6654 J. Org. Chem. 1993, 58, 6654–6661

Conformational Studies of Dihydrotetraphenylmethanes. 2. X-ray Crystallographic and Solution ^{1}H NMR Studies of *cis*-1,4-Dihydro-4-tritylbiphenyl and Its 4′-Bromo Derivative: Conformational Control by an Intramolecular Edge-to-Face Aromatic Interaction

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Received August 6, 1993[●]

X-ray structural studies of *cis*-1,4-dihydro-4-tritylbiphenyl (**2a**) and its 4′-bromo derivative **2b** reveal that, in contrast with earlier predictions based on solution NMR data, both adopt a similar congested conformation in which the cyclohexa-1,4-diene ring is almost planar, forcing the isolated aromatic ring into the π-cloud of one of the benzene rings of the trityl substituent and leading to considerable stretching of the C_1–C_{11} bond and a close intramolecular edge-to-face aromatic interaction. Variable-temperature ^{1}H NMR experiments suggest that this interaction becomes increasingly important at low temperatures. Crystals of *cis*-1,4-dihydro-4-tritylbiphenyl (**2a**) are triclinic, space group $P\bar{1}$, $Z = 2$, lattice parameters $a = 9.566(2)$ Å, $b = 10.125(1)$ Å, $c = 11.924(2)$ Å, $\alpha = 79.51(1)$, $\beta = 75.56(1)°$, $\gamma = 82.44(1)°$. 1678 independent reflections gave a final R of 0.041. Crystals of 4′-bromo-*cis*-1,4-dihydro-4-tritylbiphenyl (**2b**) are orthorhombic, space group $P2_12_12_1$, $Z = 4$, lattice parameters $a = 10.036(6)$ Å, $b = 15.785(6)$ Å, $c = 17.209(9)$ Å. 1709 independent reflections gave a final R of 0.049.

Introduction

While the conformational analysis of biphenyls is now well understood,[1] the behavior of the 1,4-dihydrobiphenyls has received much less attention. We have been particularly interested in the solid-state and solution conformational behavior of some sterically congested derivatives, particularly the stereoisomeric dihydrotritylbiphenyls **1** and **2**. For example, we have reported[2] the results of an X-ray crystallographic study of *trans*-1,4-dihydro-4-tritylbiphenyl (**1a**) and two crystalline modifications of its 4′-bromo derivative **1b**. A comparison with solution ^{1}H NMR data for these compounds led us to conclude that, contrary to earlier suggestions,[3] the cyclohexa-1,4-diene ring is almost planar in the lowest energy conformations of this structure. Furthermore, in the solid state, the trityl group appears to lock the geometry of one end of the dihydroaromatic ring, the precise nature of the favored (boat) conformation of the latter being determined by crystal packing requirements.

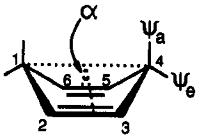
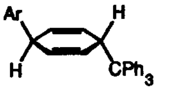
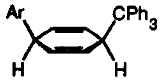


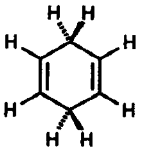
Figure 1. Puckering angle α and pseudoaxial (Ψ_a) and pseudoequatorial (Ψ_e) substituent locations within a 1,4-dihydrobenzene boat conformation.



1 a, Ar = Ph
b, Ar = p-BrC_6H_4



2 a, Ar = Ph
b, Ar = p-BrC_6H_4



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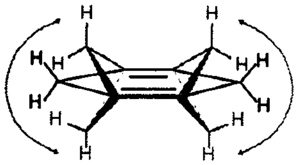

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Cyclohexa-1,4-diene (**3**) itself is thought to occupy a very shallow vibrational potential energy well in solution with a single energy minimum corresponding to a planar geometry ($\alpha = 180°$ in Figure 1),[4–6] and further support for this view comes from a recent X-ray structural study of this molecule at 153 K.[7] However, both infrared[5] and NMR spectroscopy suggest that several vibrational energy levels corresponding to a boat–boat flexing about a planar energy minimum, *e.g.*, **4**, are significantly populated at room temperature.[6] Molecular mechanics and *ab initio* molecular orbital calculations have supported this proposal.[8] So far we have been unable to ascertain whether a similar situation (i.e., a single minimum potential well)

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[●] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) This paper is a tribute to and a final publication from the Chemistry Department of Bedford College, University of London (1872–1985), where part of this study was carried out and where much key work on biphenyl stereoisomerism and clathrate formation was undertaken; *e.g.*, see: Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242. Comments in: Weber, E.; Czugler, M. In *Topics in Current Chemistry*; Weber, E., Ed.; Springer-Verlag: Berlin, Heidelberg, 1988; Vol. 149, p 47.

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pertains for the *trans*-1,4-dihydro-4-tritylbiphenyls **1**, with crystal lattice requirements distorting the shape of the potential energy well and shifting the position of the minimum, or whether the structure favors a double minimum potential energy surface with rapid equilibration in solution between relatively inverted boat conformations.[2]

We have now completed X-ray crystallographic and solution ^{1}H NMR studies of the *cis* isomers **2a**[9] and **2b**. Solution ^{1}H NMR data for **2a** have previously been interpreted as indicating a grossly puckered boat geometry ($\alpha \cong 165°$) in which the substituents are locked pseudoequatorially (Ψ_e in Figure 1).[4,10] Our results shed further light on the conformational potential energy surface for the 1,4-dihydrotetraphenylmethanes in solution and in solid state and provide a unique opportunity for a detailed comparison of the solid-state behavior of a group of closely related structures.

In addition, we discover that both *cis* isomers **2** adopt conformations in which there is a remarkably close intramolecular edge-to-face aromatic interaction. Such phenomena are now known to play an important role in protein folding[11] and molecular recognition.[12]

Experimental Section

Crystal Data. Crystallographic data for **2a** and **2b** are compared in Table I.

(a) *cis*-1,4-Dihydro-4-tritylbiphenyl (2a): $C_{31}H_{26}$, $M_w = 398$, triclinic $P\bar{1}$, $a = 9.566(2)$ Å, $b = 10.125(1)$ Å, $c = 11.924(2)$ Å, $\alpha = 79.15(1)°$, $\beta = 75.56(1)°$, $\gamma = 82.44(1)°$, $U = 1094.13$ Å^3, $D_{obs} = 1.21$ g cm^{-3}, $D_{calc} = 1.18$ g cm^{-3} for $Z = 2$. Mo Kα, $\lambda = 0.710\,69$ Å.

Preliminary photographs of a good quality crystal (0.2 × 0.2 × 0.3 mm) indicated that it had triclinic symmetry. Intensity data collection was then carried out at room temperature on an Enraf-Nonius CAD-4F diffractometer.[13] Using an ω-2θ scanning mode, data were collected automatically for half the limiting sphere in the range $\theta = 0$–$25°$. No correction for absorption was found to be necessary. Lorentz and polarization corrections were applied, and the data were scaled, sorted, and merged to give 1678 independent structure amplitudes with $I > 3\sigma$, where I is the final measured intensity and σ is the standard deviation derived from the counting statistics.

The structure was solved in space group $P\bar{1}$ by direct methods using the program MULTAN 77.[14] A block factor approximation to the full least-squares matrix was employed during the refinement of the positional and thermal parameters of the carbon atoms. All the hydrogen atoms were located during a difference Fourier synthesis. In many cases the definition was poor, making it necessary to place the hydrogen atoms geometrically after each cycle of refinement of the carbon atoms. During the final cycles of refinement, a three-term Chebyshev series was used in place of the unit weighting scheme.[15] A final R value of 4.08% ($R_w = 5.08\%$) was obtained.

Table I. Summary of Crystal Data, Intensity Collection, and Data Processing

compd	**2a**	**2b·C_6C_6**
mol form.	$C_{31}H_{26}$	$C_{37}H_{31}Br$
M_w, g mol^{-1}	398	556
cryst shape	irregular	needle
cryst size, mm	0.2 × 0.2 × 0.3	0.1 × 0.1 × 0.3
color	colorless	colorless
space grp	$P\bar{1}$	$P2_12_12_1$
cryst syst	triclinic	orthorhombic
a, Å	9.566(2)	10.036(6)
b, Å	10.125(1)	15.785(6)
c, Å	11.924(2)	17.209(9)
α, deg	79.15(1)	90
β, deg	75.56(1)	90
γ, deg	82.44(1)	90
U, Å^3	1094.13	2726.6
Z	2	4
D_{obs}, g cm^{-1}	1.21	1.30
D_{calc}, g cm^{-1}	1.18	1.32 (includes benzene)
abs correctn	none	none
radiation	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69
scan mode	ω–2θ	ω–2θ
T, K	298	143
2θ limits, deg	1–25	1–25
no. of data used, $I > 3\sigma(I)$	1678	1709
weights[13]	3-term Chebyshev[15]	3-term Chebyshev[15]
R, %	4.08	4.90
R_w, %	5.08	5.80

(b) 4′-Bromo-*cis*-1,4-dihydro-4-tritylbiphenyl (2b): $C_{37}H_{31}Br$, $M_w = 556$, orthorhombic, space group $P2_12_12_1$, $a = 10.036(6)$ Å, $b = 15.785(6)$ Å, $c = 17.209(9)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 2726.6$ Å^3, $Z = 4$, $D_{obs} = 1.3$ g cm^{-3}, $D_{calc} = 1.32$ g cm^{-3}. Mo Kα, $\lambda = 0.710\,69$ Å.

Weissenberg photographs displayed the systematic absences $h00$ ($h = 2n$), $0k0$ ($k = 2n$), indicating the space group $P2_12_12_1$ or $P2_12_12$. These were distinguished later by diffractometry; a scan of the $h00$, $0k0$, and $00l$ reflections revealed that all those with an odd index were missing, confirming the orthorhombic space group $P2_12_12_1$. A discrepancy was noted between the calculated and observed densities ($D_{calc} = 1.16$ g cm^{-3}, $D_{obs} = 1.3$ g cm^{-3}). This was caused by the presence of four molecules of benzene in the unit cell, which were subsequently located by a difference Fourier synthesis.

A temperature of −130 °C was maintained during the data collection, which was carried out as before. 1709 independent reflections were obtained after correction, scaling, and merging. Patterson methods were employed in the solution, and the refinement followed a course similar to that of *cis*-1,4-dihydro-4-tritylbiphenyl (**2a**), the benzene molecule being constrained to be a rigid body, to give a final R value of 4.90% ($R_w = 5.80\%$).

Atomic coordinates for the non-hydrogen atoms of **2a** and **2b** are listed in Table II, and selected bond lengths and bond angles for the two structures are compared in Tables III and IV respectively. The numbering scheme used for these data is shown in Figure 2. Atomic coordinates of hydrogen atoms and thermal parameters for both structures have been deposited with the Cambridge Crystallographic Data Centre.[41]

NMR Experiments. Spectra were recorded on Perkin-Elmer R24B and Bruker WH360 spectrometers as solutions in CD_2Cl_2, $CDCl_3$ and DMSO-d_6. Assignments and interproton coupling constants were determined by selective ^{1}H–^{1}H decoupling and COSY experiments.

Results and Discussion

X-ray Crystallographic Results. The solid-state geometries of *cis*-1,4-dihydro-4-tritylbiphenyl (**2a**) and its

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Table II. Atomic Coordinates for Non-Hydrogen Atoms in 2

atom	*x/a*	*y/b*	*z/c*
	(a) *cis*-1,4-Dihydro-4-tritylbiphenyl (**2a**)		
C1	0.3459(3)	0.2207(3)	0.6493(3)
C2	0.4293(4)	0.0904(3)	0.6886(3)
C3	0.5258(3)	0.0786(3)	0.7528(3)
C4	0.5639(3)	0.1937(3)	0.8001(3)
C5	0.4896(3)	0.3254(3)	0.7531(3)
C6	0.3929(3)	0.3374(3)	0.6888(3)
C7	0.7330(3)	0.2020(3)	0.7782(2)
C11	0.3627(3)	0.2458(3)	0.5169(3)
C21	0.4977(4)	0.2692(4)	0.4433(3)
C31	0.5175(4)	0.2911(4)	0.3231(3)
C41	0.4019(4)	0.2902(4)	0.2739(3)
C51	0.2672(4)	0.2671(4)	0.3451(4)
C61	0.2472(4)	0.2448(4)	0.4659(3)
C80	0.7908(3)	0.2288(3)	0.6445(2)
C90	0.8015(3)	0.3592(3)	0.5808(3)
C100	0.8485(4)	0.3804(3)	0.4595(3)
C110	0.8816(4)	0.2725(4)	0.3989(3)
C120	0.8665(4)	0.1433(3)	0.4599(3)
C130	0.8226(3)	0.1221(3)	0.5811(3)
C81	0.8090(3)	0.0718(3)	0.8356(2)
C91	0.7402(4)	−0.0102(3)	0.9359(3)
C101	0.8155(4)	−0.1194(3)	0.9902(3)
C111	0.9611(4)	−0.1494(3)	0.9473(3)
C121	1.0319(4)	−0.0682(3)	0.8488(3)
C131	0.9569(3)	0.0409(3)	0.7940(3)
C82	0.7644(3)	0.3136(3)	0.8391(3)
C92	0.6702(4)	0.3507(3)	0.9399(3)
C102	0.7033(4)	0.4461(4)	0.9968(3)
C112	0.8308(5)	0.5061(3)	0.9543(4)
C122	0.9285(4)	0.4673(3)	0.8567(3)
C132	0.8953(4)	0.3720(3)	0.8008(3)
	(b) 4′-Bromo-*cis*-1,4-dihydro-4-tritylbiphenyl (**2b**)		
Br1	0.7250(1)	0.3181(1)	0.8101(1)
C1	0.6996(9)	0.1761(7)	0.4733(5)
C2	0.5816(11)	0.2120(7)	0.4327(6)
C3	0.5839(9)	0.2576(6)	0.3670(5)
C4	0.7092(9)	0.2718(6)	0.3208(5)
C5	0.8304(9)	0.2373(6)	0.3626(6)
C6	0.8261(10)	0.1931(6)	0.4281(5)
C7	0.7287(9)	0.3699(5)	0.2970(5)
C11	0.7069(9)	0.2102(6)	0.5563(5)
C21	0.7075(10)	0.2952(6)	0.5690(5)
C31	0.7131(10)	0.3279(6)	0.6444(5)
C41	0.7175(12)	0.2723(6)	0.7066(4)
C51	0.7150(10)	0.1868(6)	0.6956(5)
C61	0.7084(10)	0.1548(6)	0.6199(5)
C80	0.7393(9)	0.4206(5)	0.3727(5)
C90	0.6237(9)	0.4560(7)	0.4067(6)
C100	0.6339(11)	0.5026(7)	0.4759(6)
C110	0.7560(15)	0.5124(6)	0.5119(5)
C120	0.8691(11)	0.4750(7)	0.4791(5)
C130	0.8600(10)	0.4291(6)	0.4103(6)
C81	0.6120(8)	0.3995(6)	0.2450(5)
C91	0.5226(10)	0.3453(6)	0.2035(5)
C101	0.4320(11)	0.3774(8)	0.1527(6)
C111	0.4133(10)	0.4637(7)	0.1441(6)
C121	0.4985(8)	0.5189(6)	0.1825(6)
C131	0.5958(12)	0.4879(6)	0.2343(6)
C82	0.8548(11)	0.3829(7)	0.2431(6)
C92	0.9157(13)	0.4608(6)	0.2401(6)
C102	1.0153(9)	0.4771(7)	0.1872(7)
C112	1.0502(11)	0.4145(7)	0.1339(6)
C122	0.9886(11)	0.3379(6)	0.1352(6)
C132	0.8854(8)	0.3215(7)	0.1889(6)
C140	0.7461	0.1860	0.0313
C141	0.8589	0.1402	0.0555
C142	0.8511	0.0894	0.1198
C143	0.7357	0.0818	0.1605
C144	0.6202	0.1245	0.1378
C145	0.6261	0.1785	0.0719

Table III. Selected Bond Lengths (Å) with esd's in Parentheses

bond	**2a**	**2b**
C(1)–C(2)	1.508(5)	1.487(14)
C(1)–C(6)	1.508(5)	1.512(13)
C(1)–C(11)	1.522(5)	1.529(12)
C(2)–C(3)	1.320(4)	1.340(14)
C(3)–C(4)	1.506(4)	1.505(13)
C(4)–C(5)	1.505(4)	1.514(13)
C(4)–C(7)	1.584(4)	1.613(11)
C(5)–C(6)	1.322(4)	1.327(13)
C(7)–C(80)	1.535(4)	1.534(12)
C(7)–C(81)	1.547(4)	1.547(12)
C(7)–C(82)	1.549(4)	1.582(14)

Table IV. Selected Bond Angles (deg) with esd's in Parentheses

	2a	**2b**
(a) Bond Angles Involving Non-Hydrogen Atoms		
C(2)–C(1)–C(6)	110.6(3)	111.1(7)
C(2)–C(1)–C(11)	111.2(3)	110.0(8)
C(6)–C(1)–C(11)	110.9(3)	112.2(8)
C(1)–C(2)–C(3)	124.9(3)	125.9(10)
C(2)–C(3)–C(4)	124.3(3)	122.7(9)
C(3)–C(4)–C(5)	110.7(3)	111.5(7)
C(3)–C(4)–C(7)	113.4(3)	112.3(7)
C(5)–C(4)–C(7)	111.4(3)	111.6(8)
C(4)–C(5)–C(6)	124.8(3)	124.5(9)
C(5)–C(6)–C(1)	124.3(3)	123.8(9)
C(1)–C(11)–C(21)	119.6(3)	119.9(8)
C(1)–C(11)–C(61)	122.2(3)	120.8(8)
(b) Bond Angles to Hydrogen[a]		
C(1)–C(2)–H(2)	117.3(3)	117.1(9)
C(1)–C(6)–H(6)	117.8(3)	118.1(8)
C(2)–C(1)–H(1)	106.6(3)	107.5(8)
C(2)–C(3)–H(3)	118.1(3)	118.6(10)
C(3)–C(2)–H(2)	117.8(3)	116.9(11)
C(3)–C(4)–H(4)	104.7(3)	104.4(8)
C(4)–C(3)–H(3)	117.6(3)	118.6(9)
C(4)–C(5)–H(5)	117.4(3)	117.8(8)
C(5)–C(4)–H(4)	104.9(3)	106.1(8)
C(5)–C(6)–H(6)	117.8(3)	118.0(9)
C(6)–C(1)–H(1)	106.8(3)	106.8(9)
C(6)–C(5)–H(5)	117.8(3)	117.7(9)
C(7)–C(4)–H(4)	111.2(3)	110.6(7)
C(11)–C(1)–H(1)	110.6(3)	108.9(7)

[a] Angles about the cyclohexadiene ring. (Note that C–H bond lengths were constrained to 1.00(1) Å.)

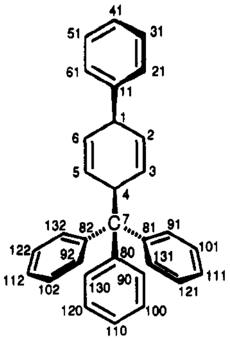

Figure 2. Numbering scheme used for the crystallographic data.

4′-bromo derivative **2b** are shown in Figures 3 and 4, respectively. Comparison with the structures of the stereoisomers **1a** and **1b** (Figure 5) immediately reveals what is perhaps the single most important (and remarkable) observation in this work, namely that the gross features of all five structures are almost identical, despite the change in the relative dispositions of the phenyl and trityl groups. The conformation of the cyclohexadiene boat remains close to planar in all five structures with α^{16} lying in the range ±172° to 180°, and this ring simply behaves as a structural hinge between the aryl and trityl groups.

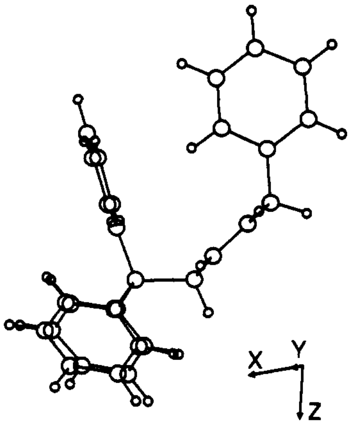

Figure 3. General view of the asymmetric unit of **2a**.

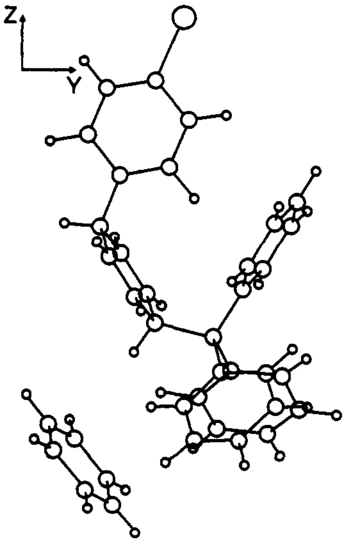

Figure 4. General view of the asymmetric unit of **2b**, showing the location of the benzene of solvation.

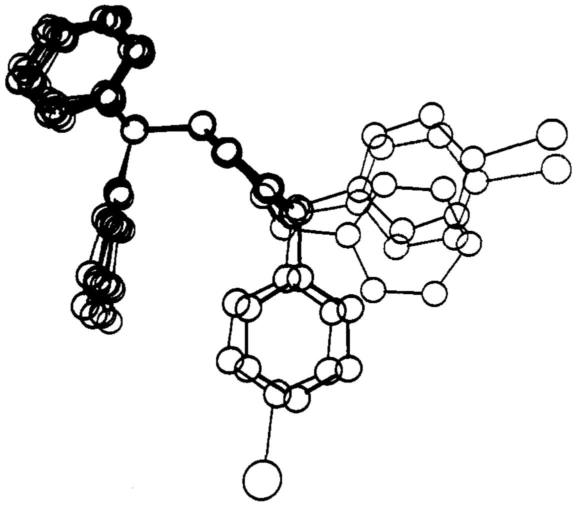

Figure 5. Overlay comparing the solid-state conformations of the *trans*- and *cis*-1,4-dihydro-4-tritylbiphenyls **1**[2] and **2** (**2a** in bold).

Both *cis* isomers **2** adopt similar conformations in which the substituents are placed pseudoequatorially. In the parent hydrocarbon **2a**, the cyclohexadiene ring has $\alpha_{\mathrm{mean}} = -175°$ but is slightly distorted being more puckered at C-4, the carbon atom bearing the trityl substituent. A similar situation is found in **2b**, but in this case the cyclohexadiene ring is almost planar, $\alpha_{\mathrm{mean}} = -178°$. In this latter structure the asymmetric unit also contains one molecule of benzene, the crystallizing solvent.[17] It should also be noted that data from the crystal of **2b** were collected at −130 °C.

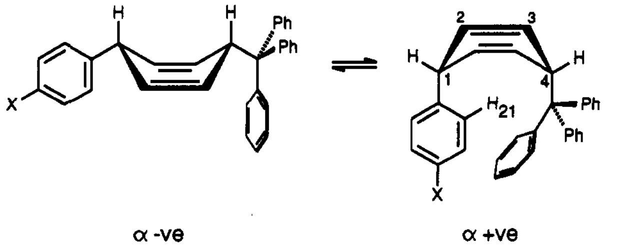

Figure 6. Effect of boat–boat inversion in the *cis*-dihydrotritylbiphenyls **2**.

For both *cis* isomers **2** the isolated phenyl substituent is oriented along the C(1)–C(4) axis of the dihydroaromatic ring in a manner similar to that found in each of the *trans* structures **1**.[2] However, this has important implications for the *cis* derivatives since when the cyclohexadiene ring is relatively planar, the ortho proton, H_{21} in **2** (see Figure 6), is forced into the π-cloud of one of the phenyl rings of the trityl substituent (see Figures 3 and 4). Indeed, in the parent hydrocarbon **2a** the proton H_{21} is located only 2.55 Å above the best plane of the remote benzene ring, while for **2b** this separation is 2.48 Å.[18] This feature is particularly significant in explaining unusual aspects of the ^{1}H NMR spectra of solutions of **2a** and **2b** (see below). As the cyclohexadiene ring conformation is changed from a planar to a more puckered geometry in which the substituents are located pseudoequatorially, the distance between the proton H_{21} and the π-cloud is increased (Figure 6). The solid-state conformation of the bromo derivative **2b** (where $\alpha = -178°$) forces the hydrogen atom H_{21} and the benzene ring to lie within the sum of their van der Waals radii (2.9 Å) (though it is not clear that a typical benzene radius of 1.7 Å is appropriate for the center of an aromatic torus). Inversion of the ring conformation so that the substituents are placed pseudoaxial exacerbates this problem, and it would seem that the solid-state conformations of **2** must approach one limit for conformational flexing of the *cis*-dihydrotritylbiphenyl skeleton. It should also be noted that the phenyl and trityl substituents adopt essentially identical orientations relative to the cyclohexadiene ring in both the *trans*-isomers **1** and the *cis*-isomers **2** (see Figure 5).[2,9]

A more detailed description of the cyclohexadiene ring geometry is conveniently provided using the torsion angles ϕ_e and ϕ_a in Figure 7. These indicate the positions of the

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(16) The angle α is that between the best planes defined by C_1–C_2–C_3–C_4 and C_4–C_5–C_6–C_1 in Figure 1; it is *positive* when the Ph_3C– group is pseudoaxial. Figure 1 also shows the pseudoaxial, Ψ_a, and pseudoequatorial, Ψ_e, positions in a boat cyclohexa-1,4-diene ring.

(17) The presence of one molecule of benezene per molecule of **2b** in the crystal is also evident from the relative integration values for aromatic and other reasonances in solution ^{1}H NMR spectra of this compound.

(18) If this benzene ring is regarded as the *xy* plane, then the proton H(21) lies at $x = 0.30$, $y = 0.00$, $z = 2.55$ Å and C(21) at $x = 0.64$, $y = 0.10$, $z = 3.49$ Å with respect to its centroid in **2a**; with H(21) at $x = 0.05$, $y = 0.04$, $z = 2.48$ Å and C(61) at $x = 0.33$, $y = 0.32$, $z = 3.46$ Å in **2b**, based on a C–H bond length of 1.0 Å.

(19) Calculations were performed using the CRYSTALS suite of programs: Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, Oxford University: Oxford, U.K. Figures were drawn using Chem-X (Chemical Design Ltd., Oxford, U.K.).

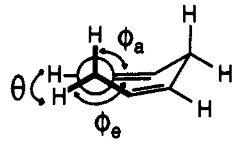

Figure 7. Torsion angles about a cyclohexa-1,4-diene ring.

Table V. Comparison of Key Structural Data for the *trans*- and *cis*-1,4-Dihydro-4-tritylbiphenyls 1 and 2, Respectively

angle (deg)/ distance (Å)	**1a**	**1b** monoclinic	**1b** orthorhombic	**2a**	**2b**
(a) Dihydrobenzene Ring Geometry (Average Values)[a]					
α^{16}	172	−173	−176	−175	−178
$\theta[H_1]$[b]	42.3	74.0	75.2	68.2	60.7
$\theta[H_4]$[b]	81.5	50.3	54.0	74.1	72.3
$\phi[C_{11}]$[b]	129.6	118.1	120.3	126.3	121.3
$\phi[C_7]$[b]	116.8	133.7	127.4	132.9	132.4
$\phi[H_1]$[b]	127.2	109.6	113.2	113.1	119.8
$\phi[H_4]$[b]	110.6	122.9	121.0	106.2	107.4
(b) Key Bond Lengths and Interatomic Distances (Average Values)[a]					
C_4–C_7	1.59	1.59	1.59	1.58	1.61
C_1–C_{11}	1.52	1.53	1.52	1.52	1.53
H_{21}–π^{18}				2.55	2.48

[a] Values were determined in CRYSTALS.[19] [b] $\theta[X_1]$ is the dihedral angle defined by X(1)–C(1)–C(2)–H(2) or X(1)–C(1)–C(6)–H(6), X = H, C; $\theta[X_4]$ by X(4)–C(4)–C(3)–H(3), X(4)–C(4)–C(5)–H(5), etc.; $\phi[X_{11}]$ by X(11)–C(1)–C(2)–C(3) or X(11)–C(1)–C(6)–C(5), etc.; see Figures 6 and 7.

pseudoequatorial and pseudoaxial substituents respectively, relative to the plane defined by one of the π-bonds in the dihydrobenzene ring. The torsion angles found in **2a** and **2b** are shown in Table V.

Another interesting feature of these structures lies in the extremely long carbon–carbon single bond C(4)–C(7) which links the central carbon atom of the trityl substituent and the dihydroaromatic ring (N.B. the *cis* isomers **2** are thermally stable in solution (DMSO) up to *ca.* 400 K). For example, in **2b** this bond is slightly over 1.61 Å which compares with values of *ca.* 1.59 Å for the corresponding bond in the *trans* isomers[2] (see Table V). These very long carbon–carbon single bonds are comparable with those found in *cis*-1,2-bis(methoxycarbonyl)-1,2-bis(*p*-nitrophenyl)cyclobutane (1.606(3) Å),[20] 4,4′-dihydro-1,3-bis(dimethylamino)-4,4′-biisoquinolyl bis(perchloate) (1.597(4) Å),[21] and 1.622–1.626 Å found in some steroidal structures.[22] The C–Ph bonds of the trityl groups of **2a** and **2b** lie within the range 1.53–1.58 Å, values which are close to those previously reported for tetraphenylmethane (1.553 Å[23]).

Comparison of the temperature factor data for the two structures **2a** (room temperature) and **2b** (143 K) as expected reveals significantly reduced motion in the latter structure. In both cases that for H_{21} has a large amplitude along the y axis ($> z > x$) and C_{110}, C_{91}, and C_{132} show rather large thermal amplitudes in the x direction. About the cyclohexadiene ring C_4 vibrates isotropically, whereas C_1 wobbles somewhat less in the yz plane, and C_7 is relatively immobile. We note that the temperature factors $U[11]$ are slightly negative for atoms C_{82} and C_{122} in the more highly absorbing bromo structure **2b**.

Figure 8 shows the similarities of the packing arrangements found in the structures of **2a** and **2b**. In both cases the molecules are arranged in columns perpendicular to the isolated 1-phenyl ring plane (Figure 8b,d). However, the need to accommodate the 4′-bromo substituent in this ring in **2b** leads to spaces in which the benzene of solvation is located. The channels running parallel with the molecular columns thus contain alternating benzene rings and bromo substituents.

^{1}H NMR Spectroscopic Studies. A detailed analysis of the nonaromatic regions of the ^{1}H NMR spectra of **2a**, supported by selective decoupling and COSY experiments, leads to the values of the coupling about the cyclohexadiene ring shown in Table VI. The homoallylic coupling constant $J_{1,4\text{-cis}}$ has a value typical for an interaction between two *cis*-protons placed in a pseudoaxial sense in a relatively planar cyclohexadiene ring.[24] The vicinal and allylic couplings also support this interpretation, particularly when compared with the corresponding values for the *trans* isomers (see Table VI), these latter being regarded as consistent with an apparently planar ring geometry.

The other important and unusual feature of the ^{1}H NMR spectra of both **2a** and **2b** lies in the unusually high-field aromatic resonance at *ca.* δ 6.3 ppm for **2a** (δ 6.15 ppm for **2b**) with an integral corresponding to two protons. This was noted in the original study of these compounds[3] but was not satisfactorily explained. In the spectrum of the parent hydrocarbon **2a** this appears as a complex multiplet which simplifies to half of an apparent AB quartet (J = 8.6 Hz) in the spectrum of **2b**. Accordingly, this signal must be assigned to either the ortho or the meta protons in the isolated aryl substituent attached to C_1 of the cyclohexadiene ring (see Figure 6). There is no significant change in this region of the spectrum when a solution of **2a** in DMSO-d_6 is heated to *ca.* 403 K so that this feature does not result from slow rotation effects on the NMR time scale. However, when a solution of **2a** in CD_2Cl_2 is cooled to 203 K, this two-proton aromatic resonance is seen to move upfield by *ca.* 0.6 ppm. Slight changes are also observed in the chemical shifts of the peaks assigned to H_1 and H_2 in both *cis* and *trans* isomers, though in these cases the resonance moves *downfield* (see Figure 9a).

As the sample is cooled, considerable line-broadening occurs, but no coalescence phenomena associated with "freezing out" of the rotation of the isolated phenyl substituent about the C_1–C_{11} bond are observed. Significant line broadening is also found in low temperature (<−50 °C) spectra of solutions of the *trans* isomers **1a** and **1b**, but this does not prevent a measurement of the homoallylic coupling at low temperatures. Very little change is noted in the magnitude of $J_{1,4\text{-trans}}$ (7.7 Hz) as sample **1** is cooled from 293 to 213 K. In contrast, when a sample of **2a** in $CDCl_3$ solution is cooled from 295 to 213 K, $J_{1,4\text{-cis}}$ is observed to decrease from 10.5 to 10.0 Hz. While the spectral lines are sufficiently broad at lower temperatures to impede satisfactory measurement of the vicinal and allylic couplings, it is notable that the magnitude of $J_{2,3}$ remains unchanged over this temperature range (see Figure 9b).

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(20) Carr, P.; Finney, J. L.; Lindley, P. F.; De Titta, G. T. *Acta Crystallogr.* **1977**, *B33*, 1022.

(21) Boyd, G. V.; Hammerich, O.; Lindley, P. F.; Mitchell, J. C.; Nicolaou, G. A.; Walton, A. R. *J. Chem. Soc., Chem. Commun.* **1985**, 885.

(22) Smith, G. W. *Acta Crystallogr.* **1975**, *B31*, 522,526. van Schalkwyk, T. G. D.; Kruger, G. J. *Acta Crystallogr.* **1974**, *B30*, 2261. See also: Beech, S. H.; Bauer, J. Y. *J. Am. Chem. Soc.* **1942**, *64*, 1142.

(23) Robbins, A.; Jeffrey, G. A.; Chesick, J. P.; Donohue, J.; Cotton, F. A.; Frenz, B. A.; Murillo, C. A. *Acta Crystallogr.* **1975**, *B31*, 2395–2399.

(24) $J_{1,4\text{-cis}}$ = *ca.* 12 Hz for α = *ca.* 145° and ca. 9.5 Hz for α = 180°, no allowance being made for substituent effects; see: Grossel, M. C. *Tetrahedron Lett.* **1980**, *21*, 1075–1078.

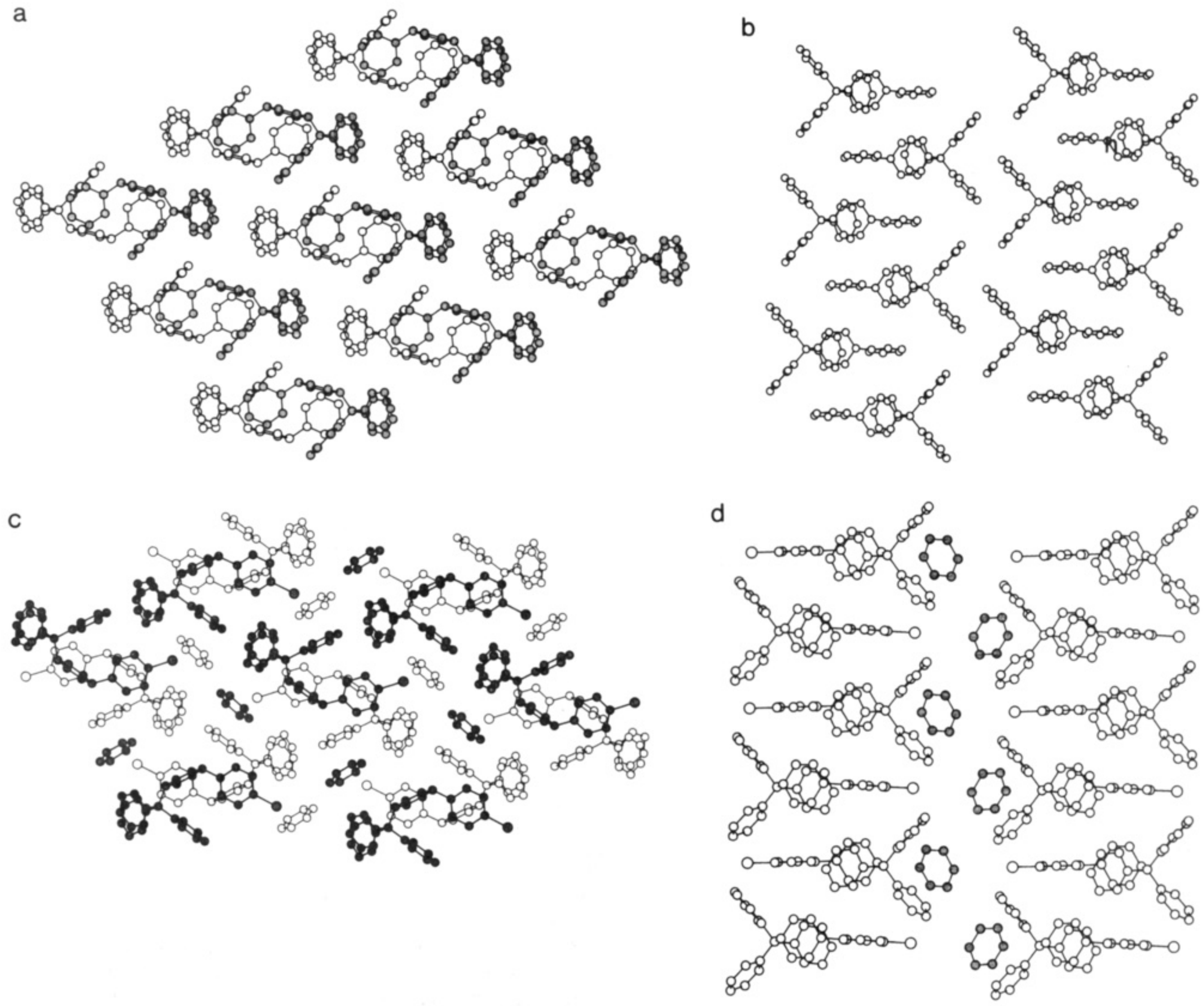

Figure 8. Packing arrangements for the *cis*-dihydrotritylbiphenyls **2**: (a and b) *cis*-1,4-dihydro-4-tritylbiphenyl (**2a**) and (c and d) 4′-bromo-*cis*-1,4-dihydro-4-tritylbiphenyl (**2b**).

Table VI. ¹H NMR Coupling Constants (±0.1 Hz) about the Dihydrobenzene Rings of 1 and 2

coupling (Hz)	2a	1a
$J_{1,2}$	2.4	2.9
$J_{1,3}$	−2.6	−2.2
$J_{1,4}$	10.5	7.7
$J_{2,3}$	10.8	10.7
$J_{2,4}$	−2.5	−2.1
$J_{3,4}$	2.8	3.3

The X-ray structures provide an explanation for the unusual behavior of the high-field aromatic absorption, since both **2a** and **2b** adopt solid-state conformations in which the aromatic proton H_{21} lies *ca.* 2.5 Å above the center of the aromatic ring defined by C_{80}–C_{130} (see Figures 3 and 4). In order to establish how the position of this proton is affected by the cyclohexadiene ring conformation, we have mapped the motion of H_{21} relative to the center of this aromatic ring as the cyclohexadiene ring is inverted, using an idealized geometry based on crystallographic data for **2a** and **2b**. This suggests that when $\alpha = -175°$ H_{21} will be *ca.* 2.8 Å above the aromatic ring compared with a distance of *ca.* 2.5 Å observed for **2a** and **2b**.[18] The model allows us to map the variation of the chemical shift of this proton with different cyclohexadiene geometries[25–27] (see Figure 10).[28] It will be seen that greater shielding of the aromatic protons at lower temperatures is entirely consistent with a flattening of the time-averaged cyclohexadiene conformation, in which both substituents remain pseudoequatorial. The same conclusions can be drawn from the decreased *cis*-homoallylic coupling constant observed at low temperatures.

Comparison with Conformations of Other Cyclohexa-1,4-diene Derivatives. Molecular mechanics calculations on the structures and conformations of 1,4-dihydrobenzene (cyclohexa-1,4-diene) (**3**)[8,29] and its 1-alkyl derivatives, e.g., **5a** and **5b**,[30] suggest that these molecules

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[25] Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

[26] Haigh, C. W.; Mallion, R. B. *Org. Magn. Reson.* **1972**, *4*, 203.

[27] Data for this plot were kindly provided by R. B. Mallion. For a detailed discussion of the relative merits of the Johnson–Bovey and Haigh–Mallion tables see: Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 303. Mallion, R. B. Nuclear Magnetic Resonance Spectroscopy in Molecular Biology. In *Proceedings of the 11th Jerusalem Symposium on Quantum Chemistry and Biochemistry*; Pullman, B., Ed.; Reidel: Dordrecht, The Netherlands, 1978; pp 183–191. Mallion, R. B. *J. Chem. Phys.* **1981**, *75*, 793–797.

[28] The values presented in Figure 10 make no allowance for rotation of the phenyl substituent in **2**. This effect would halve the predicted shifts.

[29] Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 284.

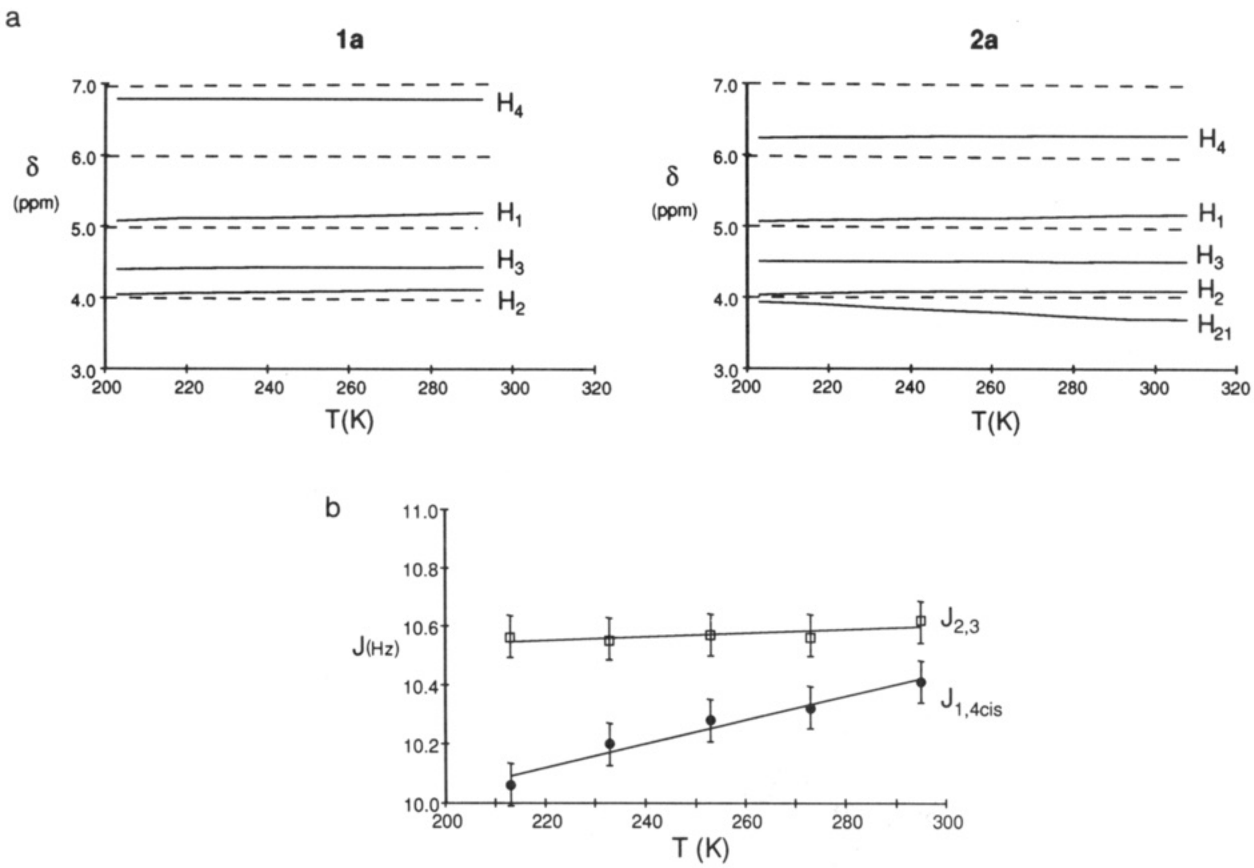


Figure 9. Temperature dependance of (a) proton chemical shifts in *trans*-1,4-dihydro-4-tritylbiphenyl (**1a**) and *cis*-1,4-dihydro-4-tritylbiphenyl (**2a**) (solutions in CH_2Cl_2; numbering as in Figure 7) and (b) the vicinal ($J_{2,3}$) and homoallylic ($J_{1,4}$) couplings about the cyclohexadiene ring of **2a** (in $CDCl_3$ solution) (solutions in CH_2Cl_2; numbering as in Figure 7).

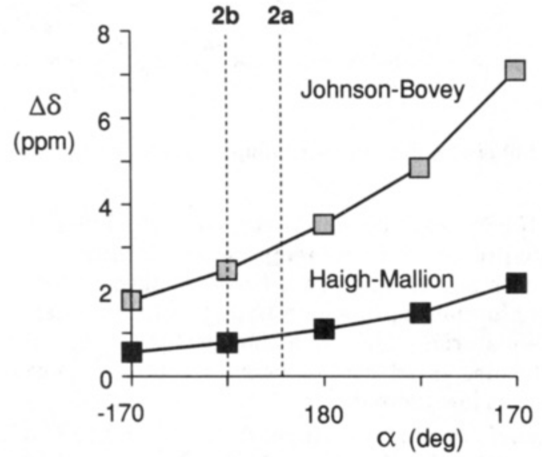
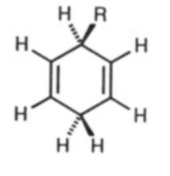


Figure 10. Predicted variation of shielding of H_{21} with dihydrobenzene geometry in **2a** and **2b** (N.B. the dashed lines indicate actual crystallographic geometries).

exist in single energy-minimum potential energy wells. That for the parent hydrocarbon is centered about a planar ring conformation, but distortion to a boat geometry having α = 160° results in an increase in energy of only 1 kcal mol^{-1}. The introduction of a 1-methyl substituent **5a** slightly puckers the ring, and further increases in substituent steric bulk lead to an even greater degree of folding. In each case the substituent is placed pseudoaxial to reduce steric interactions with the adjacent vinyl CH groups. Of particular interest is the prediction that a 1-phenyl substituent **5c** has a relatively small effect on the ring conformation and the phenyl substituent is preferentially oriented along the C(1)–C(4) axis of the dihydroaromatic ring—a result that is in accord with our crystallographic data on the isomeric dihydrotritylbiphenyls.



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a, R = Me, α_{calc} = 174°
b, R = Bu^t, α_{calc} = 160°
c, R = Ph, α_{calc} = 176°

Our studies of the dihydrotritylbiphenyls provide an interesting insight into these substituent effects, for while the *trans* isomers **1** do not show a clear preference for pseudoaxial substituent disposition despite the apparent bulk of the trityl group, such substituent location in the *cis* isomers **2** is impeded by their mutual steric interference. Thus, for the latter isomers the preferred ring conformation represents a compromise between this effect and torsional interactions. The temperature dependence of the phenyl proton chemical shift and the homoallylic coupling constant for **2** both suggest an effective flattening of the cyclohexadiene ring on cooling. These observations would seem to indicate a reduced population of higher vibrational energy levels at lower temperatures and a severely distorted potential energy well (see Figure 6).

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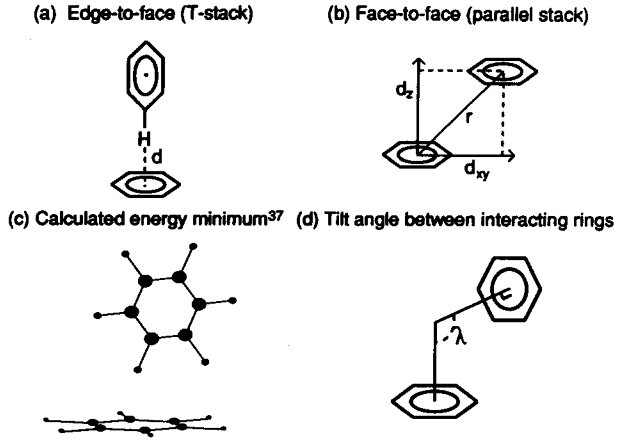
(30) Raber, D. J.; Harlee, L. E.; Rabideau, P. W.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2843–2847. Rabideau, P. W.; Wetzel, D. M.; Paschal, J. W. *J. Org. Chem.* **1982**, *47*, 3993–3994.


(a) Edge-to-face (T-stack) (b) Face-to-face (parallel stack)

(c) Calculated energy minimum[37] (d) Tilt angle between interacting rings

Figure 11. Favored geometries for aromatic π–π interactions: (a) Edge-to-face (T-stack); (b) face-to-face (parallel stack); (c) calculated energy minimum;[37] (d) tilt angle between interacting rings.

Edge-to-Face Aromatic Association (σ-π and π–π Aromatic Interactions). It is clear from Figure 5 that the solid-state conformations favored by **2a** and **2b** are typical of those adopted by other 1,4-dihydrotetraphenylmethanes. The close association of the remote aryl ring containing H_{21} and the π-cloud of ring-(C_{80}–C_{130}) is therefore all the more remarkable since there is no obvious restriction on further puckering of the cyclohexadiene ring to relieve such structural compression. It is also evident from the NMR data that this interaction occurs in solution and such a geometry cannot therefore simply be ascribed to crystal packing forces. It would therefore seem reasonable to suggest that there is an intramolecular attractive edge-to-face aromatic association present in **2a** and **2b** which helps control their conformations.

Edge-to-face aromatic interactions, which are thought to be electrostatic in origin, have been identified as important in protein structure,[11,31,32] and in the packing of simple aromatic molecules.[33] Edge-to-face ("T-stack") and face-to-face (parallel stack)[34] geometries represent two extremes of aromatic association (Figure 11a,b, respectively). Theoretical studies[35,36] on the interaction of two benzene rings have suggested an energy minimum when the two rings are perpendicular, but more recent calculations by Jorgensen and Severance[37] favor a slightly tilted T-structure (Figure 11c; $r = 4.99$ Å) as the global minimum for benzene–benzene interaction in the gas phase. The geometries of the edge-to-face interactions in **2a** and **2b** lie very close to this latter energy minimum (Table VII). In each case the relative orientation of the rings is slightly twisted in the manner observed by Gould and co-workers[32] who suggest that such a distortion improves interaction between the coordinating proton and the π-cloud. An analysis of crystal structure data relating to the association of aromatic side chains in proteins also indicates a preference for an offset geometry with a separation (centroid-to-centroid) $3.4\text{Å} < r < 6.5\text{Å}$ and a dihedral angle $\lambda > 50°$ (Figure 11).[11,31]

Table VII. Geometry of the Edge-to-Face Interaction in the *cis*-1,4-Dihydro-4-tritylbiphenyls 2 (See Figure 11)

	r (Å)	λ (deg)	d (Å) centroid → H_{21}	d (Å) centroid → C_{21}
2a	4.48	97.9	2.57	3.55
2b	4.83	100.2	2.48	3.49
calculated optimum[37]	4.99			

A number of other examples to edge-to-face aromatic interactions in the solid state have been reported[38] though in such cases the (C)H–π(centroid) separation is generally rather greater (usually *ca.* 2.80 Å). However, Hamor, Jennings, and co-workers[39] have observed a closer interaction (2.7 Å) in the *Z*-isomer of *N*-[1-(1-naphthyl)-ethylidene]-1-phenyl-2-propylamine in the solid state. This isomer is also favored in solution, and NMR experiments suggest that in this case the attractive edge-to-face interaction may be worth (*i.e.*, $\Delta H =$) *ca.* 5 kJ mol^{-1}, a value similar to that estimated for the stabilization resulting from edge-to-face association of two aromatic side chains in a protein.[31] Stoddard has recently reported a very close (2.54 Å) intermolecular interaction in the 1:1 complex formed from a cyclobis(paraquat-*p*-phenylene)-tetracation cyclophane and 1,5-dimethoxynaphthalene.[40]

Acknowledgment. Thanks are due to Dr. H. S. Rzepa (Imperial College, University of London), Dr. J. K. M. Saunders (University of Cambridge), Professor M. J. Perkins (Royal Holloway and Bedford New College, University of London) and Dr. R. B. Mallion (The King's School, Canterbury, Kent) for helpful comments.

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(31) Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995.

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(37) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

(38) Other examples of aromatic edge-to-face interactions [H-to-centroid distances (r in Figure 11) or centroid-to-centroid (d in Figure 11) distance in brackets] include the following. (i) Intramolecular: (a) Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1070–1072 ($r = 2.8$ Å). (b) Ashton, P. R.; Chrystal, E. J. T.; Mathias, J. P.; Parry, K. P.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Tetrahedron Lett.* **1987**, *50*, 6367–6370 ($r = 2.81$ Å). (ii) Intermolecular: (c) Moody, G. J.; Owusu, R. K.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Thomas, J. D. R.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 890–892. (d) Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1550–1553 ($d = 4.8, 5.1$ Å). (e) Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396–1399. (f) Ortholand, J. Y.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1394–1395 ($d = 5.17$ Å). See also: (f) Jagg, P. N.; Kelly, P. F.; Rzepa, H. S.; Williams, D. J.; Woolins, J. D.; Wylie, W. *J. Chem. Soc., Chem. Commun.* **1991**, 942–944.

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(41) The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.