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THE PREFERRED CONFORMATION OF CIS-1,4-DIHYDRO-4-TRITYLBIPHENYL: A FLEXIBLE CYCLOHEXA-1,4-DIENE

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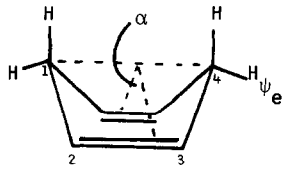
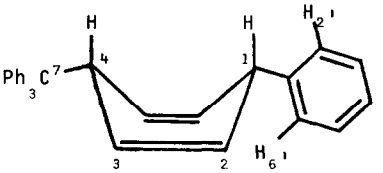
Abstract X-ray crystallographic and solution ^{1}H n.m.r. studies of cis-1,4-dihydro-4--tritylbiphenyl (2) both suggest the presence of an almost planar cyclohexa-1,4-diene ring ($\alpha_{mean} = 175^{o}$).[4]

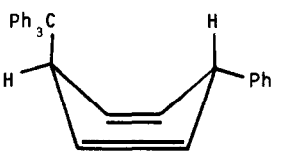
Cyclohexa-1,4-diene (1) and several of its flexible derivatives appear to favour a planar conformation.[1] In contrast, ^{1}H n.m.r. data for cis and trans-1,4-dihydro--4-tritylbiphenyl, (2) and (3) respectively, were originally thought[2,3] to indicate a locked boat conformation in which the bulky trityl substituent is located in a pseudo-equatorial (ψ_e) environment. This argument was based on the magnitude of the homoallylic couplings ($J_{1,4\ cis}$ and $J_{1,4\ trans}$ in (1)), but the availability of more data relating to the geometric dependence of these couplings with varying ring geometry (defined by the angle α[4] in (1)) has led to a reappraisal[1] of this conclusion. Indeed, it has been suggested[1] that whilst the cis-isomer (2) is probably rather puckered (approx. $\alpha \simeq 165^{o}$) with the substituents located pseudoequatorially, the trans isomer (3) may be essentially planar.



(1)



(2)



(3)

We have recently reported [5] ^{1}H n.m.r. and crystallographic studies of trans-1,4-dihydro-4-tritylbiphenyl (3) which support the suggestion that this isomer favours a relatively planar conformation having $\alpha \simeq 171.8^{\circ}$ in the crystal. However, in this structure the trityl group is located in a pseudoaxial environment. In contrast the reported ^{1}H n.m.r. data[2,6] for the cis isomer (2) suggest that in this case the substituents should be pseudoequatorial because the magnitude of $J_{1,4}$ here is greater than the maximum observed for a planar cyclohexa-1,4-diene.[1,7,8,9] Such a result is not unexpected. for pseudoaxial location of the substituents in (2) would lead to severe steric interference between them. In an attempt to gain further insight into the conformation-perturbing effect of a trityl group in (1), we have now completed crystallographic and solution ^{1}H n.m.r. studies on (2).

The molecular geometry of cis-1,4-dihydro-4-tritylbiphenyl (2) is shown in the Figure. The molecule adopts a conformation in which the cyclohexadiene ring is only slightly puckered ($\alpha_{Mean} \simeq 175^{\circ}$) though somewhat distorted ($\alpha_{C_1\text{-}Ph} \simeq 177^{\circ}$ whereas $\alpha_{C_4\text{-}CPh_3} \simeq 173^{\circ}$) and both substituents are pseudoequatorial. A particularly interesting featureof the structure is that the isolated phenyl substituent (at C-1) is oriented along the C(1)-C(4) axis of the cyclohexadiene ring. as it is in the trans isomer! This places one of the ortho protons ($H_{2'}$ or $H_{6'}$) in the r-cloud of one of the trityl phenyl substituents; the proton is situated only ca 2.5Å above the ring plane. The presence of a two proton aromatic absorption at particularly high field in the ^{1}H n.m.r. spectra of (2) and its derivatives has previously[2] been ascribed to two protons of this phenyl substituent. If the n.m.r. spectrum of (2) is studied as a function of temperature, it is found that this multiplet shifts upfield by ca 1.2 ppm as the sample is cooled from $+30^{\circ}$ to -70°. This result suggests a change in the time-averaged conformation of (2) as the solution is cooled. but rotation about the C_1-Ph bond is not frozen out on the n.m.r. time scale. The face-to-face packing of the phenyl rings of the trityl substituent and the cyclohexadiene ring which was observed[5] in the trans isomer is once again apparent here.

^{1}H n.m.r. parameters for (2) are listed in the Table. and differ slightly from those reported[6] earlier. In particular the homoallylic coupling is slightly lower than previously suggested and its magnitude is found to decrease as the solution

is cooled reaching 10.0 Hz at -30°. This is consistent with an almost planar ring conformation at low temperatures close to that found in the crystal. Unfortunately line-broadening and insolubility problems have hampered a more detailed analysis of the low temperature spectra.

In conclusion we have found further evidence to suggest that contrary to earlier interpretationsa trityl group does not lock a cyclohexadiene ring into a boat geometry, rather it favours a relatively planar ring conformation in which the controlling factor is the packing of the substituents about the central trityt carbon atom (C-7 in (2)).

Consequently cis-1,4-dihydro-4-tritylbiphenyl (2) adopts a solid state geometry in which the dihydroaromatic ring is almost planar. There are similarities between the low temperature solution n.m.r. data and the crystal geometry which suggest that this latter may reflect the energy-minimum conformation of (2). Further variable temperature n.m.r. studies of (2) are currently in progress and we are carrying out n.m.r. and crystallographic studies on cis-4'-bromo-1,4-dihydro-4-trityl-biphenyl in order to assess the generality of our observations.

Table Coupling constant data for cis-1,4-Dihydro-4-tritylbiphenyl(2)* (±0.2Hz)

J†	Value (Hz)		J†	Value (Hz)
1.2	2.4		2,3	10.8
1,3	-2.6		2.4	-2.5
1.4	10.5		3.4	2.8

* Data were obtained by computer simulation (LAOCOON 111) of a CD_2Cl_2 solution of (2) at 303K.

† Relative signs determined by spin tickling experiments.

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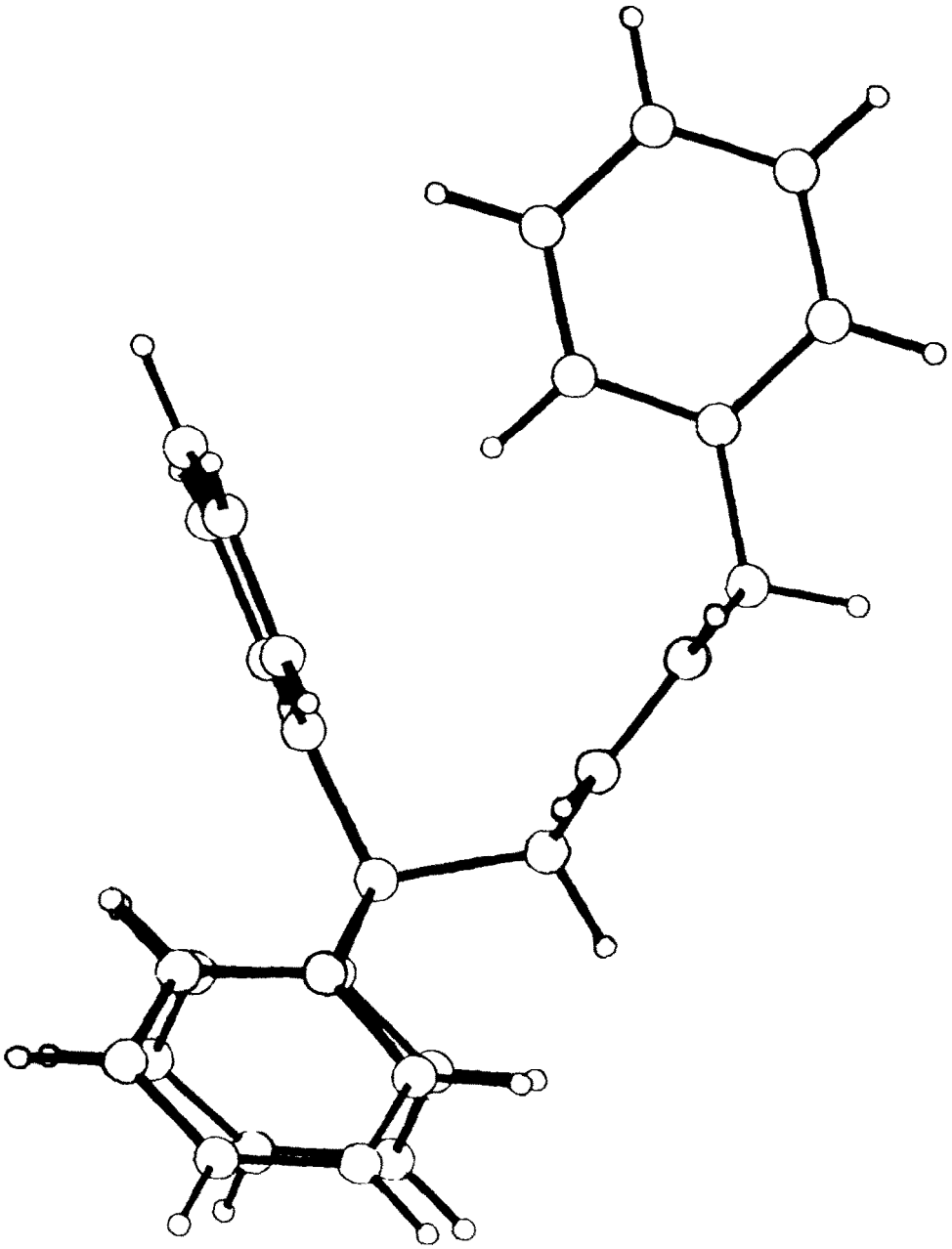

Figure The crystallographic geometry of cis-1,4-dihydro-4-tritylbiphenyl(2).