Experimental Section

Slow crystallization from $CHCl_3$–hexane of the small sample of ivaxillin remaining from the earlier work[2] gave single crystals which melted somewhat higher than reported previously: mp 181–182 °C; ^1H NMR spectrum ($CDCl_3$, 270 MHz) 4.30 (ddd, J = 10, 10, 1.5 Hz, H-8), 2.82 (quintet, J = 7.5 Hz, H-11), 2.78 (br d, J = 10 Hz, H-9a), 2.79 (br d, J = 14 Hz) and 2.74 (br d, J = 10 Hz, H-1 and H-5), 2.42 (br q, J = 7 Hz, H-7), 2.25 (dt, J = 14, 3 Hz), 2.14 (dt, J = 12.5, 3 Hz), 2.11 (br d, J = 14.5 Hz), 1.45 (dd, J = 14, 10 Hz, H-9b in 4p multiplet at 1.53–1.34 ppm), 1.39 and 1.27 (C-4 and C-10 Me), 1.23 (d, J = 8 Hz, C-11 Me); ^1H NMR spectrum (C_6D_6, 270 MHz) 3.75 (ddd, J = 11, 9, 1.5 Hz, H-8), 2.60 (br d, J = 14 Hz), 2.28 (br d, J = 10 Hz) and 2.13 (br, J = 10 Hz, H-2, H-5, and H-9a), 2.17 (quintet, J = 7.5 Hz, H-11), 1.75 (m, 2 H), 1.51 (br d, J = 15.5 Hz), 1.46 (br q, J = 7 Hz, H-7), 1.08 (dd, J = 13, 10 Hz, H-9b), 0.95 (m, 3 H), 0.89 and 0.79 (C-4 and C-10 Me), 0.77 (d, J = 5 Hz, C-11 Me).

The crystals of ivaxillin were monoclinic, space group $P2_1$, with a = 9.920 (1) Å, b = 8.743 (2) Å, c = 9.256 (1) Å, β = 117.02 (1)°, and d_{calcd} = 1.237 g cm^{-3} for Z = 2 ($C_{15}H_{22}O_4$, M_r = 266.34). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.30 × 0.30 × 0.30 mm. A total of 1037 independent reflections were measured for $\theta < 57°$ of which 1008 were considered to be observed [$I > 2.5\sigma(\mathrm{I})$]. The structure was solved by a multiple solution procedure[13] and was refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.033 and R = 0.043 for the 1008 observed reflections. The final difference map has no peaks greater than 0.2 e $Å^{-3}$.

Registry No. 5, 11014-50-9.

Supplementary Material Available: Tables II–V listing final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for compound **5** (4 pages). Ordering information is given on any current masthead page.

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Conformational Analysis of 1,4-Cyclohexadienes: Effect of a Single Bulky Substituent

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Received March 9, 1982

The conformational analysis of 1,4-cyclohexadiene (**1**), its derivatives and related compounds, has been the subject of considerable controversy.[1] Substantial efforts have been made to characterize the large, conformationally dependent, homoallylic coupling constants ($J_{1,4}$ and $J_{1,4'}$)[2] in an effort to determine geometric preferences between boat and planar forms. However, theoretical predictions as to the expected ratio of $J_{1,4}/J_{1,4'}$ for various folding angles have not always been in agreement.[3–6] There now exists sufficient experimental data to deduce preferred geometries, and it appears as though small substituents (e.g., **2**) cause little distortion from planarity. This compares favorably to the parent system itself which has been shown by far infrared,[7] force field calculations,[8] and NMR[5] to vibrate around a planar energy minimum.

Table I. Coupling Constant Data (Hertz) for 3[a, b]

$J_{1,4}$ (cis)	$J_{1,4'}$ (trans)	$J_{3,4}$	$J_{3,4'}$	$J_{1,2}$	$J_{4,4'}$
7.4	7.7	4.0	2.9	3.4[c]	22.8

[a] Run at 360 MHz in the presence of $Eu(fod)_3$. PANIC spectrum simulation indicates that first-order treatment is warranted. [b] $H_{4'}$ was assigned to the methylene signal that moved downfield fastest upon $Eu(fod)_3$ addition. See ref 13. [c] Measured both in the presence and absence of $Eu(fod)_3$.

It has been assumed that a bulky substituent at C-1 may produce a boat-shaped conformation as the energy minimum. Moreover, early suggestions[9] based on inspection of models as well as a preliminary X-ray crystallographic study with *trans*-1,4-dihydro-4-tritylbiphenyl led to the suggestion that bulky groups would preferentially occupy the pseudoequatorial position. This is in contrast with the related, 1,4-dihydronaphthalene and 9,10-dihydroanthracene systems for which pseudoaxial preference has been demonstrated.[1,10] However, since these latter systems provide considerably greater "peri" interactions than dihydrobenzenes, pseudoequatorial preference had been accepted without challenge. Recently, however, Grossel et al.[11] have reexamined the X-ray crystallographic structure of *trans*-1,4-dihydro-4-tritylbiphenyl, and their results indicate a pseudoaxial preference for the trityl group, which is, of course, assumed to be the more bulky substituent. In addition, force field calculations of 1-*tert*-butyl-1,4-dihydrobenzene indicated a boat conformation (folding angle = 160°) with the *tert*-butyl group in the pseudoaxial position.[8c] In view of these recent results, we felt that it would be important to examine (experimentally) a 1,4-cyclohexadiene with a single large substituent to determine the shape of the ring and any preferred position of the substituent. We selected **3**, since the dimethylcarbinol substituent is large and provides a suitable system for the use of shift reagents.[12,13] NMR analysis (360 MHz) was accomplished with proton–proton

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(2) For convenience and consistency with previous work, a numbering system based on 1,4-dihydrobenzene is used throughout.

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(12) The fact that the value of $J_{1,2}$ is reasonably close to $J_{3,4}$ suggests little if any conformational change caused by the shift reagent, since $J_{1,2}$ was able to be measured before the addition of $Eu(fod)_3$. This is also in agreement with previous findings that shift reagents do not alter conformations in related 1,4-cyclohexadienes.[13]

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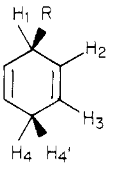
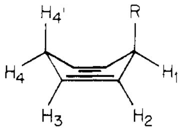
0022-3263/82/1947-3993$01.25/0 © 1982 American Chemical Society

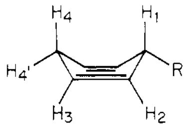
Table II. Coupling Constant Data for Various Structural Types of 1,4-Cyclohexadienes



4



5

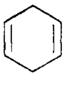


6

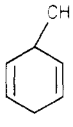
coupling constant	planar (**4**)[a]	rigid boat (**5**)[b]	rigid boat (**6**)[b]
$J_{1,4}$(cis)	8.3	2.6[c]	12.0
$J_{1,4'}$(trans)	7.5	4.7	4.7
J_{cis}/J_{trans}	1.11	<0.55	2.55
$J_{1,2}(J_{3,4})$	3.1	5.5	2.5
$J_{3,4'}$	3.0	2.5	5.5

[a] Data for compound **2** (from ref 12). [d] Data for 2,4a-dihydrotriptycene-2-carboxylic acid (from ref 13). [c] Although values for cis diequatorial coupling are not known for this geometry, a value of 2.6 Hz can be estimated by the method of Grossel (ref 6). However, his calculated values appear to be about 33% too high when compared to available experimental values.

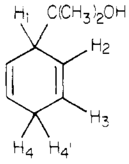
spin decoupling in the presence of Eu(fod)$_3$, and the results are presented in Table I.



1



2



3

In a planar geometry, the $J_{1,4}/J_{1,4'}$ (cis/trans) ratio has been established as about 1.1 by previous experimental data (see Table II) as well as theoretical predictions.[6] As planar 1,4-dihydrobenzene begins to pucker (boat shaped) the homoallylic coupling constants react as follows (Table II): (1) the cis diaxial value becomes considerably larger, (2) the cis diequatorial value becomes much smaller, and (3) the trans axial/equatorial value decreases slightly. Hence, a substituted 1,4-dihydrobenzene with a single substituent in the pseudoaxial position of a boat geometry would show a J_{cis}/J_{trans} ratio of less than 1.1 since the cis relationship is pseudoequatorial/pseudoequatorial. A similar geometry with a pseudoequatorial substituent would show a J_{cis}/J_{trans} ratio of more than 1.1 since the cis relationship in this case is pseudoaxial/pseudoaxial. With **3**, the value is 0.96. Hence, we can conclude that **3** exists in a boat conformation with the substituent pseudoaxial as predicted by force field calculations. This conclusion is also supported by the vicinal coupling constants since $J_{3,4}$ and $J_{1,2}$ are slightly larger than that expected for a planar geometry, indicating a slight decrease in dihedral angle. We may conclude from the magnitude of the observed values that the extent of ring puckering is quite modest, suggesting a very shallow boat. It should also be noted that this representation is an average geometry and that significant oscillations about this conformation are expected.[5,7,8c]

Experimental Section

3-(2-Hydroxy-2-propyl)-1,4-cyclohexadiene. A solution of sodium amide in 60 mL of ammonia (−78 °C) was prepared from the metal (37 mmol) and a catalytic amount of ferric chloride. 1,4-Cyclohexadiene (2 g, 25 mmol) in 10 mL of dry THF (distilled from sodium/benzophenone) was then added and stirring was continued for 1 h. Dry acetone was then added followed by aqueous ammonium chloride. Ether extraction and microdistillation afforded a colorless oil in 39% yield: bp 36 °C (2 torr); 360-MHz NMR (CDCl$_3$) δ 5.85 (AB, 4 H, 2.8), (m, 1 H), 2.65 (m, 2 H), 1.8 (s, 1 H), 1.2 (s, 6 H). Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.50; H, 9.97.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences for support of this work (P.W.R.). We also thank the Lilly Research Laboratories for use of the Bruker 360-MHz NMR spectrometer.

Registry No. 1, 628-41-1; **3**, 70338-15-7; acetone, 67-64-1.

Selectivity in Cycloadditions to Vinylheterocumulenes. [2 + 2] and [4 + 2] Cycloaddition of (Diethylamino)propyne to Vinyl Isocyanate and Vinyl Isothiocyanate[1]

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Received February 5, 1982

The mode of cycloaddition of unsaturated systems to heterocumulenes[3] varies depending on the chosen cumulative system as well as on the nature and extent of substitution at its terminal atoms. This stereochemical flexibility constitutes both a matter for mechanistic investigations and a versatile entry toward various small and medium ring size heterocycles. Particularly attractive in this respect are vinylheterocumulenes in that they have a carbon–carbon double bond adjacent to the cumulative system and can act as a 2-π-electron component by using one of the double bonds or as a 4-π-electron component by using one cumulative double bond and the vinyl group. Representative compounds of this class of heterocumulenes are vinylketenes[4] and vinylketenimines[5] whose site and peri selectivity in [2 + 2] and [4 + 2] cycloadditions have attracted considerable attention for the synthesis of four- and six-membered heterocycles. The ready availability and stability of vinyl isocyanate (**1a**) and vinyl isothiocyanate (**1b**), whose reactivities as cycloaddition partners are practically unexplored, led us to extend to these compounds our studies on cycloadditions to heterocumulenes.[6]

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(1) Supported by a grant (No. 79.02122) from the National Research Council of Italy (CNR, Rome) on the basis of a joint research project between the Department of Organic Chemistry, University of Košice, Czechoslovakia, and the Laboratory of Organic Chemistry, University of Ferrara, Italy.

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