The Preferred Conformation of Non-transoid Conjugated Dienes

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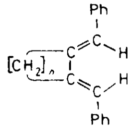
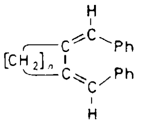
THE strong preference for the *anti*- (or *s-trans*-) conformation of open-chain 1,3-dienes is well documented[1] although not easily explained. When the *anti*-conformation is precluded, it has often been tacitly assumed that a planar *syn*- (or *s-cis*-) conformation is the best alternative, although the structural data available[1] so often reveal a dihedral angle close to the 60° of a normal *gauche* conformation that this can hardly be accidental. Unfortunately, since such diene or polyene chromophores are by necessity part of ring systems, it is impossible to draw a conclusion as to the intrinsic conformational preference. Thus, the observed dihedral angle of 18° in cyclohexa-1,3-diene[2] might be the result of an opening from 0° or a narrowing from 60°, both imposed by the ring structure. We now report chemical evidence that the non-transoid 1,4-diphenylbuta-1,3-diene chromophore, when sufficiently unconstrained, prefers a *gauche*-conformation.

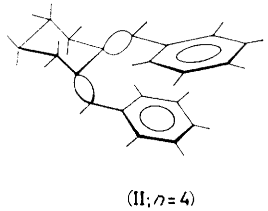
In the thermodynamic equilibrium (see Table) between the *trans,trans*- and *cis,cis*-isomers of 1,2-dibenzylidenecycloalkanes [(I) and (II)] only the former is present when the ring is five-membered ($n = 3$), as expected for a planar diene system because of the steric interference between the two phenyl groups in the latter isomers. Nevertheless, in the case of the six-membered ring ($n = 4$) there is as much as 24% of the *cis,cis*-isomer present at equilibrium. To accommodate two *cis*-phenyl groups, a dihedral angle of at least 60° is required (see Figure). That it is not the rigid cyclohexane chair which imposes such a dihedral angle between the two exocyclic double bonds, is shown by the presence of as much of the *cis,cis*- as of the *trans,trans*-isomer at equilibrium in the case of the seven-membered ring ($n = 5$). This ring is conformationally flexible[3] and could profitably have concentrated most of its inherent bond eclipsing between the benzylidene substituents if planarity had been desirable. The u.v. spectra and the chemical shift of the olefinic proton (see Table) are very similar for the six- and seven-ring *trans,trans*-isomers, and distinctly different from those of the five-ring compound. We conclude that the diene system is forced into planarity by the five-membered ring, but is allowed to assume a *gauche*-conformation in the two larger rings.



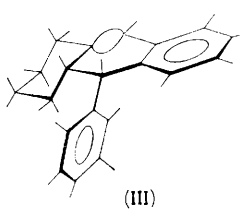
(I)



(II)



(II; $n = 4$)



(III)

Completely analogous results were obtained when the phenyl groups were replaced by β-naphthyl groups. In this case the u.v.-spectrum shows vibrational structure for the five-membered ring, but not for the others, again indicating a planar

Data for 1,2-*dibenzylidene cycloalkanes* (I) *and* (II)

	n	Configuration	(Yield)	M.p.	U.v. absorption λ_1 (log ϵ)	λ_2 (log ϵ)	Olef. in n.m.r. (δ)	Thermodynamic equilibrium	Photostationary state
(I)	5	*t,t*	(6%)	168°	335 (4·1)	238 (3·5)	6·9	100%	100%
(II)	5	*c,c*	—	—	—	—	—	0%	0%
(I)	6	*t,t*	(22%)	141°	286 (4·0)	250 (3·8)	6·6	76%	21%
(II)	6	*c,c*		82°	280 (3·7)	242 (4·0)	6·2	24%	79%
(I)	7	*t,t*	(70%)	48°	286 (4·1)	250 (3·9)	6·6	50%	16%
(II)	7	*c,c*		liquid	—	—	6·2	50%	84%

chromophore in the first case and non-planar in the others.

Very surprisingly, no trace of the *cis,trans*-isomer could ever be observed, although the equilibrium between the *trans,trans*- and *cis,cis*-isomer can be reached rapidly from both sides both thermally and catalytically (I_2 + light). Ultraviolet irradiation alone produces a photostationary state richer in the *cis,cis*-isomer (see Table). Synthesis by a Wittig reaction from cyclohexane-1,2-dione, and even from *trans*-2-benzylidenecyclohexanone, gave predominantly the *cis,cis*-isomer when the reaction was run quickly and the base (potassium t-butoxide in t-butyl alcohol) was added carefully. That the *cis,cis*-isomer is formed initially may be rationalized on the basis of the most likely conformation of the betaine[4] of the last step only if it is postulated that the intermediate 2-benzylidenecyclohexanone undergoes rapid *cis-trans* equilibration and that the *cis*-isomer reacts much faster with the ylid.

The absence of *cis,trans*-1,2-dibenzylidenecyclohexane and -heptane suggests a kind of cog-wheel mechanism for the thermal isomerization: when rotation occurs about one double bond, its momentum is transferred by hydrogen–phenyl collision to give rotation about the second double bond. It may be difficult, however, to accept this explanation for the catalyzed isomerization. It is also difficult to believe in a cyclobutene intermediate, as its closing and opening would then have to be strictly either both con- or both syn-rotatory.[5] This is unlikely under such a diversity of conditions.

The *cis,cis*-isomers are chiral molecules. Their α-CH_2-protons are non-equivalent and give therefore below ~100° a more complex pattern in the n.m.r.-spectrum than the α-CH_2-protons of the corresponding *trans,trans*-isomers, where ring inversion is not blocked. At ~100° the spectrum simplifies. No *trans,trans*-isomer could be detected after this treatment, indicating that the phenyl groups are able to slide past each other to effect racemization.

Heating converts each dibenzylidenecycloalkane *via* the *cis,cis*-isomer of the equilibrium mixture cleanly into a structurally isomeric compound. For the six-membered ring this occurs at 300° in 80% yield, and the product, m.p. 121°, was shown to be the *cis*-9-phenylhexahydroanthracene (III). The *cis,cis*-di-β-naphthylmethylidene compounds undergo this cyclization at 170°.

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