surements can be made under conditions where no significant amount of *cis*-diazene is decomposing (i.e., at temperatures below those for decomposition) and hence are more reliable than the $A_{trans(t=0)}$ value required in eq 4. Values of $\epsilon_{trans}/\epsilon_{cis}$ using eq 6 were determined prior to each kinetic run (three per diazene-solvent mixture) and the results are outlined in Table II for diazenes 1 and 4.

Values of $k(\mathrm{I})/k(\mathrm{O})$ were calculated from eq 5, using the individual average values of $\epsilon_{trans}/\epsilon_{cis}$ for each solvent and diazene, and also using the overall average value of $\epsilon_{trans}/\epsilon_{cis}$ from all solvents for each of the diazenes. In addition, the ratios $k(\mathrm{I})/k(\mathrm{O})$ were calculated, using eq 4. Although the values of $k(\mathrm{I})/k(\mathrm{O})$ varied with the choice of method for both 1 and 4, the apparent increase in $k(\mathrm{I})$ with increasing viscosity for 1 and the decrease in $k(\mathrm{I})$ for 4 was consistently observed independent of the calculation procedure.

Because there was no clearcut trend in variation of $\epsilon_{trans}/\epsilon_{cis}$ as a function of solvent, the data resulting from the use of the overall average value of this ratio for each of the diazenes were used to obtain the values of $k(\mathrm{I})$ reported in Table I for 1 and 4. Values of $k(\mathrm{N})$ were determined by subtracting values of $k(\mathrm{I})$ from values of $k(\mathrm{O})$.

Supplementary Material Available: Full experimental details of the compounds described in this study (4 pages). Ordering information is given on any current masthead page.

New Records for Sterically Congested Stilbenes: (*E*)- and (*Z*)-1-(2,2-Dimethyl-1-tetralinylidene)-2,2-dimethyltetralin[†]

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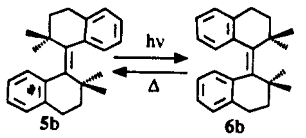
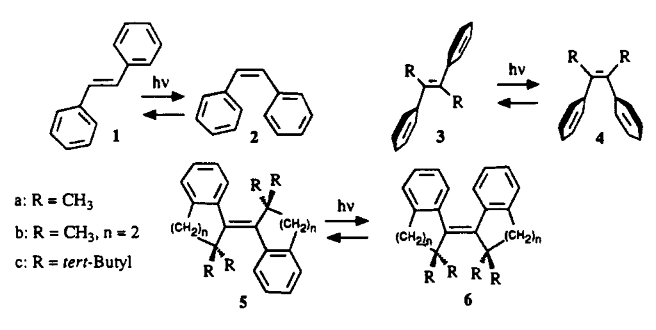
The synthesis and characterization of the isomeric, highly distorted stilbenes **5b** and **6b**, are reported. X-ray analysis showed **5b** to be twisted 36.7° at the central double bond. Isomer **6b** was unstable at room temperature, isomerizing back to **5b** with $E_a = 21 \pm 1.8$ kcal/mol. MMP2 calculations, supported by direct observations, suggested **6b** was an unsymmetrical structure twisted 73° about the central double bond.



Distortion of normally planar carbon-carbon double bonds has frequently produced strained materials with significantly altered chemical and physical properties.[1] Sterically demanding groups can introduce such structural modifications.[2] Because potential reaction channels are blocked, steric congestion frequently reduces kinetic reactivity while increasing strain energy. The important places held by (*E*)- (1) and (*Z*)-stilbene (2) in the development of photochemistry and in the evolution of many new chemical techniques make them particularly attractive for structural elaboration.[3] *E* to *Z* isomerization is particularly useful for photochemical introduction of further strain. This approach has been successful with stilbenes substituted on the carbon-carbon double bond such as (*E*)- (**3c**) and (*Z*)-di-*tert*-butylstilbene (**4c**).[3,4] The resulting steric congestion in **3c** and **4c** created novel, twisted π systems. The *Z* to *E* isomerization barrier was reduced from 42.8 (stilbene) to 32.0 kcal/mol by the *tert*-butyl substitution, the lowest recorded barrier for any symmetrically substituted stilbene.[3-5] In the cases of **3c** and **4c**, the molecule responded to the steric congestion introduced by the *tert*-butyl groups by rotation of the phenyl groups. This led to complete loss of conjugation of the phenyl rings from the central double bond. The central double bond, however, remained planar.[6] If the phenyl rings had been



[†] This paper, which was made possible by the combination of experiment and force field calculations, is dedicated to Paul von Ragué Schleyer on the occasion of his 60th birthday.

(1) (a) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *254*, 312. (b) Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Academic: New York, 1978.

(2) Sandstroem, J. *Top. Stereochem.* **1983**, *14*, 83.

(3) Saltiel, J.; Charlton, J. L. *Rearrangements in the Ground and Excited State*; DeMayo, P., Ed.; Academic: New York, 1980; p 25.

(4) (a) Lenoir, D.; Gano, J. E.; McTague, J. A. *Tetrahedron Lett.* **1986**, *27*, 5339. (b) Gano, J. E.; Park, B.-S.; Subramaniam, G.; Lenoir, D.; Gleiter, R. *J. Am. Chem. Soc.*, submitted.

(5) A push-pull substitution pattern on alkenes dramatically lowers the *Z* → *E* isomerization barrier. In contrast to 1-6, however, the barrier in push-pull substituted systems is lowered by reducing the π bond strength electronically rather than increasing the energy in the reactant.

0022-3263/90/1955-2688$02.50/0

Table I. Comparison of Measured and Calculated ^{1}H NMR Data for 5b, 6b, 6b′, and 6b″[b]

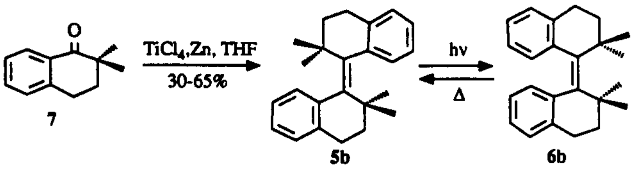
compd	source	methylene region				
5b	measd	2.80 1 H, $H4_{exo}$ m	2.80 1 H, $H4_{endo}$ m	1.73 1 H, $H3_{exo}$ $J = 7.5, 10.2, 13.5$	1.53 1 H, $H3_{endo}$ $J = 6.5, 3.5, 13.5$	
5b	calcd from X-ray struc[a]	$J = 7.90, 0.44$	$J = 8.05, 11.48$	$J = 7.90, 11.48$	$J = 8.05, 0.44$	
5b	calcd from MMP2 struc[a]	$J = 6.84, 1.04$	$J = 6.18, 12.66$	$J = 6.84, 12.66$	$J = 6.18, 1.04$	
6b	measd	2.58 1 H, $H4_{exo}$ $J = 4.5, 7.5, 15$	2.76 1 H, $H4_{endo}$ $J = 5.5, 8.5, 15$	1.95 1 H, $H3_{exo}$ $J = 4.5, 7.0, 12.5$	1.43 1 H, $H3_{endo}$ $J = 4.5, 8.5, 13$	
6b	calcd from MMP2 struc[a]	$J = 3.78, 14.69$	$J = 4.33, 2.67$	$J = 3.78, 2.67$	$J = 4.33, 14.69$	(front half)
		$J = 5.43, 1.63$	$J = 5.33, 13.89$	$J = 5.43, 13.89$	$J = 5.33, 1.63$	(back half)
		$J = 4.61, 8.16$	$J = 4.83, 8.28$	$J = 4.61, 8.28$	$J = 4.38, 8.16$	(exchanging)
6b′	calcd from MMP2 struc[a]	$J = 3.36, 14.82$	$J = 3.93, 3.04$	$J = 3.36, 3.04$	$J = 3.93, 14.82$	
6b″	calcd from MMP2 struc[a]	$J = 5.01, 13.38$	$J = 5.75, 1.71$	$J = 5.01, 1.71$	$J = 5.75, 13.38$	

[a] Cis J value given before trans. [b] See Table II for structures of **6b′** and **6b″**.

attached to the double bond, as in **5** and **6**, they could not have rotated away from nearby bulky substituents without simultaneously twisting the double bond. If such a connecting ring is small, $n = 1$ in **5** and **6**, bulky substituents, R, are drawn away from one another and steric distortion will be less significant. This is not the case where $n \geq 2$. Consequently, the synthesis of (*E*)-1-(2,2-dimethyl-1-tetralinylidene)-2,2-dimethyltetralin (**5b**) and (*Z*)-1-(2,2-dimethyl-1-tetralinylidene)-2,2-dimethyltetralin[7] (**6b**), where $n = 2$, was investigated. The final objectives were to determine what unique properties might be introduced by severe steric distortion and to provide challenging models by which current theoretical models could be tested.

Results

The coupling of sterically congested ketones in the presence of low-valent titanium reagents has proven useful in the synthesis of a wide variety of sterically congested ketones.[8] Clearly, **5b** and **6b** are approaching the limit of the capability of even this versatile reagent. Nonetheless, it proved possible to couple 2,2-dimethyl-1-tetralone (**7**) to form **5b** in 30–65% yield as a white crystalline solid.[9] Selected ^{1}H NMR (400 MHz) data for **5b** are presented in Table I. None of the isomeric **6b** (vide infra) was detected in the product mixture.



Photoisomerization of **5b** to **6b** was unsuccessful when **5b** was exhaustively irradiated in the presence or absence of triplet sensitizers (vide infra) and in the solid at 15 K. No fluorescence was observed in solution, but strong, probably excimer, fluorescence was observed in the visible region from **5b** in the crystalline solid. The absence of photoisomerization was explained when the photochemistry of **5b** was monitored by ^{1}H NMR at low temperatures. Irradiation at −70 to 0 °C immediately produced a product, **6b** (vide infra), which completely and repeatedly isomerized back to **5b** upon warming. Selected ^{1}H NMR data for **6b** are compared with those of **5b** in Table I.

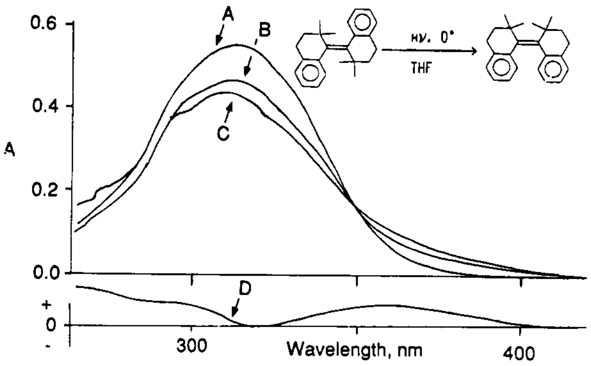


Figure 1. Absorption spectra during the irradiation of **5b** at 0 °C in THF with 254-nm light: A, 0 s; B, 120 s; C, 600 s; D, difference for C − A adjusted so no points were negative.

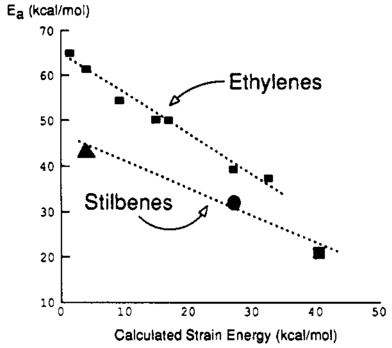


Figure 2. Measured activation energies, E_a, plotted against calculated strain energies of the *Z* isomers. Values for ethylenes cited in ref 25. Values for stilbenes cited in paper. (■) = **6b**; (●) = **4c**; (▲) = **2**.

A portion of the UV absorption spectrum of **6b** was obtained by monitoring the absorption spectrum during the 254-nm irradiation of a THF solution of **5b** at 0 °C. The changes observed during the irradiation and a difference spectrum are given in Figure 1.

Attempts to detect a low concentration of the new photoproduct, **6b**, in thermal equilibrium with **5b** at room temperature failed. Careful inspection of the ^{1}H NMR spectrum determined <0.15% of **6b** could be present. Thus ΔG_{298} for **5b** → **6b** must be ≥4 kcal/mol which was consistent with the calculated energy difference, 7.14 kcal/mol, described below. Monitoring the rate of reaction

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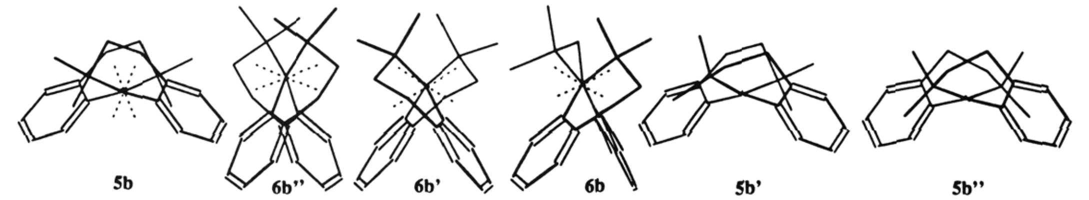
(6) Gano, J.; Park, B.-S.; Pinkerton, A. A.; Lenoir, D. *Acta Crystallogr., Sect. C*, submitted.

(7) These are more exactly named (*E*)-1-(3,4-dihydro-2,2-dimethyl-1-(2*H*)-naphthalenylidene)-1,2,3,4-tetrahydro-2,2-dimethylnaphthalene and (*Z*)-1-(3,4-dihydro-2,2-dimethyl-1(2*H*)-naphthalenylidene)-1,2,3,4-tetrahydro-2,2-dimethylnaphthalene, respectively.

(8) (a) Lenoir, D. *Synthesis*, in press. (b) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. (c) Lai, Y.-H. *Org. Prep. Proced. Int.* **1980**, *12*, 361. (d) Bottino, F. A.; Finocchiaro, P.; Libertini, E.; Reale, A.; Recca, A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 77. The term cofacial is taken to mean two flat planes sitting face-to-face of one another but not in a necessarily coplanar manner.

(9) Lemmen, P.; Lenoir, D. *Chem. Ber.* **1984**, *117*, 2300.

Table II. Calculated (MMP2 (1987)) Geometries Viewed along the C=C Bond and Heats of Formation (ΔH_f) for Lowest Energy Conformers of 5b and 6b



	5b	6b''	6b'	6b	5b'	5b''
[a]Twist of Central Bond, °	40.2	49.4	75.4	73.1	---	---
PhC=CPh Dihedral Ang.,°	148.8	-36.3	56.3	-52.53	146.3	-155.5
[b]Twist of First Phenyl, °	-43.2	-32.8	17.2	-4.67	-46.0	55.6
[b]Twist of Second Phenyl, °	-43.1	-32.8	17.2	-26.4	-47.7	55.6
ΔH_f (Calc), kcal/mole	30.94	34.02	36.01	38.08	32.90	33.4

[a] Calculated angle between p orbitals. [b] Dihedral angle between the phenyl and central double bond.

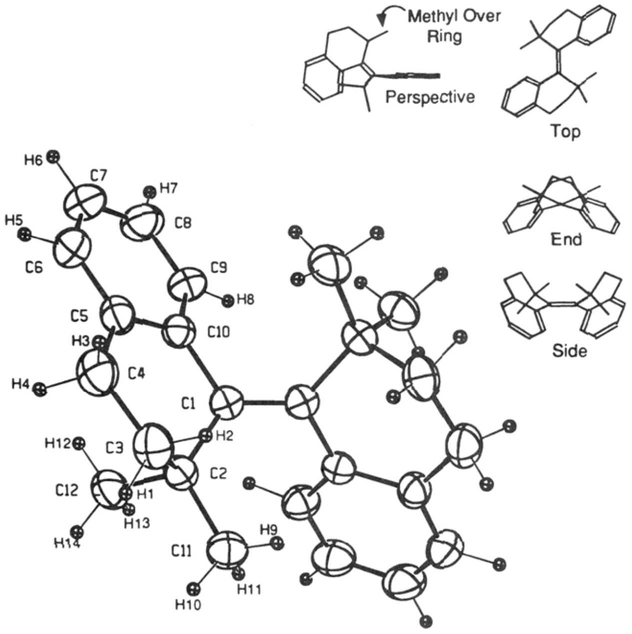


Figure 3. Structure of **5b** as determined by X-ray diffraction crystallography viewed along its twofold axis.

of **6b** to form **5b** at 4.6–19.0 °C revealed, $E_a = 21 \pm 1.8$ kcal/mol, with $A = 10^{13}$ as preexponential factor. The resulting activation energy is compared with that of other stilbenes and alkenes in Figure 2.

To determine the structures of **5b** and **6b** in solution and the structure of **5b** in the crystalline solid, X-ray diffraction crystallography and force field calculations were performed. Crystals of **5b** suitable for X-ray analysis were prepared by vacuum sublimation. The final geometry is presented in Figure 3, and important structural features are presented in Table II.

Prediction of the structures of **5b** and **6b** utilizing force field calculations proved difficult but necessary since theoretical methods were the only alternative in the study of **6b** (vide infra). As a test of the reliability of the force field method, the structure of **5b**, for which the X-ray structure had been established, was sought. In addition, this would allow comparison of the preferred conformation of **5b** in solution and the solid state. The force field program MMX was used for the initial survey.[10-12] Much to our surprise, it was impossible to unambiguously locate the proper structure for **5b** when simple trial geometries were employed in this procedure.[11] Clearly, the combination of many conformational possibilities, inherent in the "cyclohexene" system, and a highly twisted, congested molecule created a large likelihood of obtaining calculated structures that were not in the lowest energy minima.[11] Consequently, a rational search to find **5b** and **6b** was performed. The input geometries for the calculations numbered 108 different coordinates. This search revealed 15 conformers with unique geometries. Since some of the conformer energies *were very similar*, it is noteworthy to emphasize the importance of comparing the energies *and the geometries* in such studies. Five unique E geometries were obtained from 45 of the 108 calculations. The relative MMX heats of formation[12] and number of times each of the lowest energy E conformers was encountered were 0 (20 times), 1.2 (1 time), 2.3 (4 times), 4.5 (10 times), and 14.0 (10 times) kcal/mol. The geometries of the most stable E conformers were refined with the more generally available program MMP2(1987) to provide the heats of formation, structures, and geometries shown in Table II. The views presented in Table II are along the C=C bond since all other views proved useless for comparison of the structures.

Ten unique Z conformers came from the remaining 63 calculations. The relative MMX heats of formation and number of occurrences of the five lowest energy Z conformers were 0 (14 times), 0.4 (4 times), 2.9 (17 times), 3.1 (2 times), and 3.2 (2 times) kcal/mol. The three most stable conformers, **6b''**,**6b'**, and **6b**, were further refined with MMP2(1987). The geometries and energies are given in Table II.

Discussion

Many of the properties of **5b** in solution gave distinctive indications of its detailed structure. A preliminary description of some spectra has appeared.[9] The red-shifted, lowest energy band in the UV spectrum at $\lambda^{\mathrm{THF}} = 314$nm (vs $\lambda^{\mathrm{EtOH}} = 294$ nm in (E)-stilbene)[13] suggested the π

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[10] Serena Software, Box 3076, Bloomington, IN 47402.

[11] The erroneous assignment showed the difficulty in making structural assignments for such conformationally mobile systems as **5b**. Although reasonable logic, based on similarity of structures, was employed in the earlier work, a global search was not performed because creation of the plethora of intricate input structures was impossible at that time. Programs like PCMODEL make this a reasonable but still a time-consuming task at present.

[12] Since even different versions of the MMX program gave different heats of formation, only the relative values have any significance.

system in **5b** had a twisted central double bond. A distinct singlet at δ 0.64 in the ^{1}H NMR spectrum indicated two methyl groups were located over deshielding regions of the aromatic rings. The presence of two separate methyl resonances, however, revealed a separation of the four methyl resonances into two kinds on the NMR time scale. The well-resolved vicinal coupling constants in the 400-MHz ^{1}H NMR spectrum (Table I) appeared to be useful for confirmation of structural details in solution.

The X-ray crystal structure of **5b** (Figure 3) proved interesting. It was clearly not the conformer reported for **5b** on the basis of MMP2 calculations in ref 9 and shown as **5b″** in Table II.[11] Instead it corresponded to the conformer predicted to be most stable by MMP2, **5b**. The correspondence between the calculated and experimental (X-ray) structure was very good. The p orbitals in the central double bond were twisted 36.7° (40.2° via MMP2). The atoms in the central double bond were almost planar. Since pyramidalization occurred for some structures, generally, the twist angles reported are the dotted lines in Table II.[14,15] The central double bond was elongated to 1.364 Å (1.362 Å via MMP2), which can be compared to 1.318 Å for (*E*)-stilbene.[16] The bond connecting the *gem*-dimethyl group to the double bond is elongated to 1.542 Å (1.535 Å via MMP2) compared to 1.515 Å in dimethylstilbene.[17] The bond connecting the aromatic ring to the C=C bond was elongated to 1.482 Å (1.478 Å via MMP2) compared to 1.466 Å in (*E*)-stilbene.[17] The attempt by the *gem*-dimethyl group to avoid the rest of the molecule is readily seen by the closing of the $C_1C_2C_3$ angle to 102.3° (103.6° via MMP2) and the opening of the adjacent $C_2C_3C_4$ angle to 115.3° (114.3° via MMP2).

The two halves of the molecule were related by a crystallographic twofold axis perpendicular to the approximate plane of the central double bond. The ring atoms of each half of the molecule were in a single plane (e.g., C_1, C_{10}, C_9, C_8, C_7, C_6, C_5, C_4, and C_3 are all within 0.15 Å of a common plane) except for the carbon atom (0.78 Å out of the plane) bearing the *gem*-dimethyl groups. This dimethyl group tilted far out of that plane. This deformation placed one set of methyls, C_{11} and $C_{11'}$, above the aromatic rings (vide supra). Only minor pyramidalization was observed at the central double bond ($C_{1'}$ was only 0.103 Å out of the plane defined by C_1, C_2, and C_{10}). The plane of each phenyl group was twisted 44.9° (43.2° via MMP2) with respect to the double bond, thus significantly reducing the π conjugation.

The ^{1}H NMR spectrum of **5b** in solution supported a mixture of similar conformers. The dihedral angles between the adjacent methylene hydrogen atoms allowed calculation of vicinal coupling constants from the X-ray and MMP2-calculated structure of **5b**.[18] As seen in Table I, these values match very well with one another and qualitatively matched the measured values. It is evident from Figure 4, however, that a better fit with the measured coupling constants would have been obtained if the C–C–C–C dihedral angle in **5b** had been nearer 45–50° rather than the 34° found in the X-ray measurement. Consequently, it was no surprise to learn that the other somewhat higher energy conformers predicted for **5b**, **5b′**, **5b″**, and others by MMX had appreciably larger, 45–55°, C–C–C–C dihedral angles. Apparently, these other conformers of **5b**, which are not observed in the solid, are significantly populated in solution.

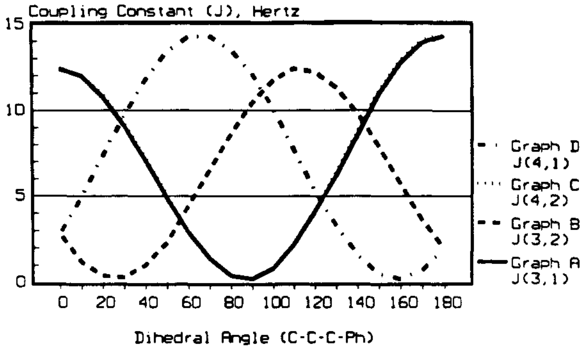
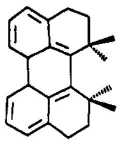


Figure 4. Vicinal coupling constants, $J_{H,H}$, for hydrogens of a CH_2CH_2Ph unit as calculated by the Karplus equation for various conformations about the C–C bond.

The structure of unstable **6b** was more difficult to establish. Structures **8** and **9** and stereoisomers of **5b** were considered reasonable candidates. Photodimer **9** was unlikely due to the steric congestion in **5b**. In any event, **9** could be ruled out on the basis of the long-wavelength UV absorption observed in **6b**. A high-energy absorption near 270 nm, typical of alkylbenzenes, would be expected for **9**.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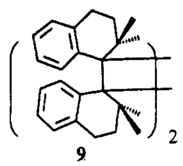
9

Dihydrophenanthrenes, like **8**, are typically present in small quantities in stilbene photochemistry if oxidizing agents are absent.[3] In the presence of oxidizing agents they can be immediately oxidized to the corresponding phenanthrenes, and the chemical yield can be quite high. In special cases they have been directly detected.[19] Dihydrophenanthrenes, however, show a long-wavelength absorption near 450 nm, which was not observed in **6b**. In addition, **8** was inconsistent with the ^{1}H NMR spectrum.

Thus, **6b** must be a highly strained *E* conformer or *Z* isomer of **5b**. Although a *Z* isomer was likely, the highly distorted nature of **6b** did not allow automatic rejection of a second *E* conformer. A number of facts can be brought to bear on the problem. The upfield-shifted aromatic hydrogen resonances observed in the ^{1}H NMR spectrum of **6b** are typical of two cofacial, or face-to-face, aromatic rings.[8] The red-shifted UV absorption in **6b** suggested the central double bond was more twisted than in **5b**, the phenyl rings were less twisted than in **5b**, or a combination thereof. The most significant, and fortuitous, observation was the failure of the vicinal coupling constants observed for **6b** to fit values calculated (Table I) by the Karplus equation for any of the calculated *Z* isomers, **6b**, **6b′**, or **6b″**. Figure 4 shows all possible combinations of the four vicinal coupling constants associated with a CH_2CH_2 unit. The coupling constants observed for **6b**, 4.5, 5.0, 7.2, and 8.5 Hz, match none of these combinations. Consequently, the observed constants must be averaged values for rapidly interconverting sites. This interconversion could not interchange the top and bottom faces of **6b** or only one

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[13] Hirayama, K. *Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compounds*; Plenum: New York, 1967; p 124.

[14] The dotted lines bisect the angle seen between the two substituent bonds when viewing down the C=C bond.

[15] For a discussion of problems of this kind, see: Ermer, O. *Aspekte von Kraftfeldrechnungen*; Wolfgang Bauer Verlag: Munich, 1981; p 65.

[16] Bernstein, J. *Acta Crystallogr.* **1975**, *B31*, 1268.

[17] Valle, G.; Busetti, V.; Galiazzo, G. *Cryst. Struct. Chem.* **1981**, *10*, 867.

[18] Haasnoot, C. A. G.; DeLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1981**, *36*, 2783, as used in MMX.

[19] Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1967**, 662.

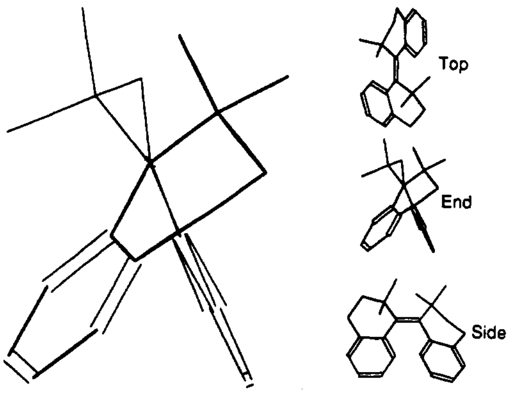

Figure 5. MMP2-calculated structure of **6b** viewed along the C=C bond.

methyl resonance and two kinds of methylene resonances would be observed. Inspection of the potential Z isomers **6b**, **6b′**, **6b″**, indicated two exchange processes must be considered: **6b″** $\rightleftarrows$ **6b′** and the racemization of **6b**. The **6b″** $\rightleftarrows$ **6b′** equilibration was ruled out because the coupling constants of the exchanging protons in **6b″** and **6b′** were almost identical. Thus, the averaged values would not have been much different from the original values shown in Table I. The racemization of **6b** had the prerequisite properties to fit the data. In **6b**, the two halves of the molecule have different conformations. The $(CH_3)_2C$ group on one end of **6b** is tilted "away from the double bond" whereas the $(CH_3)_2C$ group on the other end is tilted "toward the double bond". This is readily seen in the views directly along the central C=C bond provided in Table II and Figure 5. When these groups interchange as **6b** racemizes, the pseudoaxial protons become pseudoequatorial and vice versa. This averages the largest coupling constants with the smallest coupling constants to give calculated values of 4.61, 8.16, 4.83, and 8.28 Hz, which compare favorably with the observed values of 4.5, 7.3, 5.0, and 8.5 Hz.

Still remaining is the possibility that the new photoisomer is just a conformer of the E isomer, **5b**. Of the calculated E conformers, only **5b′**, shown in Table II, had the appropriate asymmetry to match the NMR properties of the new photoisomer. The predicted coupling constants for **5b′** gave reasonable agreement with the observed values. However, other factors led one to discounnt **5b′**. Most important of those is the similarity of the structures of **5b′** and **5b** as seen in Table II. This suggested that **5b′** and **5b** should have similar NMR and UV spectra, which was certainly not the case with the new photoisomer.

The arguments above conclude **6b**, shown in Figure 5, is the new photoisomer. It was gratifying to observe that **6b** was consistent with the other observed properties of the new isomer. The photoisomer showed upfield-shifted aromatic resonances. The positions of hydrogens H_8 and H_7 in **6b** suggest the diamagnetic anisotropy of the adjacent aromatic ring should produce an upfield shift of 0.5 and 0.3 ppm, respectively.[20] The twisted, 73.1°, central double bond in **6b** was consistent with the bathochromic shift observed in the UV absorption spectrum and inconsistent with **6b″**, which is similarly twisted to **5b**.

The structural distortions in **6b** were different from those in **5b**. The bond angles in the "cyclohexene" ring, for example, were within 3° of normal. Apparently, most of the distortion has been absorbed by the very large twist, 73.1°, in the central C=C bond. This was also reflected in the very elongated, 1.38 Å, central C=C bond. The bonds connecting the *gem*-dimethyl groups to the double bond were 1.53 and 1.54 Å compared to 1.542 Å for **5b**. The bonds connecting the aromatic ring to the double bond, however, were 1.46 and 1.47 Å compared to 1.482 Å for **5b**.

The prediction by MMP2 that **6b″** should be the most stable Z conformer and the experimental observation that **6b** was formed photochemically are revealing. Evidently, the MMP2 calculations failed to properly reproduce the relative energies of **6b″** and **6b**. The program MMP2 routinely predicts heats of formation correctly, within a few kcal/mol, for molecules with relatively normal geometries because it has been parametrized for such molecules. For molecules with extreme structural distortions, such as **6b″** and **6b**, less success would be expected. In this instance, likely the discrepancy lies primarily in the parameterization of the twisting feature about the central C=C bond. At high twist angles the introduced strain is calculated to be too great. An alternative explanation would involve photoexcited **5b** relaxing to a geometry similar to **6b** before it reached the geometry of **6b″**. In that event, **6b″** could be the second most stable isomer but it would never be seen. The single piece of evidence bearing on this point was the failure to observe any other isomer of **5b** by ^1H NMR. If **6b″** were really only 3.01 kcal/mol less stable than **5b**, it seemed likely it should have been detected.

The isomerization barrier of **6b** to **5b** was measured between 4.6 and 19.0° and found to be $E_a = 21 \pm 1.8$ kcal/mol. This value is 11 kcal/mol lower than the nearest reported isomerization barrier for a symmetrically substituted stilbene.[4a] It is compared with other such barriers in Figure 2. A simple, linear relationship, the top line in Figure 2, has been reported between the Z/E isomerization barrier and the calculated strain energy in simple, sterically congested alkenes.[25] The entire decrease in the alkene isomerization barrier was explained by the increase in energy of the reactants due to steric congestion. Even though the structural differences between stilbenes are much greater than those of the simple alkenes, the plot in Figure 2, bottom line, shows a similar relationship apparently exists for stilbenes. The different slopes, $0.88^{\text{ethylenes}}$ and $0.7^{\text{stilbenes}}$, show the stilbenes are less responsive to steric congestion.

Experimental Section

(*E*)-1-(2,2-Dimethyltetralinylidene)-2,2-dimethyltetralin (5b). The synthesis and characterization of **5b** have been previously reported, including a low-resolution ^1H NMR spectrum and mp 195 °C.[9] High-resolution 400-MHz ^1H NMR (−30 °C, cyclohexane-d_{12}/diethyl-d_{10} ether): δ 1.10 (s, 3 H), 0.64 (s, 3 H) 2.80 (m, 1 H), 2.80 (m, 1 H), 1.73 (ddd, $J_{H,H}$ = 7.5, 10.2, 13.5, 1 H), 1.53 (ddd, $J_{H,H}$ = 3.5, 6.5, 13.5, 1 H), 7.11–6.96 (m, 4 H). In

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[20] (a) It should be noted that the lower energy Z conformer, **6b″**, would show similar shifts of 0.5 and 0.4 ppm, respectively. (b) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969; p 95.

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Table III. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2
C1	0.03675 (8)	0.1665 (3)	0.2552 (1)	2.49 (3)
C2	0.08324 (9)	0.0904 (3)	0.3327 (1)	2.80 (3)
C3	0.12327 (9)	−0.1170 (3)	0.3017 (1)	3.63 (4)
C4	0.17275 (9)	−0.0694 (3)	0.2352 (1)	3.93 (4)
C5	0.14597 (8)	0.1126 (3)	0.1771 (1)	3.05 (3)
C6	0.18662 (9)	0.1817 (4)	0.1146 (1)	4.09 (4)
C7	0.1659 (1)	0.3599 (4)	0.0650 (1)	4.52 (4)
C8	0.1035 (1)	0.4765 (3)	0.0774 (1)	4.18 (4)
C9	0.06201 (9)	0.4083 (3)	0.1382 (1)	3.24 (4)
C10	0.08108 (8)	0.2227 (3)	0.18746 (9)	2.58 (3)
C11	0.0428 (1)	0.0054 (3)	0.4037 (1)	3.83 (4)
C12	0.13779 (9)	0.2695 (3)	0.3654 (1)	3.71 (4)
H1[a]	0.1509 (9)	−0.187 (3)	0.349 (1)	2.2 (4)
H2[a]	0.0850 (9)	−0.236 (3)	0.2808 (9)	2.1 (4)
H3[a]	0.180 (1)	−0.211 (3)	0.202 (1)	3.2 (5)
H4[a]	0.2214 (9)	−0.023 (3)	0.261 (1)	2.4 (4)
H5[a]	0.233 (1)	0.100 (3)	0.108 (1)	3.4 (5)
H6[a]	0.1957 (9)	0.405 (3)	0.021 (1)	2.6 (4)
H7[a]	0.089 (1)	0.613 (3)	0.043 (1)	3.6 (5)
H8[a]	0.0148 (9)	0.491 (3)	0.150 (1)	2.1 (4)
H9[a]	0.0042 (8)	−0.108 (3)	0.385 (1)	1.7 (4)
H10[a]	0.0792 (9)	−0.077 (3)	0.443 (1)	2.0 (4)
H11[a]	0.0211 (8)	0.133 (3)	0.433 (1)	1.8 (4)
H12[a]	0.1663 (9)	0.330 (3)	0.322 (1)	2.0 (4)
H13[a]	0.111 (1)	0.404 (3)	0.390 (1)	3.0 (4)
H14[a]	0.1714 (9)	0.201 (3)	0.412 (1)	2.4 (4)

[a] These atoms were refined isotropically.

an effort to detect **6b** in the presence of **5b**, a concentrated sample of **5b** was analyzed by ^{1}H NMR. The aromatic region of **6b**, which was well separated from the aromatic region of **5b**, showed no evidence, <0.15%, of the presence of **6b**.

(*Z*)-1-(2,2-Dimethyltetralinylidene)-2,2-dimethyltetralin (6b): 400-MHz ^{1}H NMR (−30 °C, cyclohexane-d_{12}/diethyl-d_{10} ether) δ 1.59 (s, 3 H), 1.13 (s, 3 H), 2.76 (ddd, $J_{H,H}$ = 5.5, 8.5, *15*, 1 H), 2.58 (ddd, $J_{H,H}$ = 4.5, 7.5, 15.0, 1 H), 1.95 (ddd, $J_{H,H}$ = 4.5, 7.0, 12.5, 1 H), 1.43 (ddd, $J_{H,H}$ = 4.5, 8.5, 13, 1 H), 6.82 (d, $J_{H,H}$ = 7.0, 1 H), 6.72 (dd, $J_{H,H}$ = 7.0, 1.7, 1 H), 6.49 (d, $J_{H,H}$ = 7.3, 1 H), 6.42 (d, $J_{H,H}$ = 7.5, 1 H).

(*E*)-1-(2,2-Dimethyltetralinylidene)-2,2-dimethyltetralin: MMX and MMP2 Calculations. Any force field program suitable for these calculations needed to consider the π contribution to the energy. The commonly employed version of the popular program MM2 is deficient in this regard and gives unreasonable results. Both MMX (Serena Software) and MMP2(80) (available from Molecular Design Limited) were suitable. Since the VAX version of MMX gave absolute heats of formation that differed significantly from other versions of MMX and from MMP2, only relative MMX values are reported here. Likewise, final energies and geometries were calculated by MMP2 since these calculations should be readily reproducible in other laboratories. Since MMX and its companion program, PCMODEL, offered a particularly convenient means of creating, handling, and displaying a large number of structures, it was chosen for the initial rational search with the recognition that some further refinement of the final structures with MMP2 would be necessary. Exploratory calculations showed that each half of the molecule was typically planar except for a section that was tipped out of the common plane. This tipped part was either the *gem*-dimethyl group, the adjacent methylene group, or the combined *gem*-dimethyl/methylene unit. Consequently, it was useful to construct six templates (with PCMODEL). Each consisted of half of the whole molecule (split through the C=C bond) having one of the out-of-plane units tipped up or down. Three of these templates with the out-of-plane units tipped in the same direction were copied for use as the other half of the molecule. The three left halves were successively combined with each of the six right halves to give 18 starting geometries. Six input geometries were generated from each of these 18 geometries by rotating about the central bond in 60° increments. This gave 108 input geometries. Another 108 geometries, which were mirror images of the first set, were ignored. Calculation of the minimum-energy geometry from each starting geometry with MMX took 55 h of VAX cpu time. For the final refinement, MMP2(80) calculations were performed on the unique MMX geometries with the Cyber computer at the Rechenzentrum at the University of Erlangen.

Rate of 6b → 5b Isomerization. A solution of **5b** in THF was outgassed and sealed in a quartz NMR tube. The tube was maintained at −78 °C as it was irradiated in an unsilvered, quartz Dewar flask with two low-pressure mercury (PenRay) lamps for 20–30 min. The sample was then quickly transferred into the precooled probe of a JEOL FX90Q NMR spectrometer. The disappearance of the absorptions from **6b** in the aromatic region were monitored with time. This experiment was performed over an NMR probe temperature range of 4.6–19.0 °C. The NMR probe temperature was calibrated before and after each measurement. Least-squares analysis provided individual rate constants and their associated errors. A linear least-squares analysis of the rate constants, with appropriate statistical weighting based on the error in each rate constant, led to $E_a = 21.4 \pm 1.8$ kcal/mol and $A = 1.4 \times 10^{13}$.

(*E*)-1-(2,2-Dimethyltetralinylidene)-2,2-dimethyltetralin: X-ray Analysis. A colorless crystal of $C_{24}H_{28}$ having approximate dimensions of 0.25 × 0.22 × 0.09 mm was cut from a larger needle and mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix were determined by using the setting angles of 25 reflections, $12 < \theta < 14°$. The monoclinic cell parameters and calculated volume are as follows: a = 18.622 (2) Å, b = 5.957 (1) Å, c = 16.428 (2) Å, β = 95.17 (1)°, V = 1815.0 Å^3. For Z = 4 and fw = 316.49 the calculated density is 1.16 g/cm^3. From the systematic absences of hkl, $h + k = 2n + 1$, and from subsequent least-squares refinement, the space group was determined to be $C2/c$ (No. 15).

Data were collected at 21 ± 1 °C using the θ–2θ scan technique. A total of 2449 reflections were collected, of which 2281 were unique and not systematically absent. An anisotropic decay correction was applied to adjust for the 2.2% loss in total intensity. The correction factors on I ranged from 0.913 to 1.038, with an average value of 0.982.

Lorentz and polarization corrections were applied. The linear absorption coefficient is 0.6 cm^{-1} for Mo Kα radiation. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0.925 to 0.996, with an average value of 0.960.

The structure was solved by direct methods. A total of 11 phase sets were produced from 218 reflections (minimum E of 1.56) and 2092 relationships. All non-hydrogen atoms were located from an E map prepared from the most probable phase set. Hydrogen atoms were located from a difference Fourier synthesis, and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares where the function minimized has $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[23] Only the 1137 reflections having intensities >3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 165 variable parameters: $R_1 = 0.037$; $R_2 = 0.046$.

All calculations were performed on a VAX 11/750 computer using SDP/VAX.[24]

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Supplementary Material Available: Experimental details of X-ray structure determination and tables of positional and thermal parameters, general temperature factor expressions, bond distances, bond angles, torsional angles, and least-squares planes (13 pages). Ordering information is given on any current masthead page.