Tetrahedron Letters No. 52, pp 5229 - 5232.
0040-4039/78/1222-5229$02.00/0

THE EFFECT OF BULKY SUBSTITUENTS ON THE CONFORMATION OF CYCLOHEXA-1,4-DIENE

M. C. Grossel*

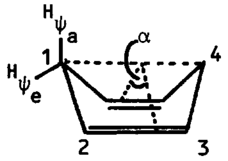
Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY

and

A. K. Cheetham* and J. M. Newsam

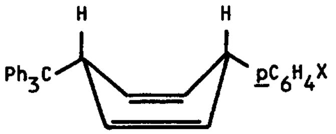
Chemical Crystallography Laboratory, Hooke Building, 9 Parks Road, Oxford, OX1 3RJ

Simple derivatives of cyclohexa-1,4-diene (1) appear to favour a planar ring conformation.[1] It has been suggested,[2,3] however, that bulky substituents at C-1 or C-4 force the ring into a boat conformation,[4] and space filling models indicate[3] that the substituent is located in a pseudoequatorial environment (ψ_e) in order to minimise steric interactions.

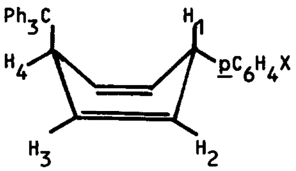


(1)

Among the earliest cyclohexadiene derivatives studied were cis- and trans-1,4-dihydro-4-tritylbiphenyl (2) and (3a) respectively. It was thought [2,3] that the large homoallylic coupling in the cis isomer (2) [ca. 11 Hz] reflects such a highly puckered conformation in which favourable overlap between the C(1)-H and C(4)-H σ-bonds and the p-orbitals of the π-bond optimises the long range coupling interaction. Further evidence for the conformation-locking effect of the trityl substituent was obtained[3] from a preliminary X-ray crystallographic study of the trans-4'-bromo derivative (3b). This suggested that the cyclohexadiene ring was puckered with $\alpha \simeq 165^{\circ}$ and with the trityl group in a pseudoequational position. ^1H n.m.r. data for the trans isomer (3a) revealed a homoallylic coupling $J_{1,4\ trans}$ of ca. 7.5 Hz from which an angle of pucker $\alpha \simeq 166^{\circ}$ was deduced. More recent n.m.r. data suggest that, for a planar cyclohexadiene ring, $J_{trans} \simeq 8.3$ Hz, but that this value should fall to ca. 4.7 Hz when the ring is highly



(2),X = H



(3) a, X = H
b, X = Br

puckered (α ≈ 145°). This result would suggest that the cyclohexadiene ring in (3) should be relatively flat. Indeed we have re-examined the n.m.r. data for (3a) [see Table] and find that $\underline{J}_{\text{homoallyl}}$ is slightly larger than previously reported[3,5] supporting this conclusion, as do the measured allylic couplings.[6]

In view of the incomplete nature of the earlier work, and in the light of the more recent n.m.r. results, we have determined the crystal and molecular structure of trans-1,4-dihydro-4-tritylbiphenyl; the molecular geometry is shown in the Figure. The cyclohexadiene ring is relatively flat (α = 171.8°) in agreement with the ^{1}H n.m.r. data. Surprisingly, however, the location of the substituents is the opposite of that previously suggested i.e. the trityl group is located pseudoaxially. It is interesting to note that the trityl group does not adopt the propeller conformation found in tetraphenylmethane[7] but rather the rings favour an eclipsed conformation.

Our results suggest that caution should be exercised in the use of space-filling models for predicting the effect of substituents on the conformation of a cyclohexa-1,4-diene ring. However, solution n.m.r. data may provide a more reliable probe and we are currently studying the structures of the 4'-bromo compound (3b) and cis isomers (2) of 1,4-dihydro-4-tritylbiphenyl. (X = H,Br).

REFERENCES and NOTES

1. P.W. Rabideau, Acc. Chem. Res., 11, 141 (1978)

2. L. J. Durham, J. Studebaker, and M.J. Perkins, *Chem. Comm.*, 456 (1965).
3. D. J. Atkinson, and M.J. Perkins, *Tetrahedron Lett.*, 2335 (1969).
4. The angle α is that between the planes defined by C(1)-C(2)-C(3)-C(4) and C(4)-C(5)-C(6)-C(1) in (1), which is numbered as a 1,4-dihydrobenzene for convenience.
5. L. Benati, M. Tiecco, A. Tundo, and F. Taddei, *J. Chem. Soc. B*, 1443 (1970).
6. M.C. Grossel, and R.C. Hayward, *J.C.S. Perkin II*, 851 (1976).
7. A. Robbins, G.A. Jeffrey, J.P. Chesick, J. Donohue, F.A. Cotton, B.A. Frenz, and C.A. Murrillo, *Acta Cryst.*, *B31*, 2395 (1975).

Table. Coupling Constant Data for *trans*-1,4-Dihydro-4-tritylbiphenyl (3a) [*]

J[†]	Value (Hz)	J[†]	Value (Hz)
1,2	2.9	2,3	10.7
1,3	-2.2	2,4	-2.1
1,4	7.7	3.4	3.3
	± 0.2 Hz		± 0.2 Hz

[*] Data were obtained by computer simulation (LAOCOON III) of a CD_2Cl_2 solution of (3a) at 303K.

[†] Relative signs determined by spin-tickling experiments.

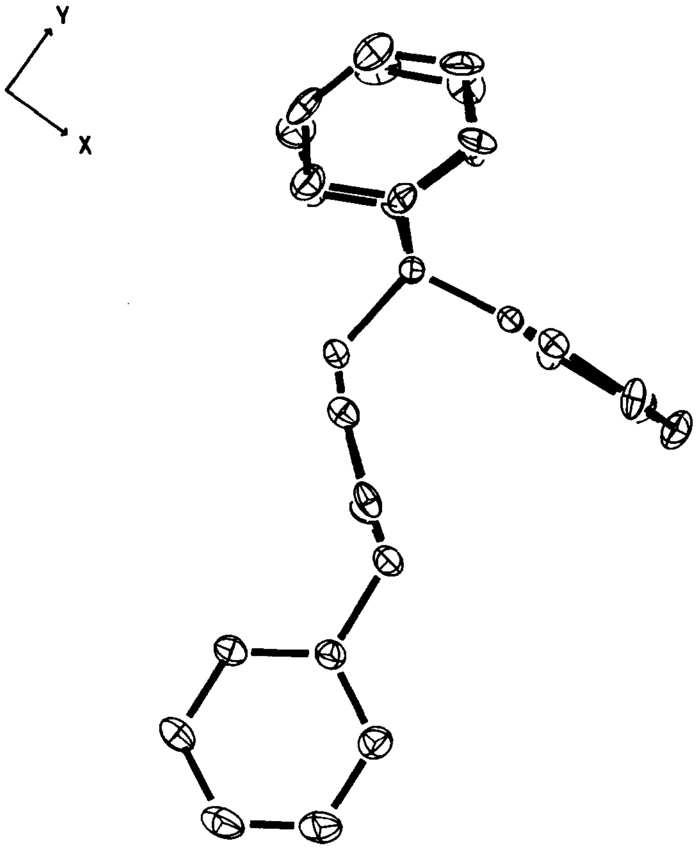


Figure. The crystallographic geometry of trans-1,4-dihydro-4-tritylbiphenyl (3a) [carbon skeleton only].

(Received in UK 20 October 1978)