new chemical techniques make them particularly attractive

Distortion of normally planar carbon–carbon double bonds has frequently produced strained materials with significantly altered chemical and physical properties. Sterically demanding groups can introduce such structural modifications. 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. 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). 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. 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. 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 Ragut Schleyer on the occasion of his 60th birthday.

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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 $A_e = 21 \pm 1.8$ kcal/mol. MMP2 calculations, supported by direct observations, suggested 6b was an unsymmetrical structure twisted 73° about the central double bond.

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.

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-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.

![Figure 1](image)

**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](image)

**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.


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

\(^{8}\)(Lemmen, P.; Lenoir, D. Chem. Ber. 1984, 117, 2300.)

### Table I. Comparison of Measured and Calculated \(^1\)H NMR Data for 5b, 6b, 6b', and 6b''

<table>
<thead>
<tr>
<th>compd</th>
<th>measured</th>
<th>source</th>
<th>methylene region</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>2.80</td>
<td>H, H(_{4\text{exo}})</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m</td>
<td>1.53</td>
</tr>
<tr>
<td>6b</td>
<td>2.68</td>
<td>H, H(_{4\text{endo}})</td>
<td>1!56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m</td>
<td>1.43</td>
</tr>
<tr>
<td>6b'</td>
<td>3.36</td>
<td>H, H(_{3axo})</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m</td>
<td>3.78</td>
</tr>
<tr>
<td>6b''</td>
<td>4.01</td>
<td>H, H(_{3\text{endo}})</td>
<td>4.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m</td>
<td>4.33</td>
</tr>
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</table>

\( ^{\text{a}}\)Cis \( J \) value given before trans. \( ^{\text{b}}\)See Table II for structures of 6b' and 6b''.

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

<table>
<thead>
<tr>
<th>Conformer</th>
<th>ΔHf (Calc), kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>-4.62</td>
</tr>
<tr>
<td>6b</td>
<td>-4.76</td>
</tr>
<tr>
<td>6b'</td>
<td>-4.77</td>
</tr>
<tr>
<td>6b''</td>
<td>-4.78</td>
</tr>
<tr>
<td>5b'</td>
<td>-4.79</td>
</tr>
<tr>
<td>5b''</td>
<td>-4.80</td>
</tr>
</tbody>
</table>

*Calculated angle between p orbitals. *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.

The structure of 6b to form 5b at 4.6-19.0 °C revealed Eo = 21 ± 1.8 kcal/mol, with A = 1013 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 formation11 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.10 The red-shifted, lowest energy band in the UV spectrum at λTHF = 314 nm (vs λRiOH = 294 nm in (E)-stilbene)13 suggested the π

(10) Serena Software, Box 3076, Bloomington, IN 47402.
system in 5b had a twisted central double bond. A distinct singlet at \( \delta 0.64 \) 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 1) 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 \( \phi \) orbitals in the central double bond were twisted 36.7° (40.2° via MMP2). The torsion angles reported are the dotted lines in Table II.\(^{12,13}\) 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 seen by the closing of the \( \delta C_{1}C_{2}C_{3} \) angle to 102.3° (103.6° via MMP2) and the opening of the adjacent \( \gamma C_{1}C_{2}C_{3} \) 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., \( C_{1}, C_{1b}, C_{9}, C_{9b}, C_{7}, C_{7b}, C_{5}, C_{6} \), 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, \( C_{1b} \) and \( C_{1b} \), above the aromatic rings (vide supra). Only minor pyramidalization was observed at the central double bond (\( C_{1b} \) 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 \( \pi \) 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 angles in 5b had been nearer 45–50° rather than the 54° found in the X-ray measurement. Consequently, it was no surprise to learn that the other some-

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(14) The dotted lines bisect the angle seen between the two substit- ent 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.
(18) Hassnoot, C. A. G.; DeLeeuw, F. A. A. M.; Altona, C. Tetrahedron 1981, 36, 2783, as used in MMX.
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" = 6b' and the racemization of 6b. The 6b" = 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)_2C group on one end of 6b is tilted “away from the double bond” whereas the (CH)_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 discount 5b". Most important of these 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. The twisted, 73.1°, central double bond in 6b was consistent with the baxocromatic 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 MM2 that 6b" should be the most stable Z conformer and the experimental observation that 6b was formed photochemically are revealing. Evidently, the MM2 calculations failed to properly reproduce the relative energies of 6b" and 6b. The program MM2 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 'H NMR. If 6b" were really only 0.31 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 15.0° 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. 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 $\Delta E$ isomerization barrier and the calculated strain energy in simple, sterically congested alkenes. 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 for stilbenes, 0.74 for 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 'H NMR spectrum and mp 195 °C. High-resolution 400-MHz 'H NMR (−30 °C, cyclohexane-d$_2$, diethyl-d$_2$ ether), 0.64 (s, 3 H), 2.80 (m, 1 H), 2.80 (m, 1 H), 1.73 (dd, $J_{HH} = 1.3, 3.5, 13.5, 1$ H), 1.53 (dd, $J_{HH} = 3.5, 6.5, 13.5, 1$ H), 7.11–6.96 (m, 4 H), 7.11–6.96 (m, 4 H).

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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 565.
an effort to detect 6b in the presence of 5b, a concentrated sample of 5b was analyzed by 1H 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.

(E)-1-(2,2-Dimethyltetralinylidene)-2,2-dimethyltetralin: X-ray Analysis. A colorless crystal of C_{20}H_{22} that has a brownish color, was collected at 21 ± 1 °C using the 6-28 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 K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix were determined by using the setting angles of 1 reflection, 12 < 15°. The monoclinic cell parameters and calculated volume are as follows: \(a = 16.622\) Å, \(b = 5.957\) Å, \(c = 16.428\) Å, \(\beta = 95.17\)°, \(V = 1815.0\) Å\(^3\). For \(Z = 4\) and \(fw = 316.49\) the calculated density is 1.16 g/cm\(^3\). From the systematic absences of 4klh and khlh, \(h + k = 2n + 1\), and from subsequent least-squares refinement, the space group was determined to be C2/c (No. 15).

The technical assistance of R. Schramm is gratefully acknowledged. Anomalous dispersion effects were included in \(\lambda\) and \(\beta\). The structure was refined in full-matrix least squares where the function minimized has \(\Sigma w(|F_{o}| - |F_{c}|)^2\) and the weight \(w\) is defined as \(4F_{o}^2/c^2(F_{c}^2)^2\). Scattering factors were taken from Cromer and Waber.\(^{21}\) Anomalous dispersion effects were included in \(F_{o}\); the values of \(\Delta\rho'\) and \(\Delta\rho''\) were those of Cromer.\(^{20}\) 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: \(R_1 = 0.037\), \(R = 0.046\).

All calculations were performed on a VAX 11/750 computer using SPC/PAX.\(^{24}\)

Acknowledgment. The technical assistance of R. Roesner, B. Reinold, and K. W. Schramm is gratefully acknowledged as is the financial assistance of the University of Toledo de Arce Fund, the Ohio Research Challenge Program, the UT A&S Instrumentation Center, and the Fonds der Chemischen Industrie.

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.