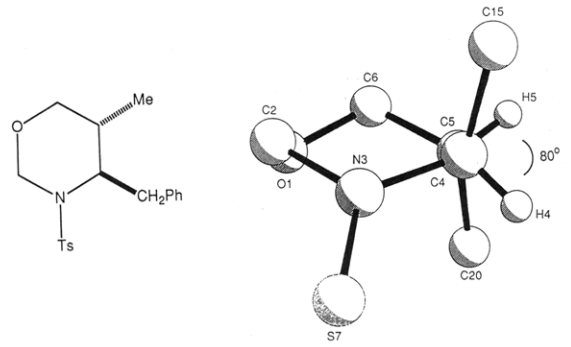


Figure 1. Pictorial and abbreviated PLUTO representations of *anti*-tetrahydro-1,3-oxazine **3**.

chemistry of some 1,3-amino alcohols, including compounds **1** and **2**. Our initial attempts to do this focused on coupling constant analyses of the tetrahydro-1,3-oxazines **3** and **4**, prepared as shown in Scheme I. This paper illustrates that such stereochemical assignments based on ^1H NMR coupling constants can be misleading.

The coupling constants J_{AB} for heterocycles **3** and **4** are <0.5 and 4.6 Hz. Intuitively, one might predict that the larger coupling constant corresponds to the anti compound **3**, where an unusually small trans diaxial coupling could be attributed to a distorted chair geometry. However, single-crystal X-ray diffraction studies[2] of compounds **3** and **4** prove that this is not so; it is the syn compound **4** that displays the larger J_{AB} coupling.

Comparison of the solid-state structures of compounds **3** and **4** reveals the cause of this unexpected observation. Abbreviated PLUTO diagrams are shown in Figures 1 and 2, and the supporting Table I gives important bond parameters for these materials. Both structures are based upon chair cyclohexane conformations with axial benzyl substituents and "pseudoaxial" *N*-tosyl groups; steric interactions between the benzyl and tosyl fragments are thereby minimized. The methyl substituent of the anti derivative **3** adopts an axial position; hence, the torsional angle between hydrogen atoms A and B is 80°. For the syn derivative **4**, the corresponding methyl substituent resides in an equatorial position such that the hydrogen atoms A and B of this substance rest at a torsional angle of 50°.

The Karplus relationship predicts that dihedral angles of 50° and 80° correspond to coupling constants of approximately 3.2 and 0.0 Hz, respectively. These values are close to those observed (4.6 and <0.5 Hz), providing evidence that the solid-state structure of these materials is a reliable representation of their solution conformations. Furthermore, difference NOE studies show that there is a 3% enhancement between H_A and H_B for the anti compound **3** and a 6% enhancement between the corresponding hydrogens of the syn isomer **4**, observations which are also consistent with the similar solution and solid-state structures for each of these compounds. Coupling constants between H_A and H_B are almost identical when the sample is prepared in $CDCl_3$ and in C_6D_6; if π-stacking were significant in determining the solid-state structure of these cyclic derivatives, the solvent would be expected to have a greater effect.

Findings described in this note indicate that stereochemical assignments based on coupling constant analyses of tetrahydro-1,3-oxazines must be treated with caution.[3]

Table I. Selected Bond Distances and Angles for 3 and 4

	3	4
	Distances (Å)	
S7–N3	1.615 (3)	1.643 (5)
C2–O1	1.406 (5)	1.412 (7)
C6–O1	1.438 (6)	1.429 (9)
C2–N3	1.454 (5)	1.445 (9)
C4–N3	1.476 (4)	1.490 (8)
C4–C15	1.532 (5)	1.550 (7)
C5–C20	1.521 (6)	1.50 (1)
C5–C6	1.514 (7)	1.51 (1)
	Angles (deg)	
C2–O1–C6	108.6 (3)	109.6 (5)
C2–N3–C4	116.3 (3)	113.1 (4)
C2–N3–S7	120.2 (3)	117.6 (5)
C4–N3–S7	123.5 (2)	116.3 (4)
O1–C2–N3	111.4 (4)	114.1 (5)
N3–C4–C5	108.7 (3)	109.0 (5)
N3–C4C15	108.3 (5)	110.1 (5)
C5–C4–C15	115.9 (3)	113.4 (5)
C20–C5–C6	111.4 (4)	111.5 (6)
C20–C5–C4	111.4 (3)	114.5 (6)
C6–C5–C4	110.7 (4)	110.7 (5)
O1–C6–C5	111.5 (4)	112.0 (5)

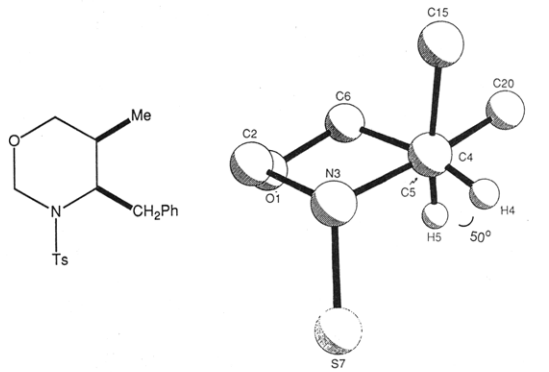


Figure 2. Pictorial and abbreviated PLUTO representations of *syn*-tetrahydro-1,3-oxazine **4**.

Experimental Section

Preparation of *anti*-Tetrahydro-1,3-oxazine 3. Tosyl amide **1** (70 mg, 0.2 mmol) was dissolved in 5 mL of dry THF. Sodium hydride (50% dispersion in oil, 30 mg, 0.6 mmol) was added, followed by ~10 mg of NBu_4I. The mixture was stirred for a few

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(2) For **3**: orthorhombic space group $P2_12_12_1$ (No. 19); refinement converged with $R = 0.038$; $R_w = 0.049$. For **4**: monoclinic space group $P2_1$ (No. 4); refinement converged with $R = 0.046$, $R_w = 0.056$.

(3) Coupling constants were used for stereochemical assignments of similar systems in a recent paper (although their stereochemical assignments were supported by an X-ray crystal structure determination): Barluenga, J.; Joglar, J.; Gonzalez, F. L.; Fustero, S. *Tetrahedron Lett.* **1989**, *30*, 2001. The heterocycles considered therein contained a more pyramidal nitrogen; syn and anti isomers did exhibit very different coupling constants.

minutes, then bromochloromethane (30 μL, 0.4 mmol) was added, and the mixture was heated to 60 °C for 4 h with stirring. On cooling, the suspension was diluted with 50 mL of Et_2O, washed twice with water, and dried over $MgSO_4$. Evaporation of the solvent and flash chromatography (15–20% ethyl acetate/hexane eluant) gave 42 mg (61%) of **3**, a white crystalline solid (R_f = 0.3 in 15% ethyl acetate/hexane eluant), which was recrystallized from CH_2Cl_2: mp 108–109 °C. ^1H NMR (300 MHz) in C_6D_6: δ 0.67 (d, 7.0 Hz, 3 H), 1.22 (m, 1 H), 1.88 (s, 3 H), 2.78 (dd, 13.5 and 9.6 Hz, 1 H), 2.96 (dd, 13.5 and 5.3 Hz, 1 H), 3.13 (dd, 11.5 and 2.5 Hz, 1 H), 3.45 (dd, 11.5 and 2.9 Hz, 1 H), 4.05 (m, 1 H), 4.39 (d, 11.1 Hz, 1 H), 5.48 (d, 11.1 Hz, 1 H), 6.75 (m, 2 H), 7.07 (m, 5 H), 7.71 (m, 2 H). ^{13}C NMR (75.42 Hz) in $CDCl_3$: δ 17.2 (CH_3), 21.3 (CH_3), 29.1 (CH), 37.7 (CH_2), 58.8 (CH), 67.9 (CH_2), 72.9 (CH_2), 126.4 (CH), 126.9 (CH), 128.4 (CH), 129.2 (CH), 129.3 (CH), 137.6 (C), 143.0 (C). Mass spectrum: calcd for $C_{26}H_{31}NO_3S$ 345.13985, found 345.14039.

Preparation of *syn*-Tetrahydro-1,3-oxazines 4. Tosyl amide **2** gave 41 mg (59%) of **4**, a colorless solid (R_f = 0.3 in 15% ethyl acetate/hexane eluant) when subjected to the sequence described above: mp 136–139 °C. ^1H NMR (300 MHz) in C_6D_6: δ 0.26 (d, 7.1 Hz, 3 H), 1.90 (s, 3 H), 2.03 (m, 1 H), 2.52 (m, 2 H), 3.08 (t, 11.6 Hz, 1 H), 3.38 (dd, 11.6 and 4.5 Hz, 1 H), 4.31 (m, 1 H), 4.4 (d, 11.8 Hz, 1 H), 5.59 (d, 11.8 Hz, 1 H), 6.72 (m, 2 H), 7.06–7.21 (m, 5 H), 7.62 (m, 2 H). ^{13}C NMR (75.42 Hz) in $CDCl_3$: δ 13.69 (CH_3), 21.26 (CH_3), 30.67 (CH_2), 31.70 (CH), 57.53 (CH), 68.39 (CH_2), 71.98 (CH_2), 126.08 (CH), 126.94 (CH), 128.1 (CH), 128.9 (CH), 129.10 (CH), 137.59 (C), 142.81 (C). $[\alpha]_D$ 68.5°, c = 0.0044 in $CHCl_3$. Mass spectrum: calcd for $C_{26}H_{31}NO_3S$ 345.13985, found 345.14039.

X-ray Diffraction Analyses. Crystals of **3** and **4** were mounted on glass fibers and fixed with epoxy cement. Data were collected on a Rigaku AFC5S single-crystal, automated diffractometer using Mo Kα radiation. Unit cell parameters based on 23 reflections for **3** and 21 reflections for **4** were obtained and after data reduction indicated the monoclinic and orthorhombic cells given in Table I, respectively. Symmetries expected for the monoclinic and orthorhombic cells were confirmed via intensity measurements of Laue symmetry equivalent reflections. Intensity statistics on the collected data indicated both cells to be eccentric as expected, given the known chiral nature of the starting materials. Structure determination for **3** and **4** followed the same procedures. Structure solution was accomplished by using SHELX86[4] followed by full-matrix least-squares refinements using TEXSAN (2.0).[5] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were included in calculated positions but not refined (the placement of the hydrogen atoms on the methyl groups was based originally upon reasonable hydrogen locations found in the Fourier difference maps and subsequently idealized). For **4**, equivalent reflections were measured and were averaged in the final least-squares cycles. Data were corrected for LP and included terms for anomalous dispersion. No corrections were necessary for decay nor absorption [μ = 1.86 cm^{-1} (Mo Kα) for both determinations].

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Registry No. **1**, 124443-33-0; **2**, 124443-34-1; **3**, 124443-35-2; **4**, 124443-36-3.

Supplementary Material Available: ORTEP diagrams and tables of positional parameters and B(eq), crystallographic data collection and refinement parameters, and anisotropic thermal parameters for compounds **3** and **4** (14 pages). Ordering information is given on any current masthead page.

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Bridging of the [2.2]Paracyclophane Nucleus by a Phenanthrene Unit[1]

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Polycyclic hydrocarbons consisting of aromatic subunits held in a rigid perpendicular arrangement are of interest not only for stereochemical and structural reasons but also as model compounds for the investigation of electronic interactions between orthogonal π-systems. Recently several "orthogonal cyclophanes" have been described that are formally composed out of biphenyl units whose benzene parts are held in strict orthogonality by molecular bridges.[2-5] For the synthesis of these novel aromatic systems, the intermediate generation and trapping of various [2.2]paracyclophynes[3,4,6] as well as the electrocyclic ring closure of 1,2,9,10-tetravinyl[2.2]paracyclophanedienes[5,7] have been particularly valuable.

We now introduce a new method for aromatic bridging of an already existing [2.2]paracyclophane unit that makes use of the throughly studied stilbene–phenanthrene photocyclization[8] and creates a novel bridge consisting of a condensed aromatic system.

Results and Discussion

Starting from 4,13-diformyl[2.2]paracyclophane (**3**), which is readily available in gram quantities by our paracyclophane synthesis from 1,2,4,5-hexatetraene (**1**) and propiolic aldehyde (**2**),[9,10] a double Grignard reaction with phenylmagnesium bromide in tetrahydrofuran is carried out first (Scheme I). The resulting diol **4**, formed in 95% yield, is stereochemically homogeneous as judged from its chromatographic behavior and spectroscopic data. Since the infrared spectrum of **4** is dominated by a very strong band at 3300 cm^{-1} and the OH groups appear as a broad peak at δ = 4.4 in the ^1H NMR spectrum we assume that strong intramolecular hydrogen bonding occurs and the diastereomer obtained has the structure shown in Scheme I. This would imply the (reasonable) assumption that the Grignard reagent has attacked **3** from the "outside" exclusively. Oxidation with pyridinium chlorochromate (PCC) in refluxing methylene chloride converts **4** into the diketone **5**, again in near quantitative yield (96%). Although the conformation of **5** was not explicitly determined, we believe that its carbonyl groups—rather than the phenyl substituents—point toward the ethano bridge. For a number of alkyl ketones this arrangement has been

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