that for C_1–C_2 so that our measurements with their large uncertainties provide no experimental evidence on the point. Some supporting evidence is available in the results of X-ray diffraction investigation of [4.4.2]propella-3,8-diene-11,12-dione,[15] a molecule with a CBD subunit, and *trans*-3,4-di-*tert*-butylcyclobutane-1,2-dione[17] The first of these has distances of 1.551 (3) Å, 1.534 (3) Å, and 1.572 (3) Å for the bonds corresponding to C_1–C_2, C_1–C_4, and C_3–C_4 in CBD; the second has distances of 1.560 (3) Å, 1.527 (2) Å, and 1.560 (3) Å. Thus the C_1–C_2 type distance is in each case longer than normal and the C_1–C_4 type smaller than its neighbors.

The C=O bond length in CBD (r_g = 1.194 (2) Å) is about 0.02 Å shorter than those found in aliphatic ketones. We attribute the shortening to diminished nonbond repulsions involving the C=O and adjacent bonds, and the oxygen atom and geminal carbons. Since the proximity of the opposing bonds and atoms depends most importantly on the CCC bond angle at the base of the carbonyl group, the C=O bond length should decrease as this angle decreases. This is observed to be the case: In CBD and in the similar propelladienedione and *tert*-butyl compounds mentioned above the C=O bond lengths are respectively 1.194 (2) Å, 1.192 (2) Å, and 1.191 (2) Å, (C=O base angles $\sim$90°); and in 2-cyclopentane-1,4-dione,[18] and *p*-benzoquinone[19] (C=O base angles respectively 108.2 (4)° and 118.1 (3)°) the C=O bond lengths are 1.208 (2) Å and 1.225 (2) Å.

The measured amplitudes of vibration are generally in good agreement with those calculated from our assumed force field. The agreement is poorest for the ring bonds. However, we attribute no special significance to this fact because the values of these amplitudes are highly correlated with the values of the distances which bear large uncertainties.

Acknowledgment. We are grateful to Professor J. M. Conia for providing us with the sample of CBD, to Lise Hedberg for advice with the force field calculations, and to the National Science Foundation which supported this work through Grant No. CHE 74-13527 and No. CHE 78-04258.

Supplementary Material Available: Tables of total intensities, final backgrounds, average molecular intensities, symmetry coordinates, force constants, and calculated frequencies (11 pages). Ordering information is given on any current masthead page.

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Conformational Studies of Dihydrotetraphenylmethanes. 1. X-ray Crystallographic and Solution ^{1}H NMR Studies of *trans*-1,4-Dihydro-4-tritylbiphenyl and Its 4′-Bromo Derivative: Boat–Boat Inversion in a Congested Cyclohexa-1,4-diene

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Contribution from the Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, England, and the Department of Chemistry, Bedford College University of London, Regent's Park, London, NW1 4NS, Enland. *Received January 9, 1981*

Abstract: Single-crystal X-ray diffraction measurements on 1,4-dihydro-4-tritylbiphenyl and on two crystal modifications of its 4′-bromo derivative reveal that the three molecular structures are remarkably similar, the only variation being the sense of puckering of the cyclohexa-1,4-diene ring. Crystals of 1,4-dihydro-4-tritylbiphenyl are orthorhombic, space group *Pnam*, $Z = 4$, lattice parameters a = 10.083 (1), b = 12.128 (2), c = 18.247 (5) Å; 1201 independent reflections gave a final R of 0.050. The orthorhombic form of 4′-bromo-1,4-dihydro-4-tritylbiphenyl has space group *Pnam*, $Z = 4$, a = 13.012 (2), b = 17.264 (3), c = 10.431 (1) Å; 894 independent reflections gave a final R of 0.046. In contrast, the monoclinic form has space group *Pc*, $Z = 2$, a = 9.011 (1), b = 16.187 (3), c = 8.463 (2) Å, β = 108.98 (1)°; 1205 independent reflections gave a final R of 0.041. Comparison of the three structures suggests that the cyclohexa-1,4-diene ring in 1,4-dihydro-4-tritylbiphenyls exists in either a shallow potential well with a single minimum corresponding to an essentially planar cyclohexadiene geometry or a double-minimum potential well in which there is rapid boat inversion. There is no evidence for the highly puckered boat conformation previously suggested. A reassessment of the ^{1}H NMR data for these compounds also supports this view. The close similarity of the molecules analyzed provides a rare opportunity for the evaluation of the relative importance of intramolecular interactions and intermolecular or "packing" forces on the solid-state geometries of these molecules. It is concluded that while the steric requirements of the dihydrotetraphenylmethane molecule prescribe an essentially planar cyclohexa-1,4-diene geometry, the exact conformation of the ring is controlled by crystal packing requirements.

Introduction

Long-range ^{1}H NMR coupling constants provide a convenient probe into the solution conformations of organic molecules.[1] In principle, for a derivative of cyclohexa-1,4-diene (**1**),[2] an analysis of vicinal couplings could indicate the overall ring conformation. However, such couplings are generally small when saturated carbon centers are involved, and the effect of large variations in ring geometry may be reflected by only slight changes in the magnitudes of such short-range interactions.[3] Allylic couplings,[4]

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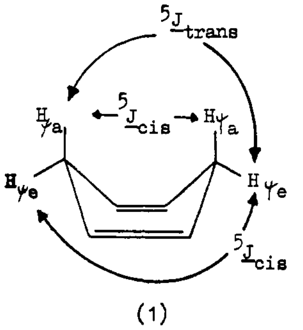
over four bonds, are potentially more useful. For cyclohexadiene derivatives there is good agreement between observed and calculated coupling constants so that measured values may be interpreted in terms of molecular geometry.[5-7] However, these interactions are relatively insensitive to the extent of ring puckering when this becomes large,[5] and, more seriously, the small values of such coupling constants limit the precision with which they can be determined experimentally. Considerable emphasis has therefore been placed on the interpretation of homoallylic couplings.[8]

Homoallylic coupling occurs over five bonds and thus encompasses the entire cyclohexadiene ring framework. It attains a maximum value when the bonds to the coupled protons are nearly parallel.[9-11] Fortunately, this maximum is apparently of the order of 12 Hz[6,8,11,12] which is substantially larger than the maximum allylic coupling (ca. 3 Hz) and can be measured experimentally with good precision. Further, this coupling varies relatively uniformly with the extent of ring puckering which can be defined by the angle α.[13] We may distinguish four coupling pathways [see **1**], though for a symmetrically puckered ring the two trans pseudo-axial–pseudo-equatorial couplings are identical.



(1)

For a planar cyclohexa-1,4-diene, $^5J_{cis}$ is thought to be ca. 9.2–9.6 Hz,[8,10,11,14,15] rising to a maximum of ca. 12 Hz for α = ca. 145°.[8,9,11,12] $^5J_{trans}$, however, is significantly smaller and values in the range 7.1–8.04 Hz have been reported for supposedly planar derivatives.[15] In addition $^5J_{trans}$ falls with increasing ring puckering, having a value of 4.3 Hz when α = ca. 145°.[12] Since $^5J_{cis}$ and $^5J_{trans}$ vary in different senses with α, the ratio of the two can provide a more accurate indicator of the ring conformation than the actual magnitudes of the couplings themselves.[9,11,15] Calculated homoallylic coupling constants as yet show only a qualitative agreement with experiment.[9,10,11,15,16] We have determined the exact molecular geometries of systems in which homoallylic coupling may be accurately measured. This has allowed us to establish a direct correlation between coupling constant values and dihydroaromatic ring conformations in rigid structures. However, we have also found that solid-state conformations of flexible, 1,4-dihydrobenzoic acids are closely related to those adopted in solution[7] despite possible perturbations arising from packing effects in the crystal.

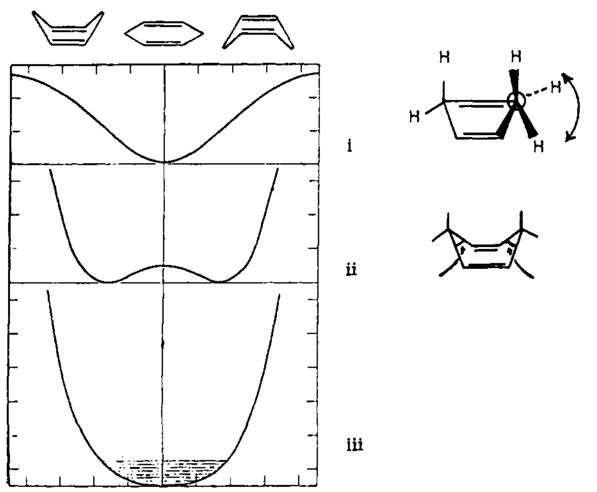


Figure 1. Factors controlling the shape of the cyclohexa-1,4-diene potential energy well (after Laane and Lord[17]): (i) torsional strain, (ii) angle strain, (iii) overall effect.

One effect which may complicate the interpretation of long time-scale spectroscopic data (e.g., ^{1}H NMR spectra) is that due to thermal vibration.[9,14] The shape of the potential well occupied by the cyclohexa-1,4-diene ring is governed mainly by two factors, namely, torsional strain about the C(1)–C(2), etc., bonds and angle strain (see Figure 1).[17] The former favors a planar structure while the latter is minimized in a boat conformation having α = ca. 150°. The combination of these two effects apparently produces a shallow single-minimum potential energy well in which the lower vibrational levels may be readily populated thermally. Indeed far-IR measurements on cyclohexa-1,4-diene itself[17] suggest that at room temperature in the gas phase there is a significant population of energy levels corresponding to large amplitude boat ⇌ boat vibrations about a planar energy-minimum geometry. A similar situation is believed to exist in solution,[14] for the magnitude of $^5J_{trans}$ about 1,4-dihydrohexadeuteriobenzene varies with temperature in a manner which suggests that the population of the higher vibrational levels is reduced at lower temperatures, resulting in a more nearly planar time-averaged geometry.[14] The introduction of substituents will distort this picture and may lead to a steepening of the potential well, or a shift in the energy minimum to a puckered conformation (as, for example, in 2,6-dimethyl-1,4-dihydrobenzoic acid[7]), or give rise to a double minimum potential energy surface.[18,19] This latter situation is found for 1,4-dihydronaphthalenes and 9,10-dihydroanthracenes.[8,9,20-22]

However, substituents may also directly affect the magnitude of the observed homoallylic coupling through electronic interactions.[4,7,11,12] C-1 substitution exerts little influence on the homoallylic couplings,[6,7] but substituents on the vinylic carbon atoms may modify the π-electron density by mesomeric or inductive effects.[7,23] Such influences have served merely to confuse the experimental interpretations.[7,9,15] A large single substituent can also greatly modify the shape of the cyclohexa-1,4-diene potential energy well. For example, the bulky trityl group could act as a conformational lock, and it has been suggested[24] that with this

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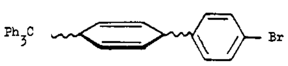
group located at C-1, a cyclohexadiene ring would be forced into a highly puckered boat geometry with the trityl group adopting a pseudo-equatorial position. ^{1}H NMR data on several 1,4-dihydro-4-tritylbiphenyls were considered to support this view.[25] For example, the measured cis-homoallylic coupling for **2a** was reported to be ca. 11 Hz, a value which was thought to be consistent with a highly folded ring geometry.[25] In a more recent analysis of the spectrum of **2a**, however, a slightly smaller value of 10.5 Hz was found.[26] When this is compared with the corresponding couplings in hexadeuterio-1,4-dihydrobenzene (J_{cis} = 9.6 Hz)[27] and 1,4-dihydropentadeuteriobenzoic acid (J_{cis} = 9.2 Hz),[10] both of which are believed to be essentially planar, doubt is cast on the original suggestion that the dihydroaromatic ring is highly puckered in the dihydrotritylbiphenyls. Further, the spectra of the cis isomers **2a** and **3a** show a remarkably high-field two-proton aromatic absorption (at ca. τ 3.8) assigned[24] to the ortho protons of the isolated phenyl substituent, the presence of which cannot be convincingly explained through conformations in which the substituents are placed in a pseudo-equatorial environment.

(2) a, cis
b, trans



(3) a, cis
b, trans

In view of these ambiguities we have reexamined in detail the solution ^{1}H NMR spectra of the cis and trans isomers of 1,4-dihydro-4-tritylbiphenyl (**2**) and their 4′-bromo derivatives (**3**). We have also completed X-ray crystallographic studies on each of these materials. Preliminary reports of the results obtained for the cis and trans isomers of the parent hydrocarbon (**2**) have already appeared.[28,29] A particularly interesting feature of the crystal structure of the trans system (**2a**) is that, contrary to previous suggestions, the trityl substituent occupies a pseudo-axial position. For both isomers (**2**) the cyclohexadiene ring is almost planar (α_{cis} = ca. 175°,[28] α_{trans} = ca. 172° [29]). This is in marked contrast to the preliminary results of an earlier crystallographic study of the *trans*-4′-bromo derivatives (**3b**) in which the trityl substituent was found to occupy the *pseudo-equatorial* position of a more highly puckered cyclohexadiene ring (α = 165°).[25,30] In order to obtain more accurate structural information, we have reexamined the structure of this material. Further, as 4′-bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (**3b**) occurs in two distinct crystalline forms, it presents an unusual opportunity for examining the same molecular system in differing crystal environments.

In this paper we present the results of solution ^{1}H NMR studies and single-crystal X-ray measurements on both modifications of **3b** together with a detailed discussion of the results from the parent hydrocarbon (**2b**). Details of our work on the cis isomers **2a** and **3a** will follow.[31]

Experimental Section

The three sets of intensity data were collected on an Enraf-Nonius CAD-4F diffractometer[32] and, to optimize clarity, the basic experimental details for each analysis are tabulated in Table I. Salient features of the analyses are described below. All crystallographic calculations were performed on the Oxford University 1906A computer, using the CRYSTALS suite of programs.[33] Atomic scattering factors were taken from Cromer and Mann[34] and Spagna[35] (H only). In the final cycles of refinement, truncated three-term Chebyshev polynomials were used as the weighting schemes,[36] and, in all three cases, there was no evidence for secondary extinction and corrections for anomalous dispersion and absorption were unnecessary.

Table I. Experimental Details for the Three X-ray Crystallographic Analyses

	parent	OTBR	MTBR
photographic survey	yes	no	no
reflection conditions	$h0l$, $h = 2n$ $0kl$; $k + l = 2n$	$h0l$, $h = 2n$ $0kl$, $k + l = 2n$	$h0l$, $l = 2n$
crystal size	0.3 mm cube	0.25 mm cube	0.4 × 0.2 × 0.1 mm
unit cell definition[a]			
no. of reflections	22	25	22
θ range	$15 < \theta < 18°$	$16 < \theta < 18°$	$15 < \theta < 19°$
data collection			
max θ	25°	25°	26°
geometry mode	bisecting	bisecting	FLAT (see text)
scan type, $w - n\theta$, $n =$	1.67	1.33	1.33
no. of measd reflections	3072	3247	2924
data reduction			
corrections	Lorentz polarization	Lorentz polarization	Lorentz polarization
rejection criterion	$I \leqslant 3\sigma_I$[b]	$I \leqslant 3\sigma_I$	$I \leqslant 3\sigma_I$
no. of independent structure factor moduli	1201	894	1205
structure refinement			
least-squares matrix	full	full	block-diagonal
hydrogen refinement	xyz	xyz, U[iso]	xyz
no. of variables	200	220	365
no. of H constraints	66	65	96
R	0.0496	0.0458	0.0413
R_w	0.0575	0.0543	0.0443

[a] Data relating to the reflections used in the least-squares optimization of the unit cell parameters and orientation matrix. [b] σ_I refers to the standard deviation derived from the counting statistics.

(a) Parent Hydrocarbon: *trans*-1,4-Dihydro-4-tritylbiphenyl. Crystal data: $C_{31}H_{26}$ M = 398, orthorhombic, space group *Pnam*, a = 10.083 (1), b = 12.128 (2), c = 18.247 (5) Å, U = 2231.4 Å^3, Z = 4, d_o = 1.17, d_c = 1.18 g cm^{-3}, Mo Kα radiation, λ = 0.71069 Å, μ = 0.7 cm^{-1}.

The parent hydrocarbon (**2b**) was prepared as previously described[37] and recrystallized from light petroleum (bp 60–80 °C) in the form of rhombs. The systematic absences (Table I) are consistent with twoo space groups, *Pna*2$_1$ and *Pnam*. For structure solution, in the expectation that intramolecular symmetry would be absent, the noncentrosymmetric *Pna*2$_1$ was assumed and MULTAN[38] was partially successful in that approximate coordinates for nearly half the nonhydrogen atoms were extracted from one of the resulting phase sets. The remainder of the molecular skeleton was obtained by a combination of least-squares and Fourier calculations. After subsequent refinement, all the hydrogen atoms were located in a difference Fourier synthesis and their coordinates were included as variables in refinement, although subject to a series of Waser-type constraints on bond lengths and angles.[33,39] While refinement was possible, with only limited instability, in *Pna*2$_1$ it became clear that the structure possesses an intramolecular mirror plane. Indeed, Hamilton's significance test[40] shows that the noncentrosymmetric *Pna*2$_1$ is invalid even at the α = 0.5 level. The centrosymmetric *Pnam* was

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therefore taken to be the correct choice of space group. The final residuals were $R = 0.0496$ and $R_w = 0.0575$.

(b) Orthorhombic Form of 4′-Bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (OTBR). Crystal data: $C_{31}H_{25}Br$, $M = 447.4$, orthorhombic, space group *Pnam*, $a = 13.012$ (2), $b = 17.264$ (3), $c = 10.431$ (1) Å, $U = 2343.2$ Å^3, $d_c = 1.35$ g cm^{-3} for $Z = 4$; Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 18.8$ cm^{-1}.

A crystalline sample of the 4′-bromo derivative (**3b**) was kindly supplied by K. P. Lam and M. J. Perkins. This sample had been prepared as previously described[37] and was recrystallized from light petroleum (bp 60–80 °C). An optical examination of the sample revealed the occurrence both of rhombs and of clusters of elongated plates, but no needles were apparent. A well-formed rhomb was selected and, as the unit cell derived on the diffractometer was in good agreement with that reported by Atkinson,[30] we proceeded to collect intensity data (Table I). The position of the bromine atom was deduced from a Patterson synthesis and, using this for a phasing model, all of the anticipated carbon atoms were located in a $|F_o|$ Fourier synthesis. The systematic absences (Table I) imply that this system suffers from the same space group ambiguity as the parent hydrocarbon, although, in this case (presumably because of the heavy weighting by the bromine), refinements in $Pna2_1$ were unstable. In the subsequent analysis we found no evidence in favor of the noncentrosymmetric symmetry and, therefore, in common with the parent, *Pnam* was taken to be the correct space group. After refinement, all the expected hydrogen atoms were located in a difference Fourier synthesis. Their coordinates and isotropic thermal parameters (U[iso]) were refined subject to a series of Waser-type constraints on bond lengths and angles. In an additional constraint, the U[iso]'s for H(1) and H(4) were linked to the mean-square deviations of C(1) and C(4), respectively, in the direction of the C–H bond. This was necessary because U[iso] for both these protons had become negative during earlier refinements. The final residuals were $R = 0.0458$ and $R_w = 0.0543$.

(c) Monoclinic Form of 4′-Bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (MTBR). Crystal data: $C_{31}H_{25}Br$, $M = 447.4$, monoclinic, space group *Pc*, $a = 9.011$ (1), $b = 16.187$ (3), $c = 8.463$ (2) Å, $\beta = 108.98$ (1)°, $U = 1167.4$ Å^3, $d_c = 1.36$ g cm^{-3} for $Z = 2$, Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 18.8$ cm^{-1}.

Crystals of the monoclinic form of the 4′-bromo derivative (**3b**) were taken from a second preparation similar to the above (i.e., (b)). Crystallization from light petroleum (bp 60–80 °C) at ca. 25 °C afforded crystals of two distinct forms, in approximately equal quantities. These consisted of rhombs and well-faceted plates. Again no needles were apparent, although some of the plates were elongated perpendicular to the crystallographic b axis. One of the plate-like crystals was selected for analysis on the diffractometer and the derived unit cell is in good agreement with that reported by Atkinson[30] (Table I). Because of the shape of the crystal, data collection was implemented using the FLAT mode.[32] Each reflection was measured at the value of rotation about the scattering vector which resulted in minimum absorption, subject to some restraints on this rotation imposed by the geometry of the diffractometer hardware.

The systematic absences (Table I) are consistent with two space groups, *Pc* and *P2/c*. The latter would imply that the molecule has a center of symmetry or an intramolecular twofold axis, neither of which is in accord with the molecular configuration. The noncentrosymmetric *Pc* was therefore assumed and confirmed by the subsequent analysis. For structure solution, coordinates for the bromine atom were taken from Atkinson[30] and the remainder of the molecular skeleton was elucidated by successive least-squares and $|F_o|$ Fourier calculations. *Pc* is a polar space group, in which the position of the molecule may be defined arbitrarily along the x and z axes. To circumvent instabilities in the refinement, therefore, the sum of the shifts along the x and z axes were each constrained to be zero.[33,39] After further refinement of the atomic coordinates and anisotropic thermal parameters, all the anticipated hydrogens were found in electron density difference syntheses. Their coordinates were refined, subject to Waser-type constraints as above, although their isotropic temperature factors were fixed at U[iso] = 0.05. The final residuals are $R = 0.0413$ and $R_w = 0.0443$.

Bond lengths and interatomic distances found in the three structures are listed inTable II, while Table III compares interatomic angles. The numbering scheme employed is shown in Figure 2; OTBR and MTBR refer to the orthorhombic and monoclinic forms of 4′-bromo-1,4-dihydro-4-tritylbiphenyl (**3b**), respectively.

Table II. Bond Lengths (Å) and Interatomic Distances (Å), with Estimated Standard Deviations in Parentheses

	parent	OTBR	MTBR
C(1)–C(7)	1.592 (5)	1.591 (11)	1.593 (11)
C(1)–C(2)	1.496 (4)	1.507 (8)	1.518 (11)
C(1)–C(6)	1.496 (4)	1.507 (8)	1.487 (12)
C(2)–C(3)	1.333 (4)	1.315 (9)	1.326 (12)
C(5)–C(6)	1.333 (4)	1.315 (9)	1.326 (12)
C(3)–C(4)	1.497 (4)	1.494 (8)	1.487 (13)
C(4)–C(5)	1.497 (4)	1.494 (8)	1.512 (12)
C(4)–C(11)	1.525 (6)	1.523 (12)	1.533 (12)
C(7)–C(21)	1.541 (3)	1.547 (8)	1.541 (12)
C(7)–C(31)	1.541 (3)	1.547 (8)	1.554 (11)
C(7)–C(41)	1.534 (5)	1.538 (12)	1.541 (12)
C(7)–C(4)	3.705	4.264	4.322
C(7)–C(11)	5.183	5.551	5.558
C(4)–C(41)	3.765	4.129	4.281
C(11)–C(41)	5.285	5.607	5.737
C(11)–C(12)	1.379 (6)	1.371 (14)	1.389 (13)
C(11)–C(16)	1.392 (6)	1.393 (13)	1.351 (13)
C(12)–C(13)	1.394 (6)	1.378 (14)	1.363 (14)
C(13)–C(14)	1.378 (7)	1.355 (14)	1.355 (14)
C(14)–C(15)	1.378 (7)	1.368 (14)	1.375 (14)
C(15)–C(16)	1.379 (6)	1.378 (13)	1.417 (13)
C(14)–Br		1.915 (9)	1.935 (7)
C(21)–C(22)	1.392 (4)	1.376 (8)	1.384 (12)
C(31)–C(32)	1.392 (4)	1.376 (8)	1.399 (12)
C(21)–C(26)	1.391 (4)	1.389 (8)	1.393 (12)
C(31)–C(36)	1.391 (4)	1.389 (8)	1.380 (13)
C(22)–C(23)	1.386 (4)	1.381 (9)	1.382 (14)
C(32)–C(33)	1.386 (4)	1.381 (9)	1.392 (14)
C(23)–C(24)	1.377 (5)	1.359 (9)	1.340 (15)
C(33)–C(34)	1.377 (5)	1.359 (9)	1.377 (15)
C(24)–C(25)	1.370 (5)	1.351 (9)	1.340 (14)
C(34)–C(35)	1.370 (5)	1.351 (9)	1.377 (15)
C(25)–C(26)	1.387 (4)	1.393 (10)	1.394 (13)
C(35)–C(36)	1.387 (4)	1.393 (10)	1.403 (14)
C(41)–C(42)	1.394 (3)	1.394 (8)	1.408 (12)
C(41)–C(46)	1.394 (3)	1.394 (8)	1.371 (12)
C(42)–C(43)	1.391 (4)	1.381 (10)	1.383 (11)
C(45)–C(46)	1.391 (4)	1.381 (10)	1.393 (12)
C(43)–C(44)	1.373 (4)	1.376 (10)	1.360 (13)
C(44)–C(45)	1.373 (4)	1.376 (10)	1.370 (13)
C(1)–H(1)	1.07 (3)	1.09 (2)	1.08 (4)
C(2)–H(2)	1.05 (2)	1.05 (2)	1.07 (4)
C(6)–H(6)	1.05 (2)	1.05 (2)	1.09 (5)
C(3)–H(3)	1.04 (2)	1.05 (2)	1.07 (4)
C(5)–H(5)	1.04 (2)	1.05 (2)	1.08 (4)
C(4)–H(4)	1.07 (3)	1.09 (2)	1.08 (4)
C(12)–H(12)	1.05 (3)	1.08 (1)	1.11 (4)
C(13)–H(13)	1.06 (3)	1.08 (1)	1.05 (4)
C(14)–H(14)	1.07 (3)		
C(15)–H(15)	1.08 (3)	1.08 (1)	1.05 (4)
C(16)–H(16)	1.06 (3)	1.08 (1)	1.10 (4)
C(22)–H(22)	1.04 (2)	1.08 (1)	1.06 (4)
C(32)–H(32)	1.04 (2)	1.08 (1)	1.08 (4)
C(23)–H(23)	1.05 (2)	1.08 (1)	1.09 (4)
C(33)–H(33)	1.05 (2)	1.08 (1)	1.08 (4)
C(24)–H(24)	1.05 (2)	1.08 (1)	1.08 (4)
C(34)–H(34)	1.05 (2)	1.08 (1)	1.08 (4)
C(25)–H(25)	1.04 (2)	1.08 (1)	1.07 (4)
C(35)–H(35)	1.04 (2)	1.08 (1)	1.06 (4)
C(26)–H(26)	1.04 (2)	1.08 (1)	1.08 (4)
C(36)–H(36)	1.04 (2)	1.08 (1)	1.09 (4)
C(42)–H(42)	1.04 (2)	1.08 (1)	1.08 (4)
C(46)–H(46)	1.04 (2)	1.08 (1)	1.02 (4)
C(43)–H(43)	1.04 (2)	1.08 (1)	1.03 (4)
C(45)–H(45)	1.04 (2)	1.08 (1)	1.08 (4)
C(44)–H(44)	1.04 (3)	1.08 (1)	1.06 (4)

Results and Discussion

X-ray Crystallographic Results. In the solid state, *trans*-1,4-dihydro-4-tritylbiphenyl (**2b**) adopts a conformation in which the cyclohexadiene ring has a boat geometry ($\alpha_{mean} = +172.1°$)[13] with the trityl substituent placed pseudo-axially (see Figure 3a).[29] In contrast, both crystalline modifications of 4′-bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (**3b**) have a pseudo-equatorial trityl substituent, and the cyclohexadiene ring is inverted relative to (**2b**) (see Figures 3b and 3c); for the orthorhombic form $\alpha_{mean} = -176.3°$, whereas in the monoclinic structure $\alpha_{mean} = -172.9°$.[13] In all three cases the cyclohexadiene ring is more puckered at C-1, the carbon bearing the trityl substituent, than at C-4 [compare, for example, the torsion angles C(5)–C(6)–C(1)–C(7) and C-(6)–C(5)–C(4)–C(11) in Table IV].

Table III. Interatomic Angles (deg) with Estimated Standard Deviations in Parentheses

	parent	OTBR	MTBR
C(2)-C(1)-C(7)	111.2 (2)	111.4 (4)	110.7 (6)
C(6)-C(1)-C(7)	111.2 (2)	111.4 (4)	113.3 (6)
C(2)-C(1)-C(6)	111.8 (3)	110.6 (8)	111.1 (7)
C(1)-C(2)-C(3)	123.6 (3)	124.1 (6)	123.2 (7)
C(1)-C(6)-C(5)	123.6 (3)	124.1 (6)	125.0 (7)
C(2)-C(3)-C(4)	124.6 (3)	125.4 (6)	125.2 (8)
C(6)-C(5)-C(4)	124.6 (3)	125.4 (6)	123.6 (8)
C(3)-C(4)-C(11)	110.8 (2)	111.3 (5)	110.4 (7)
C(5)-C(4)-C(11)	110.8 (2)	111.3 (5)	110.6 (7)
C(3)-C(4)-C(5)	110.9 (3)	110.3 (8)	111.1 (7)
C(1)-C(7)-C(21)	111.9 (2)	110.0 (5)	110.6 (6)
C(1)-C(7)-C(31)	111.9 (2)	110.0 (5)	111.5 (6)
C(1)-C(7)-C(41)	104.9 (3)	106.0 (6)	106.4 (7)
C(21)-C(7)-C(31)	103.1 (3)	103.5 (7)	103.8 (7)
C(21)-C(7)-C(41)	112.6 (2)	112.7 (4)	113.1 (7)
C(31)-C(7)-C(41)	112.6 (2)	112.7 (4)	111.6 (6)
C(12)-C(11)-C(4)	121.6 (4)	122.4 (9)	120.6 (8)
C(16)-C(11)-C(4)	119.8 (4)	120.8 (9)	120.7 (8)
C(12)-C(11)-C(16)	118.7 (4)	116.9 (9)	118.7 (8)
C(11)-C(12)-C(13)	120.6 (5)	121.9 (1.0)	121.0 (1.0)
C(12)-C(13)-C(14)	119.8 (5)	119.3 (1.0)	119.9 (9)
C(13)-C(14)-Br		120.0 (9)	120.0 (7)
C(15)-C(14)-Br		118.4 (9)	118.5 (8)
C(13)-C(14)-C(15)	120.1 (4)	121.6 (1.0)	121.5 (8)
C(14)-C(15)-C(16)	119.9 (5)	118.2 (1.0)	117.6 (1.0)
C(15)-C(16)-C(11)	120.9 (5)	122.1 (9)	121.3 (9)
C(7)-C(21)-C(22)	119.8 (3)	119.6 (6)	121.8 (8)
C(7)-C(31)-C(32)	119.8 (3)	119.6 (6)	117.6 (7)
C(7)-C(21)-C(26)	123.1 (3)	122.5 (6)	120.6 (7)
C(7)-C(31)-C(36)	123.1 (3)	122.5 (6)	123.8 (7)
C(22)-C(21)-C(26)	116.6 (3)	117.5 (6)	117.4 (8)
C(32)-C(31)-C(36)	116.6 (3)	117.5 (6)	118.5 (8)
C(21)-C(22)-C(23)	122.0 (3)	121.2 (6)	121.3 (9)
C(31)-C(32)-C(33)	122.0 (3)	121.2 (6)	119.8 (9)
C(22)-C(23)-C(24)	119.9 (3)	120.2 (6)	119.7 (9)
C(32)-C(33)-C(34)	119.9 (3)	120.2 (6)	121.1 (9)
C(23)-C(24)-C(25)	119.4 (3)	120.4 (7)	119.8 (9)
C(33)-C(34)-C(35)	119.4 (3)	120.4 (7)	120.4 (9)
C(24)-C(25)-C(26)	120.6 (3)	119.9 (7)	120.7 (1.0)
C(34)-C(35)-C(36)	120.6 (3)	119.9 (7)	119.3 (9)
C(25)-C(26)-C(21)	121.5 (3)	120.8 (7)	121.0 (9)
C(35)-C(36)-C(31)	121.5 (3)	120.8 (7)	120.9 (9)
C(7)-C(41)-C(42)	120.7 (2)	120.2 (5)	121.0 (8)
C(7)-C(41)-C(46)	120.7 (2)	120.2 (5)	120.7 (7)
C(42)-C(41)-C(46)	118.2 (3)	119.2 (9)	117.4 (8)
C(41)-C(42)-C(43)	120.7 (3)	119.9 (8)	120.9 (8)
C(41)-C(46)-C(45)	120.7 (3)	119.9 (8)	120.7 (8)
C(42)-C(43)-C(44)	120.1 (3)	120.6 (9)	120.7 (9)
C(44)-C(45)-C(46)	120.1 (3)	120.6 (9)	121.2 (8)
C(43)-C(44)-C(45)	120.2 (4)	119.8 (1.1)	119.0 (9)
C(2)-C(1)-H(1)	108 (1)	107 (1)	108 (2)
C(6)-C(1)-H(1)	108 (1)	107 (1)	107 (2)
C(7)-C(1)-H(1)	106 (2)	109 (2)	107 (2)
C(1)-C(2)-H(2)	118 (1)	118 (2)	117 (2)
C(1)-C(6)-H(6)	118 (1)	118 (2)	117 (2)
C(3)-C(2)-H(2)	118 (1)	118 (2)	120 (2)
C(5)-C(6)-H(6)	118 (1)	118 (2)	118 (2)
C(2)-C(3)-H(3)	118 (1)	116 (2)	117 (2)
C(6)-C(5)-H(5)	118 (1)	116 (2)	118 (2)
C(4)-C(3)-H(3)	117 (1)	119 (2)	117 (2)
C(4)-C(5)-H(5)	117 (1)	119 (2)	118 (2)
C(3)-C(4)-H(4)	107 (1)	108 (1)	108 (2)
C(5)-C(4)-H(4)	107 (1)	108 (1)	107 (2)
C(11)-C(4)-H(4)	110 (2)	108 (2)	109 (3)

A detailed comparison of the three structures reveals several common features. Firstly, the phenyl and trityl substituents are almost superimposable. This feature is emphasized by an overlay of the structures shown (Figure 4). Secondly, there is face-to-face pairing of the rings of the dihydrotetraphenylmethane fragment, and, thirdly, the ring plane of the remote phenyl substituent is approximately perpendicular to the plane containing C(2)-C(3)-C(5)-C(6) of the cyclohexadiene ring (see Figures 3 and 4). These features are also observed for the cis isomers **2a**[28] and **3a**.[31]

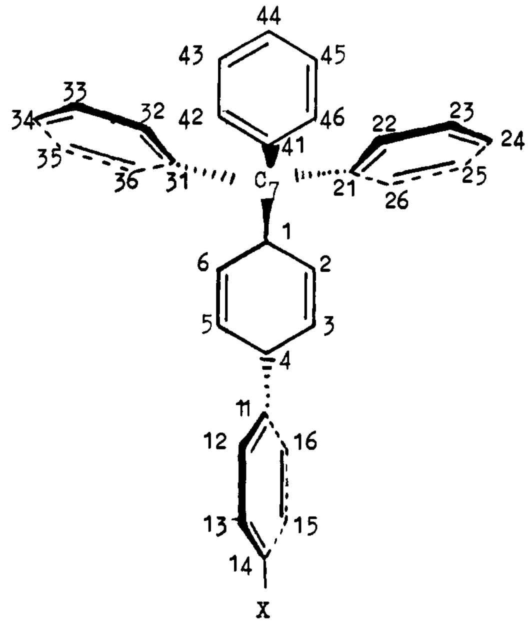


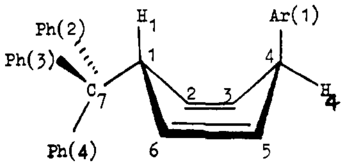
Figure 2. The numbering scheme employed for the crystallographic data.

Table IV. Selected Torsional Angles (Deg)[a]

X_A	C_B	C_C	X_D	parent	OTBR	MTBR
C(3)	C(2)	C(1)	C(7)	−116.8	−127.4	−133.2
C(5)	C(6)	C(1)	C(7)	(116.8)	(127.4)	134.2
C(3)	C(2)	C(1)	H(1)	127.2	113.2	110.6
C(5)	C(6)	C(1)	H(1)	(−127.2)	(−113.2)	−108.6
H(2)	C(2)	C(1)	C(7)	73.6	44.2	40.8
H(6)	C(6)	C(1)	C(7)	(−73.6)	(−44.2)	−44.7
H(2)	C(2)	C(1)	H(1)	−42.3	−75.2	−75.4
H(6)	C(6)	C(1)	H(1)	(42.3)	(75.2)	72.6
C(2)	C(3)	C(4)	C(11)	−129.6	−120.3	−116.9
C(6)	C(5)	C(4)	C(11)	(129.6)	(120.3)	119.2
C(2)	C(3)	C(4)	H(4)	110.6	121.0	123.9
C(6)	C(5)	C(4)	H(4)	(−110.6)	(−121.0)	−121.8
H(3)	C(3)	C(4)	C(11)	38.4	64.7	72.5
H(5)	C(5)	C(4)	C(11)	(−38.4)	(−64.7)	−64.9
H(3)	C(3)	C(4)	H(4)	−81.5	−54.0	−46.6
H(5)	C(5)	C(4)	H(4)	(81.5)	(54.0)	54.0
C(43)	C(42)	C(41)	C(7)	−173.1	−173.8	−172.9
C(45)	C(46)	C(41)	C(7)	(173.1)	(173.8)	172.4

[a] A positive angle indicates an anticlockwise rotation when viewed along C_B–C_C.

The face-to-face pairing of the dihydrotetraphenylmethane fragment (Figure 3) contrasts with the propellor conformation observed in tetraphenylmethane itself.[41] It arises from the interactions between the hydrogen atom at C-1 and the adjacent phenyl rings (see **4**). The origin of the preferred orientation of the 4-phenyl substituent is less clear, as in solution there is free rotation about the C(4)–C(11) bond in the related cis compounds **2a** and **3a**.[28,31]



(4) a, Ar(1) = C_6H_5-

b, Ar(1) = p-Br-C_6H_4-

There are three further structural features which are common to the *trans*-1,4-dihydro-4-tritylbiphenyls. The C(1)–C(7) bond is exceptionally long (1.591 to 1.593 Å; see Table II) in comparison

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(41) Robbins, A.; Jeffrey, G. A.; Chesick, J. P.; Donohue, J.; Cotton, F. A.; Frenz, B. A.; Murrillo, C. A. *Acta Crystallogr., Sect. B* **1975**, *31*, 2395.

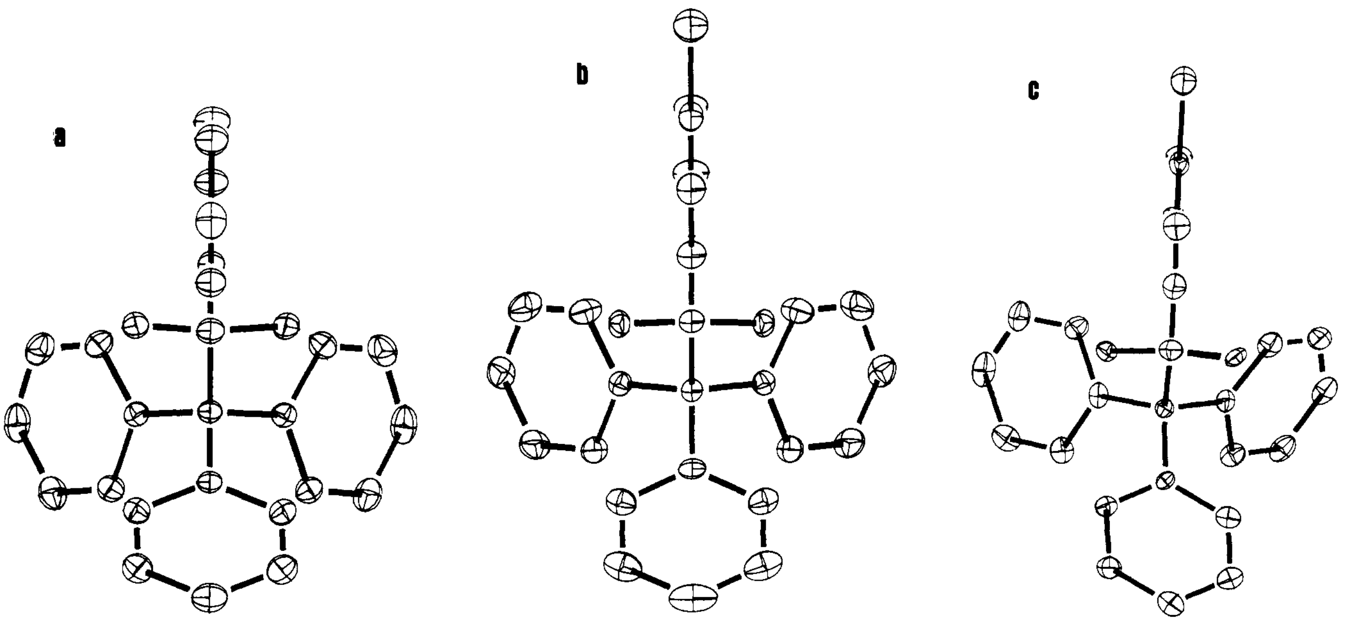

Figure 3. View along C(1)–C(4) showing the relative dispositions of the phenyl groups and the puckering of the cyclohexa-1,4-diene ring (note the inversion of the cyclohexadiene ring between **2b** and **3b**). (In this and subsequent figures the thermal ellipsoids represent 50% probability surfaces). (a) *trans*-1,4-dihydro-4-tritylbiphenyl (**2b**). (b) Orthorhombic 4′-bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (**3b**). (c) Monoclinic 4′-bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (**3b**).

with typical C–C single bonds (1.54 Å), and the C–aryl bond lengths reported for tetraphenylmethane (1.553 Å).[41] The angles C(*n*2) - C(*n*1) - C(*n*6), *n* = 1–4, are consistently less than 120°. Finally, the phenyl substituent, Ph(4), is significantly tilted toward the cyclohexadiene ring (see **4** and Figure 4) by an angle of ca. 7°. This is reflected in the torsion angle C(43)–C(42)–C(41)–C(7) (see Table IV) which would ideally be 180°. All these distortions must arise from an attempt to minimize the considerable steric interactions present in the dihydrotritylbiphenyl skeleton.

In each cyclohexadiene ring the double bond angles are forced slightly open from the expected 120° (values for angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4), for example, range from 123.2 to 125.4°, see Table III). Puckering of the cyclohexadiene ring in *trans*-1,4-dihydro-4-tritylbiphenyl (**2b**) is, however, in the *opposite* sense from that found for the two structures of the 4′-bromo compound (**3b**). This suggests that the potential energy well for the cyclohexadiene ring is very shallow and centered around an almost planar configuration, or has a double minimum, a point which will be considered in more detail below. In either case, the inversion of the cyclohexadiene ring from **2b** to **3b** must reflect the influence of the bromine substituent on the intermolecular crystal-packing forces (see Figure 5).

The unsymmetrical nature of the cyclohexadiene boats found in all three structures, as evidenced by the torsion angles in Table IV, probably results from the unusual steric requirements of a pseudo-equatorial trityl substituent. The slight distortion observed in the three trans structures reported here is also evident in the structures of their cis isomers.[28,31]

As the degree of ring puckering (i.e., α) increases, the molecular volume is reduced. The orthorhombic form, with the more nearly planar cyclohexadiene ring, has the higher unit cell volume and the higher crystallographic symmetry; this suggests that it is a high-temperature modification. The monoclinic structure also shows a skew-boat geometry[42] about the C(1)–C(4) axis of the cyclohexadiene ring. This is precluded in the orthorhombic case where there is a mirror plane coincident with the C(1)–C(4) axis. The crystallization at room temperature yields each form in approximately equal quantities. The energy difference between the two crystal modifications must therefore be small and, if the system is in thermodynamic equilibrium during crystallization, the phase transformation must occur close to room temperature.

Table V. Comparison of Some Solid-State Structural Features of the Dihydrotritylbiphenyls

		3b	
	2b	orthorhombic	monoclinic
deviation of C(7) from least-squares best plane[a] (Å) (max dev,[b] Å)	0.16 (0.001)	0.15 (0.004)	0.17 (0.020)
α,[c] deg	+172.1	−176.3	−172.9

[a] Best plane is defined through C(41)–C(44), C(42)′, C(43)′ (′ referring to the mirror plane related atoms) for 2b and orthorhombic 3b, and by C(41)–C(46) for monoclinic 3b. [b] This is the maximum deviation of atoms which define the *best* plane used from the least-squares best plane. [c] See ref 13.

Table VI. Comparison of Experimental and Calculated[a] Values for ^1H–^1H Coupling Constants around the Cyclohexa-1,4-diene Ring in 2b and 3b

J, Hz	2b		3b		
	obsd[a]	calcd[b]	obsd[a]	OTBR calcd[b]	MTBR calcd[b]
1, 2	2.9	3.9 (4.8)	2.9	2.9 (3.7)	2.8 (3.6)
1, 3	−2.2	−0.7 (−1.6)	−2.1	−2.0 (−2.6)	−2.3 (−2.8)
1, 4	7.7	5.9 (5.9)[c]	7.3	6.2 (6.1)[c]	6.0 (6.0)[c]
2, 3	10.7		10.6		
2, 4	−2.1	−2.4 (−2.9)	−2.2	−1.1 (−2.0)	−0.8 (−1.7)
3, 4	3.3	2.8 (3.5)	3.1	3.5 (4.5)	3.8 (4.7)

[a] ^1H NMR spectra of solutions of 2b and 3b in $CDCl_3$ and CD_2Cl_2 were recorded on a Perkin-Elmer R32 and a JEOL FX90Q NMR spectrometer. Relative signs of coupling constants were determined by spin-tickling experiments. Spectra were simulated using the program LAOCOON III. [b] Calculated from torsion angles given in Table IV. The principal values are derived from data of Grossel, Hayward, and Perkins,[5,9] while those in parentheses use the calculations of Marshall and co-workers[10] (the calculated homoallylic couplings obtained by the latter have been divided by a factor of 2; see Figure 6 and ref 11). [c] Values calculated from the mean crystallographic angle of pucker α[13] of the cyclohexadiene ring (see Table V).

Solution ^1H NMR Studies. Solution ^1H NMR data relating to the cyclohexadiene ring components of *trans*-1,4-dihydro-4-tritylbiphenyl (**2b**) and its 4′-bromo derivative (**3b**) are presented

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(42) This is the first example of a skew boat geometry for a cyclohexa-1,4-diene ring, but see: Dallinga, G.; Toneman, L. H. *J. Mol. Struct.* **1967**, *1*, 117.

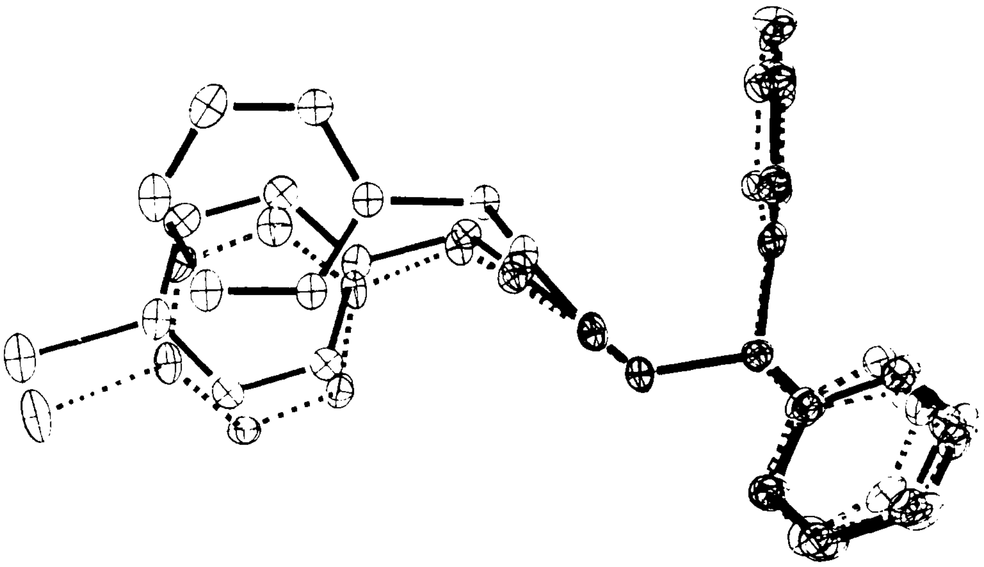

Figure 4. An overlay of the molecular geometries of **2b**, and orthorhombic and monoclinic **3b**. The molecules are drawn to the same scale and are arranged such that the C(1)–C(7) bonds are coincident. The parent hydrocarbon is recognized by the absence of the apical substituent and by the opposite sense of puckering in the central cyclohexadiene ring. The molecular geometry found in the monoclinic modification is indicated by the dashed bonds.

Table VII. Fractional Atomic Coordinates for *trans*-1,4-Dihydro-4-tritylbiphenyl (2b) with Estimates of Standard Deviations in Parentheses

atom	*X*/*A*	*Y*/*B*	*Z*/*C*
C(1)	0.1245 (2)	0.5236 (3)	0.2500
C(2)	0.1564 (2)	0.4739 (2)	0.1271 (3)
C(3)	0.2130 (2)	0.4044 (2)	0.1277 (3)
C(4)	0.2514 (2)	0.3649 (3)	0.2500
C(7)	0.1334 (2)	0.6542 (3)	0.2500
C(11)	0.2580 (2)	0.2396 (3)	0.2500
C(12)	0.3253 (3)	0.1879 (4)	0.2500
C(13)	0.3299 (3)	0.0731 (4)	0.2500
C(14)	0.2669 (3)	0.0107 (4)	0.2500
C(15)	0.1993 (3)	0.0616 (4)	0.2500
C(16)	0.1949 (2)	0.1750 (4)	0.2500
C(21)	0.0949 (1)	0.7078 (2)	0.1303 (3)
C(22)	0.1154 (2)	0.8129 (2)	0.0891 (3)
C(23)	0.0763 (2)	0.8704 (3)	−0.0063 (3)
C(24)	0.0156 (2)	0.8231 (3)	−0.0644 (3)
C(25)	−0.0047 (2)	0.7187 (3)	−0.0281 (3)
C(26)	0.0338 (1)	0.6619 (3)	0.0687 (3)
C(41)	0.2165 (2)	0.6740 (3)	0.2500
C(42)	0.2557 (1)	0.6766 (2)	0.3686 (3)
C(43)	0.3318 (2)	0.6827 (3)	0.3681 (4)
C(44)	0.3692 (2)	0.6857 (4)	0.2500
H(1)	0.0665 (15)	0.5082 (28)	0.2500
H(2)	0.1276 (11)	0.4839 (15)	0.0379 (23)
H(3)	0.2250 (11)	0.3632 (15)	0.0401 (23)
H(4)	0.3049 (15)	0.4014 (28)	0.2500
H(12)	0.3740 (15)	0.2347 (24)	0.2500
H(13)	0.3822 (15)	0.0355 (24)	0.2500
H(14)	0.2703 (17)	−0.0770 (22)	0.2500
H(15)	0.1501 (15)	0.0126 (24)	0.2500
H(16)	0.1427 (15)	0.2126 (25)	0.2500
H(22)	0.1612 (11)	0.8485 (19)	0.1325 (19)
H(23)	0.0942 (12)	0.9492 (18)	−0.0336 (19)
H(24)	−0.0146 (11)	0.8646 (19)	−0.1371 (18)
H(25)	−0.0511 (11)	0.6833 (19)	−0.0710 (18)
H(26)	0.0165 (11)	0.5833 (18)	0.0960 (19)
H(42)	0.2276 (13)	0.6731 (8)	0.4587 (24)
H(43)	0.3590 (13)	0.6833 (8)	0.4584 (24)
H(44)	0.4260 (15)	0.6903 (8)	0.2500

in Table VI. The two sets of data are identical to within the limits of precision of the measurements, and we therefore suggest that the two compounds adopt similar conformations in liquid solution. This is not unexpected, for the bromine atom is sufficiently remote from the rest of the molecule for it to have little influence on interactions about the cyclohexadiene ring.

Table VIII. Fractional Atomic Coordinates for Orthorhombic *trans*-4′-Bromo-1,4-dihydro-4-tritylbiphenyl (3b) with Estimates of Standard Deviations in Parentheses

atom	*X*/*A*	*Y*/*B*	*Z*/*C*
Br(1)	0.1295 (1)	0.1590 (1)	0.2500
C(1)	0.6057 (6)	−0.1649 (5)	0.2500
C(2)	0.5961 (4)	−0.1157 (4)	0.3688 (6)
C(3)	0.5774 (4)	−0.0409 (4)	0.3675 (7)
C(4)	0.5618 (7)	0.0072 (5)	0.2500
C(7)	0.7098 (6)	−0.2132 (5)	0.2500
C(11)	0.4563 (7)	0.0455 (6)	0.2500
C(12)	0.4441 (8)	0.1243 (6)	0.2500
C(13)	0.3483 (8)	0.1584 (6)	0.2500
C(14)	0.2634 (8)	0.1129 (7)	0.2500
C(15)	0.2705 (8)	0.0338 (6)	0.2500
C(16)	0.3670 (9)	0.0009 (6)	0.2500
C(21)	0.7146 (5)	−0.2685 (3)	0.3665 (6)
C(22)	0.8082 (5)	−0.2955 (4)	0.4084 (7)
C(23)	0.8148 (5)	−0.3498 (5)	0.5053 (8)
C(24)	0.7281 (6)	−0.3789 (4)	0.5596 (7)
C(25)	0.6346 (6)	−0.3543 (4)	0.5205 (8)
C(26)	0.6270 (6)	−0.2998 (4)	0.4224 (8)
C(41)	0.7972 (5)	−0.1532 (5)	0.2500
C(42)	0.8330 (5)	−0.1225 (4)	0.1348 (8)
C(43)	0.9044 (5)	−0.0633 (4)	0.1359 (9)
C(44)	0.9394 (7)	−0.0333 (6)	0.2500
H(1)	0.5405 (25)	−0.2047 (22)	0.2500
H(2)	0.6152 (9)	−0.1414 (18)	0.4570 (25)
H(3)	0.5794 (10)	−0.0132 (18)	0.4570 (25)
H(4)	0.6199 (27)	0.0524 (20)	0.2500
H(12)	0.5115 (20)	0.1611 (19)	0.2500
H(13)	0.3402 (30)	0.2208 (9)	0.2500
H(15)	0.2024 (19)	−0.0022 (19)	0.2500
H(16)	0.3733 (30)	−0.0616 (8)	0.2500
H(22)	0.8791 (15)	−0.2740 (13)	0.3678 (20)
H(23)	0.8903 (14)	−0.3717 (13)	0.5296 (23)
H(24)	0.7347 (27)	−0.4207 (7)	0.6364 (11)
H(25)	0.5664 (17)	−0.3680 (14)	0.5749 (21)
H(26)	0.5553 (14)	−0.2692 (13)	0.4108 (23)
H(42)	0.8058 (16)	−0.1465 (14)	0.0450 (19)
H(43)	0.9300 (17)	−0.0402 (14)	0.0450 (20)
H(44)	0.9933 (10)	0.0144 (8)	0.2500

The homoallylic couplings lie within the range reported for dihydrobenzenes considered to be essentially planar (see Introduction). For example, 1,4-dihydrohexadeuteriobenzene has $J_{1,4\text{-trans}} = 8.0$ Hz[27] (but see also ref 14), whereas in 1,4-dihydropentadeuteriobenzoic acid and 1,4-dihydrobenzyl alcohol $J_{1,4\text{-trans}} = 7.6$[10] and 7.4 Hz,[12] respectively. Even smaller trans-

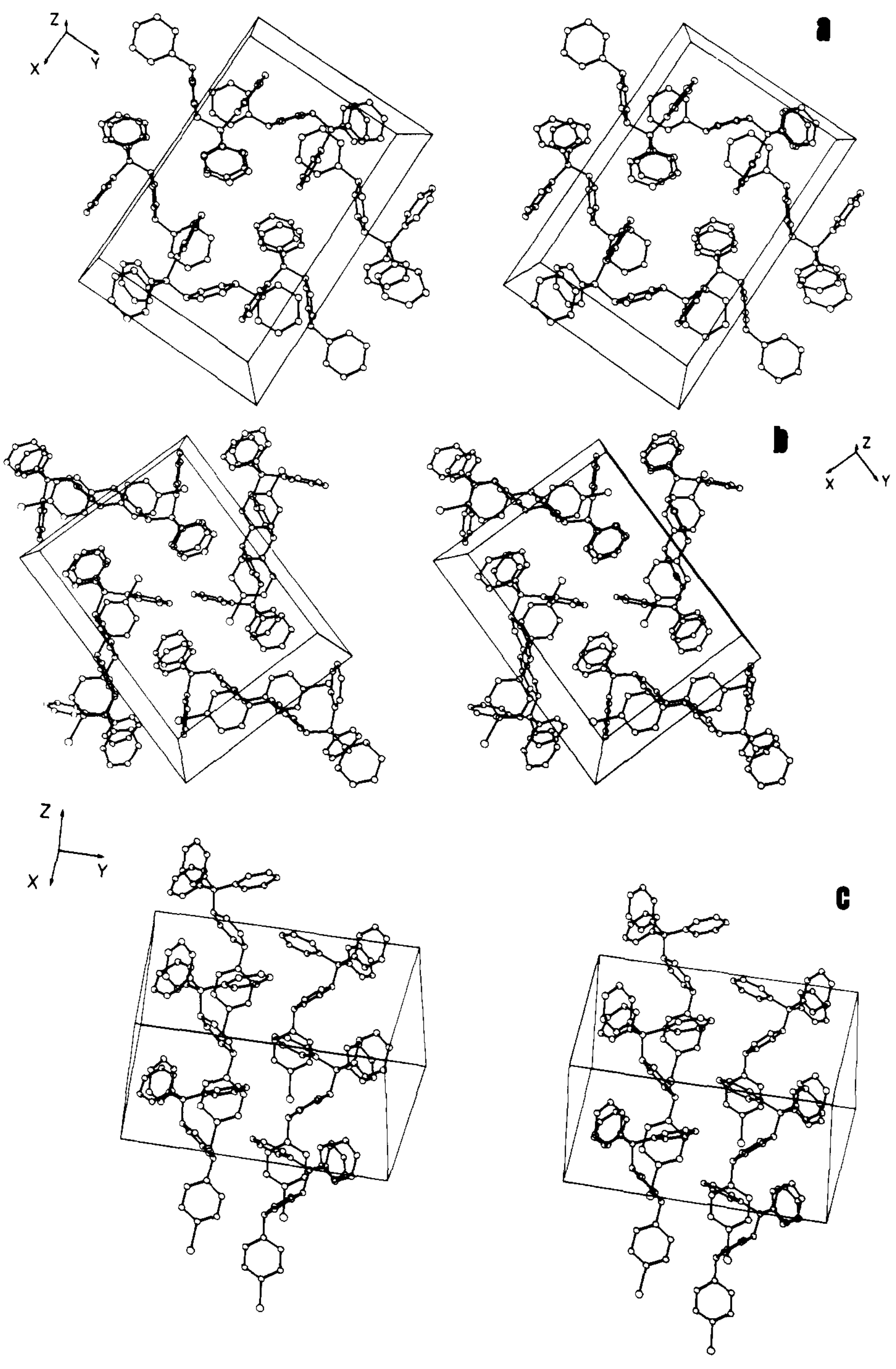

Figure 5. Stereoscopic projection showing the packing of molecules within the crystal lattice. The parent hydrocarbon (**2b**) and the orthorhombic form of **3b** have the same space group symmetry although their packing arrangements differ. The local environments of the monoclinic and orthorhombic modifications of **3b** are also clearly quite different: (a) *trans*-1,4-dihydro-4-tritylbiphenyl (**2b**), (b) orthorhombic 4′-bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (**3b**), (c) monoclinic 4′-bromo-*trans*-1,4-dihydro-4-tritylbiphenyl (**3b**).

homoallylic couplings have been reported for 1,4-dihydro-3,5-dimethylbenzoic acid[7] and its benzyl alcohol,[15] structures in which there is also evidence for a planar ring conformation. It is not yet clear why such a range of homoallylic coupling constant values is found. Possible factors include electronic substituent effects and distortion of the shape of the vibrational potential well by substituents. A change of the C-1 substituent from carboxyl to hydroxymethyl or 2-(2-hydroxypropyl) has little influence on the magnitude of $J_{1,4\text{-trans}}$ in dihydro aromatic rings,[7] and accordingly electronic C-1 substituent effects would seem to be relatively unimportant. The more likely explanation, and one which may rationalize the comparatively wide range of homoallylic couplings for "planar" dihydrobenzenes arises from the high flexibility of the cyclohexadiene ring itself. Substituents will modify the shape of the vibrational potential well.[14] This will result in different populations of the various boat–boat inversion vibrational levels at a particular temperature and will consequently lead to different "time-averaged" NMR couplings even though in each case the potential well may have a single, essentially planar, energy minimum.

The similarity of the vicinal couplings $J_{1,2}$ and $J_{3,4}$ in the *trans*-1,4-dihydro-4-tritylbiphenyls (**2b** and **3b** (Table VI)) which are opposite in sense (when one is pseudo-axial, the other is pseudo-equatorial) provides strong evidence for a planar time-averaged ring conformation. The same conclusion may be drawn from a comparison of the observed allylic couplings $J_{1,3}$ and $J_{2,4}$. We have also calculated vicinal and allylic coupling constant values using carbon skeleton positions determined crystallographically

Table IX. Fractional Atomic Coordinates for Monoclinic *trans*-4′-Bromo-1,4-dihydro-4-tritylbiphenyl (3b) with Estimates of Standard Deviations in Parentheses

atom	*X*/*A*	*Y*/*B*	*Z*/*C*
Br(1)	1.0031 (6)	0.3364 (1)	0.0009 (6)
C(1)	0.4490 (11)	0.2283 (6)	0.5884 (11)
C(2)	0.3599 (10)	0.2618 (6)	0.4161 (11)
C(3)	0.4095 (11)	0.3252 (7)	0.3476 (12)
C(4)	0.5579 (11)	0.3713 (6)	0.4259 (12)
C(5)	0.6382 (11)	0.3429 (6)	0.6034 (11)
C(6)	0.5862 (11)	0.2813 (6)	0.6744 (11)
C(7)	0.3337 (10)	0.2145 (6)	0.6944 (11)
C(11)	0.6678 (11)	0.3620 (6)	0.3215 (12)
C(12)	0.7136 (12)	0.4306 (7)	0.2504 (13)
C(13)	0.8104 (13)	0.4229 (7)	0.1566 (14)
C(14)	0.8634 (10)	0.3473 (7)	0.1316 (11)
C(15)	0.8212 (13)	0.2772 (7)	0.1983 (14)
C(16)	0.7212 (13)	0.2869 (7)	0.2961 (14)
C(21)	0.1966 (10)	0.1575 (6)	0.6001 (11)
C(22)	0.0486 (11)	0.1662 (6)	0.6144 (12)
C(23)	−0.0701 (13)	0.1107 (7)	0.5403 (15)
C(24)	−0.0436 (13)	0.0464 (6)	0.4428 (13)
C(25)	0.0998 (12)	0.0358 (7)	0.4306 (13)
C(26)	0.2211 (12)	0.0906 (6)	0.5081 (12)
C(31)	0.4161 (10)	0.1672 (6)	0.8594 (11)
C(32)	0.3372 (12)	0.1618 (7)	0.9766 (11)
C(33)	0.4000 (14)	0.1143 (7)	1.1200 (13)
C(34)	0.5378 (15)	0.0743 (6)	1.1498 (13)
C(35)	0.6195 (12)	0.0795 (7)	1.0380 (12)
C(36)	0.5581 (14)	0.1271 (6)	0.8928 (14)
C(41)	0.2795 (12)	0.3010 (5)	0.7285 (11)
C(42)	0.3629 (11)	0.3455 (6)	0.8731 (11)
C(43)	0.3245 (12)	0.4264 (5)	0.8948 (12)
C(44)	0.2094 (12)	0.4662 (7)	0.7737 (13)
C(45)	0.1303 (12)	0.4245 (6)	0.6301 (12)
C(46)	0.1664 (11)	0.3427 (6)	0.6063 (11)
H(1)	0.4944 (44)	0.1680 (29)	0.5724 (46)
H(2)	0.2464 (69)	0.2356 (45)	0.3543 (70)
H(3)	0.3287 (69)	0.3502 (44)	0.2360 (75)
H(4)	0.5289 (45)	0.4359 (29)	0.4306 (47)
H(5)	0.7388 (84)	0.3774 (45)	0.6783 (61)
H(6)	0.6470 (69)	0.2690 (41)	0.8062 (74)
H(12)	0.6656 (54)	0.4918 (29)	0.2659 (55)
H(13)	0.8434 (50)	0.4758 (27)	0.1031 (61)
H(15)	0.8597 (100)	0.2185 (29)	0.1746 (107)
H(16)	0.6873 (54)	0.2328 (28)	0.3535 (70)
H(22)	0.0256 (43)	0.2163 (29)	0.6833 (58)
H(23)	−0.1862 (53)	0.1190 (26)	0.5506 (57)
H(24)	−0.1359 (51)	0.0023 (28)	0.3865 (57)
H(25)	0.1188 (49)	−0.0141 (33)	0.3573 (78)
H(26)	0.3374 (54)	0.0804 (24)	0.5008 (68)
H(32)	0.2279 (56)	0.1939 (32)	0.9580 (46)
H(33)	0.3340 (47)	0.1074 (37)	1.2058 (53)
H(34)	0.5882 (50)	0.0402 (44)	1.2639 (69)
H(35)	0.7273 (55)	0.0475 (30)	1.0595 (47)
H(36)	0.6247 (48)	0.1342 (30)	0.8070 (54)
H(42)	0.4580 (56)	0.3155 (23)	0.9672 (60)
H(43)	0.3860 (56)	0.4569 (23)	1.0033 (55)
H(44)	0.1852 (66)	0.5291 (32)	0.7897 (66)
H(45)	0.0370 (74)	0.4544 (24)	0.5325 (72)
H(46)	0.1070 (54)	0.3126 (23)	0.4982 (55)

in the solid state (see Table VI). While we do not yet consider the computed data to be of sufficient precision to allow direct comparison with the solution experiments, they do serve to emphasize that small deviations from planarity can introduce significant differences in the magnitudes of comparable couplings. We can therefore conclude that the ^{1}H NMR data in Table VI point to essentially planar solution conformations for both **2b** and **3b**.

There is, however, also the possibility of a boat–boat inversion which is rapid for the NMR time scale. Figure 6 indicates the predicted geometric dependence of J_{vic}, J_{allyl}, and $J^{\mathrm{trans}}_{\mathrm{homoallyl}}$ for a relatively planar cyclohexa-1,4-diene ring. The mean values to be expected from rapid inversion between two equivalent but relatively inverted boat geometries are also shown. In this latter situation *none* of the couplings is at all sensitive to the conformation of the cyclohexadiene ring for 170° ≤ α ≤ 180°. Variable-temperature ^{1}H NMR experiments on solutions of **2b** and **3b** have proved uninformative so far. When solutions of samples in CD_2Cl_2 are cooled below 0 °C line-broadening occurs and the solubility of each compound decreases rapidly. We have therefore been unable to obtain satisfactory high-resolution spectra over a sufficiently wide temperature range to allow any conclusions to be drawn concerning the temperature dependence of the various coupling constants. However, there is no evidence for significant changes in chemical shift, in marked contrast with the behavior of the *cis*-dihydrotritylbiphenyls **2a** and **3a**.[28]

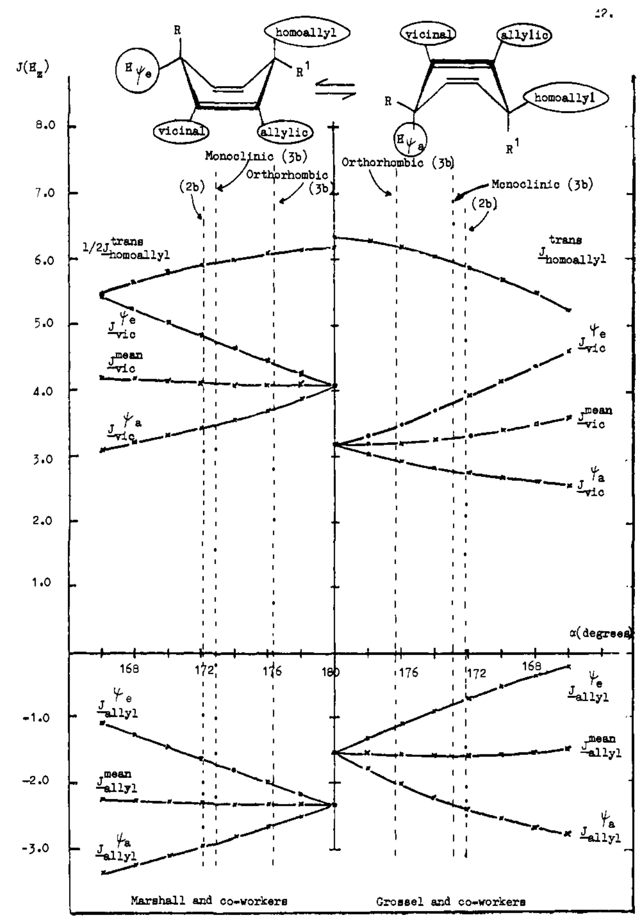

Figure 6. Predicted conformational dependence of vicinal, allylic, and homoallylic couplings about a relatively planar cyclohexa-1,4-diene ring. The data are based on calculations of Marshall, Faehl, McDaniel, and Ledford[10], and Grossel, Perkins, and Hayward.[5,9,11,43] The couplings J_{mean} demonstrate the effect of rapid boat–boat inversion assuming a 50:50 population of equivalent but relatively inverted boat conformations. (For a discussion of the use of $^1/_2J_{\mathrm{homoallyl}}$ from Marshall's calculations, see ref 11.)

Conclusions

We have established that the crystal structures of *trans*-1,4-dihydro-4-tritylbiphenyl (**2b**) and of two crystalline modifications of its 4′-bromo derivative (**3b**) adopt conformations in which the dihydrobenzene ring is slightly puckered. In each case the gross features of the molecular geometry are similar and they appear to be determined by the steric requirements of the dihydrotetraphenylmethane skeleton. The effect of external "packing" forces appears to be small and can be accommodated by slight changes in the conformation of the dihydro aromatic ring. ^{1}H NMR studies suggest that in solution both **2b** and **3b** favour a conformation in which the cyclohexa-1,4-diene geometry is essentially planar. It is not, however, clear whether this ring exists in a shallow single minimum potential well or in a double minimum well with a low energy barrier separating conformations ap-

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(43) Vicinal coupling constant data are yet to be published (Grossel, M. C., unpublished results) but have been discussed elsewhere; see ref 7.

proximating to those seen in the solid state. Since the boat-boat inversion barrier is evidently very low, such a distinction may not readily be resolved. This study has provided a unique opportunity for using crystallographic techniques to probe a molecular vibration in solution.

Acknowledgment. We are grateful to Professor M. J. Perkins (Chelsea College, University of London) for his help and advice.

Supplementary Material Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters for carbon, hydrogen, and bromine, and final observed and calculated structure amplitudes (30 pages). Ordering information is given on any current masthead page.

Electronic Structure of Vinylamine. Proton Affinity and Conformational Analysis

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Abstract: Wave functions for vinylamine (**1**), ethylidenimine (**2**), and methylenimine (**3**) have been obtained at two levels of SCF theory, PRDDO and ab initio. All geometries were optimized at the level of PRDDO. A gradeint calculation with a DZD basis confirmed that the nitrogen is pyramidal in vinylamine. The ab initio calculations of the proton affinities of **1**, **2**, and **3** were performed with STO-3G, DZ, DZD, and DZP basis sets. The values for the PA's using the DZP basis relative to PA(NH_3) = 0.0 are −20.1, −14.9, and −4.6 kcal/mol for **1**–**3**, respectively. The energy difference with the DZP basis set between **1** and **2** is found to be 5.2 kcal/mol with **2** being more stable. The difference between C-protonation (iminium ion) and N-protonation (enammonium ion) of **1** is 18.3 kcal/mol favoring C-protonation. The rotation barrier about the C–N bond in vinylamine has been used to estimate a value of 6 kcal/mol for the strength of the conjugative interaction in **1**. The inversion barriers in the conjugated and nonconjugated forms of **1** were found to be low, 1.5 and 4.2 kcal/mol, respectively. Charge distributions show a significant delocalization of positive charge to the α carbon in the iminium ions. The ionization potentials determined from Koopmans' theorem are typical of those found in amines for **2** and **3**. The ionization potential for **1** is predicted to be quite low, 8.70 eV.

Introduction

Enamines $R_2C{=}CR'NR''_2$ are extremely important in a number of synthetic processes.[1] The reactions of enamines are strongly dependent on their electronic structure, particularly with regard to the nature of the conjugative interaction to the nitrogen. Although numerous substituted enamines have been synthesized, the simplest member of this group, vinylamine (**1**), is difficult to prepare and has not been studied in detail experimentally. Some experimental information about this molecule is available from flow tube studies in which its microwave spectrum was measured.[2] A detailed analysis of the microwave results has also been presented.[3] The proton affinity of vinylamine has been determined from a combination of theoretical calculations and measurements from ion cyclotron resonance spectroscopy.[4] However, most of our information about this simple compound has come from theoretical studies[5–8] which have been done either at the PRDDO level[5,9] or at the ab initio level with the STO-3G[10] and 4-31G basis sets.[11]

Ethylidenimine (**2**) is an isomer of vinylamine; the C-protonated form of vinylamine is identical with N-protonated form of the imine. Although this molecule also cannot be readily prepared and stored, its microwave spectrum[12] and matrix IR spectrum[7] have been obtained. Several theoretical studies of **2** have been published[13,14] and its proton affinity has been determined experimentally.[4] The simplest imine, methylenimine (**3**), is again not readily available for experimental studies,[15–17] and our knowledge of this model compound has come mostly from theory.[13,15,18–20]

Table I. Values for N-H Bond Distances for ab Initio Calculations[a]

basis	$r(\text{N-H})_{\text{pyr}}$[b]	$r(\text{N-H})_{\text{pl}}$[c]	$r(\text{N}^+\text{-H})$
PRDDO	1.033	1.008	1.040
DZ	0.995	0.989	1.012
DZD	1.003	0.991	1.014
DZP	1.001	0.989	1.012

[a] All distances in Å. From optimizations on NH_3 and NH_4^+ from ref 26. [b] Pyramidal nitrogen. These values are also employed in the imine calculations. [c] Planar nitrogen; ref 27.

As part of our program to obtain detailed information about the microscopic behavior of enamines and imines,[-1] especially with

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