The Conformations of *cis*- and *trans*-Isomers of Benzylideneanilines: ^{1}H Nuclear Magnetic Resonance and Optical Spectroscopic Studies

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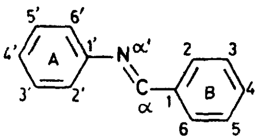
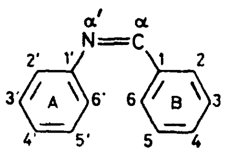
The conformations of the *cis*- and *trans*-isomers of benzylideneanilines were studied by two spectroscopic approaches. Effects of *trans–cis* isomerization on diamagnetic shielding in the ^{1}H n.m.r. spectra suggest only a limited deviation of the aniline ring from the 1-α-α′-1′ plane in the *trans*-isomers in the absence of steric hindrance due to methyl substitution. Similar conclusions are suggested by the intensity-lowering effects of *trans–cis* isomerization and of methyl substitution on the first electronic absorption band. Such effects also indicate that the first electronic transition extends over the whole molecule as in stilbene and rule out the possibility that the aniline ring is perpendicular to the 1-α-α′-1′ plane in either isomer of benzylideneaniline.

DURING the last few years n.m.r. spectroscopy has been successfully applied to several problems of structure and conformation determination of unstable photoisomers.[1] The most important structural parameter obtained experimentally from the ^{1}H n.m.r. spectrum of an unstable intermediate is the extent of diamagnetic shielding felt by a particular group of nuclei. This quantity, expressed as a shielding shift Δ, is related by the ring current model (see below) to two geometrical parameters ρ and z, ρ being the in-plane and z the out-of-plane component of the vector connecting a given nucleus with the centre of the shielding ring. ρ and z are thus determined once the set of atomic co-ordinates of the intermediate is known. For unstable intermediates, as in the present work, this is never the case and one has to resort to computed molecular structures (*cf.* ref. 1).

In the present paper we apply this approach in a qualitative sense to a series of thermally unstable *cis*-photoisomers † of variously substituted benzylideneanilines.[3] Progressive methyl substitution at the α- and *ortho*-(2,6,2′,6′) ring positions will be used as a tool for introducing varying extents of torsion around the C–N 1′-α′ bond and the C–C 1-α bond in both *trans*-(*E*) and *cis*-(*Z*) isomers.



trans (*E*)



cis (*Z*)

The definition of torsional angles θ and of bond angles ϕ is as follows

Angle	Defining atoms
θ_N	6′-1′-α′-α
θ_C	6-1-α-α′
ϕ_N	1′-α′-α
ϕ_C	1-α-α′

We shall also consider the effects of these distortions on the electronic absorption spectra of the *cis*- and *trans*-isomers. The systematic analysis of these effects allows an unambiguous characterization of the first electronic transition to be made in these molecules, and provides additional information about their geometry.

Though *cis–trans* photoisomerization has been studied for several benzylideneanilines,[4-6] little information could be obtained in these studies on the geometry of the *cis*-isomers besides that available from the optical spectra.

During the course of this work the n.m.r. spectra of the *cis*-isomers of substituted 4-dimethylamino-*N*-benzylideneanilines were reported by Kobayashi *et al.*[7,8] Their work is of particular relevance to the present study as dimethylamino-substitution was shown [9] to favour (at least in the case of the *trans*-forms) a planar conformation unlike that existing in other benzylideneanilines.

Several different molecular conformations of *trans*-benzylideneanilines have been observed in the crystalline state.[10a] (a) First, there is a conformation with considerable torsion of ring A about the C–N bond but with limited torsion about the C–C single bond. The values in the parent compound (1) (θ_N 55°, θ_C −10°) are typical,[10b] and similar values are obtained for the 2,4-dichloro-, the 4′-carboxylic acid, the 4-methyl-4′-nitro-, and the 4′-bromo-derivatives.[10a] (b) Secondly, there is a planar conformation, observed in the metastable form of 4,4′-dichloro-, 4,4′-dibromo-, and 4-nitro-4′-dimethylamino-benzylideneaniline. (c) Finally, there is a non-planar conformation with significant torsion about both C–N and C–C single bonds as in the stable modification of 4,4′-dichlorobenzylideneaniline ($\theta_N = \theta_C = 25°$).

Whether the *trans*-isomers retain a similar geometry in solution remains largely an open question (as in many other cases) because both the barriers to torsion about the single bonds such as the 1′-α′ and the 1-α bond and the energy differences between the conformers are small.[10b] However, the low value of the oscillator strength of the first electronic transition in benzylideneaniline suggests a strong deformation (relative to the geometry of *trans*-stilbene). In most MO studies of benzylideneanilines, various extents of torsion about the 1′-α′ bond were thus suggested though other types of deformation were also considered. Among the geometries

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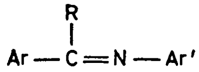
† Recent nomenclature [2] designates the two geometrical isomers as *E* (*trans*) and *Z* (*cis*).

considered in the more recent literature one should note: ' perpendicular ' geometries, *e.g.* θ_N 90, ϕ_N 180, ϕ_C 120° [11] or θ_N 90°, ϕ_N 117, ϕ_C 53°; [12a] ' benzylideneaniline-crystal ' geometry, θ_N 40—60°; [12b] a ' linear ' form, $\theta_N = \theta_C = 0$, ϕ_N 156, ϕ_C 128°.[13]

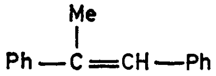
In the present study we included compounds (1)—(10),



$$\mathrm{Ar{-}\overset{\overset{\Large R}{|}}{C}{=}N{-}Ar'}$$

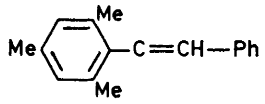
(1) Ar = Ar′ = Ph, R = H
(2) Ar = Ar′ = Ph, R = Me
(3) Ar = Ph, Ar′ = 2,4,6-$Me_3C_6H_2$, R = H
(4) Ar = Ph, Ar′ = 2,4,6-$Me_3C_6H_2$, R = Me
(5) Ar = Ph, Ar′ = 2,6,-$Me_2C_6H_3$, R = Me
(6) Ar = Ar′ = 2,4,6-$Me_3C_6H_2$, R = H
(7) Ar = Ph, Ar′ = β-$C_{10}H_7$, R = H
(8) Ar = Ph, Ar′ = β-$C_{10}H_7$, R = Me
(9) Ar = β-$C_{10}H_7$, Ar′ = Ph, R = H
(10) Ar = β-$C_{10}H_7$, Ar′ = Ph, R = Me
(15) Ar = 4-$Me_2NC_6H_4$, Ar′ = Ph, R = H
(16) Ar = 4-$Me_2NC_6H_4$, Ar′ = 2,6-$Me_2C_6H_3$, R = H
(17) Ar = 2-Me-4-$Me_2NC_6H_3$, Ar′ = Ph, R = H

Ph—CH=CH—Ph
(11)

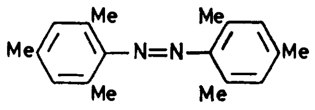


$$\mathrm{Ph{-}\overset{\overset{\Large Me}{|}}{C}{=}CH{-}Ph}$$

(12)



(13)



(14)

and also for comparison purposes stilbene (11), α-methylstilbene (12), 2,4,6-trimethylstilbene (13), and 2,2′,4,4′,6,6′-hexamethylazobenzene (14).

RESULTS AND DISCUSSION

N.M.R. Spectra.—The percentages of the *cis*-isomers of the benzylideneanilines in the photostationary state (measured by spectrophotometry, at −100 °C) is given in Table 1. Typical 90-MHz n.m.r. spectra, before and after u.v. irradiation are given in Figure 1. These experiments were carried out at −70°. The ^{1}H n.m.r. data for the α-group R, for the *o*- and *p*-methyl groups, and for the ring *meta*-protons are summarized in Table 2. The chemical shift differences Δ are relative to the values for the *trans*-isomers. For comparison, some n.m.r. data for the three 4-dimethylamino-*N*-benzylideneanilines (15)—(17) [7,8] are listed in Table 3.

Analysis of Shielding Effects: Proton and Methyl Protons at the α-Position.—Of all the magnetic intramolecular shielding effects to which the α groups are subjected only the interaction with ring A is changed by the *trans–cis* isomerization process. The results obtained with *trans*- and *cis*-stilbene (see below) seem to justify the neglect of other effects at this stage such as those due to the shielding effects of the nitrogen lone pair. The magnetic shielding effects will be analysed according to the ring currents model [14] using the parametrization and numerical values of Johnson and Bovey.[14a,b,] *

TABLE 1

Irradiation wavelength λ and photostationary state composition

Compound	(1)	(2)	(3)	(4)	(5)
λ/nm	313 [b]	366 [b]	313 [b]	366 [c]	366 [c]
% *cis* [a]	85	65	75	45	66
Compound	(6)	(7)	(8)	(9)	(10)
λ/nm	366 [b]	313 [b]	366 [c]	313 [b]	366 [c]
% *cis* [a]	33	80	40	80	68

[a] Percentage *cis*-isomer in photostationary state mixture. [b] Methylcyclohexane solution. [c] Methylene chloride solution.

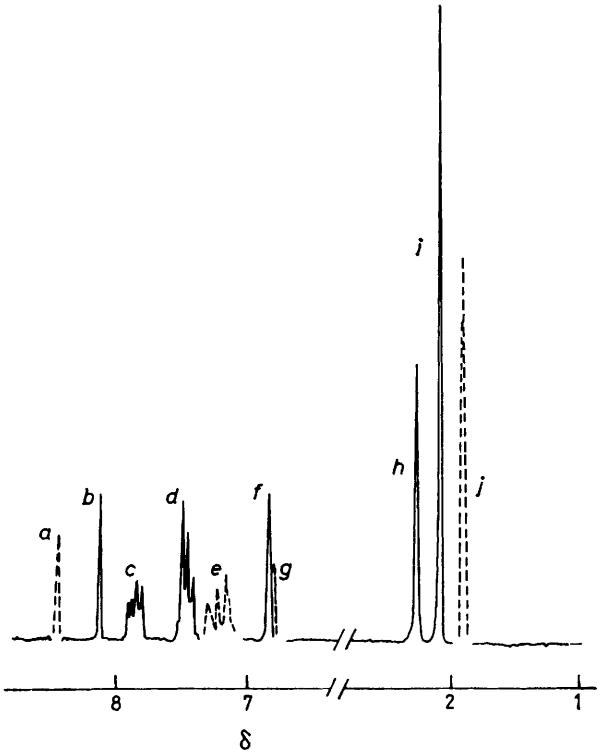


FIGURE 1 Low temperature 90-MHz ^{1}H n.m.r. spectra of *trans*- (——) and *cis*- (– – – –) isomers of (3) both in CD_2Cl_2 at −70 °C. Concentration 4.5 × 10^{-2}M. Assignments: a, b, α; f, g, 3′-, 5′-H; i, j, 2′-, 6′-methyl; h, 4′-methyl

On the basis of the effect of the *trans–cis* isomerization on the chemical shift of the α-proton H^α (or of the α

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* The shielding values predicted by the Haigh and Mallion model [14c] are too low to account for the effects observed here. These authors have noted that the shielding predicted by this model are underestimated for protons above rings and in their close proximity.[14c]

methyl protons, CH_3^{α}) the molecules of Tables 2 and 3 can be divided into two groups. In group a [compounds (2)—(6), (8)—(10), and (16)] the chemical shift difference $\Delta^{\alpha}[\Delta^{\alpha} = \delta(cis) - \delta(trans)]$ is positive. In group b [(7), (15), (17), and model compounds (11) and (12)] Δ^{α} is negative. As shown by the shielding effects calculation on the five models (Tables 4 and 5) the difference between the two groups is mainly due to the near planarity of the *trans*-isomers in group b. Thus in the *trans*-benzylideneaniline model I (Table 4), z, the out-of-plane component of the position of H^{α} relative to the centre of ring A is obviously zero, subjecting H^{α} to a large deshielding effect of −0.7 p.p.m. However, in the other *trans*-models II and IV z is *ca.* 2 Å, but ρ, the in-plane component of the position of H^{α} is smaller than in I (*ca.* 3 *versus* 3.6 Å in I) and thus only small shielding effects result, −0.10 p.p.m. in II, 0 in IV. The *cis*-models III and V are all necessarily twisted about the 1-α bond. z is *ca.* 1 Å in both but ρ (*ca.* 4.5 Å) is significantly larger than in the *trans*-models leading to deshielding contributions of 0.3 p.p.m. in both. The theoretical shielding differences for H^{α} due to *trans*–*cis* isomerization in several hypothetical molecules are given in Table 5. Process I ⟶ III, resulting in a negative Δ effect of −0.40 on H^{α}, describes the isomerization effects in group b. Processes II ⟶ III, IV ⟶ V, and II ⟶ V all result in similar positive Δ effects of 0.3—0.2 p.p.m. These describe the shielding changes on H^{α} in molecules in group a. The predicted Δ values for both groups a and b are fairly representative of the experimental shielding changes in H^{α} and CH_3^{α} listed in Tables 2 and 3.

TABLE 2

90-MHz ^1H N.m.r. chemical shifts (CD_2Cl_2; δ from Me_4Si) of *trans*- and *cis*-isomers of benzylideneanilines (1)—(10) and of related molecules (11)—(14). Δ Denotes the chemical shift change relative to *trans*-isomer

	C(R)=N			*o*-CH_3			*p*-CH_3			*m*-H		
Compound	*trans*	*cis*	Δ	*trans*	*cis*	Δ	*trans*	*cis*	Δ	*trans*	*cis*	Δ
(1)	8.50	*a*										
(2)	2.15	2.44	+0.29									
(3)	8.11	8.45	+0.34	2.12	1.88	−0.24	2.28	2.28	0.0	6.82	6.80	−0.02
(4)	2.06	2.56	+0.50	1.95	1.95	0.0	2.28	2.19	−0.10	6.89	6.71	−0.18
(5)	2.08	2.58	+0.50	1.99	1.99	0.0						
(6)	8.56	8.69	+0.13	{2.15 2.55	{1.87 2.01	{−0.28 −0.46	{2.29 2.34	{2.21 2.25	{−0.08 −0.09	{6.98 6.92	{6.76 6.76	{−0.22 −0.16
(7)	8.64	8.51	−0.13									
(8)	2.29	2.59	+0.30									
(9)	8.65	*a*										
(10)	2.37	2.64	+0.27									
(11)	7.10 [b]	6.55 [b]	−0.55									
(12)	2.31	2.24	−0.07									
(13)	{6.55 [c] 7.08			2.30	2.06	−0.24	2.23	2.23	0.0	6.86	6.80	−0.06
(14)				2.37	1.89	−0.48	2.30	2.20	−0.10	6.98	6.76	−0.22

[a] Too unstable to be measured. [b] In $CDCl_3$. [c] Proton next to trimethylphenyl ring.

TABLE 3

60-MHz ^1H Chemical shifts (δ from Me_4Si) of *trans*- and *cis*-4-dimethylaminobenzylideneanilines (15)—(17), as reported in ref. 7. Δ defined as in Table 2

	α-H			2-H		
Compound	*trans*	*cis*	Δ	*trans*	*cis*	Δ
(15)	8.41	8.21	−0.20	7.85	7.09	−0.76
(16)	8.15	8.37	0.22	7.87	7.03	−0.84
(17)	8.63	8.53	−0.10	8.03 [a]	6.65 [a]	−1.38

[a] 6-H.

Because of insufficient thermal stability, δ(*cis*) is unavailable for (1) and (9). However, by analogy with the other molecules of group b, it seems very likely that $\Delta^{\alpha} = \delta(cis) - \delta(trans)$ will be negative for these.

TABLE 4

Theoretical shielding effects on H^{α} (in p.p.m.) in some models of benzylideneanilines. ρ and z are the two components of the radius vector from centre of shielding ring A to H^{α}. ρ lies in the plane of ring A and z is the component along the hexad axis

Model	θ_N(°)	θ_C(°)	ρ(Å)	z(Å)	Shielding (p.p.m.)
I Planar *trans*	0	0	3.60	0	−0.70
II 60° *trans*	60	0	3.12	1.79	−0.10
III 60° *cis*	60	0	4.56	0.99	−0.30
IV 90° *trans*	90	0	2.95	2.06	0
V 90° *cis*	90	0	4.53	1.15	−0.30

TABLE 5

Theoretical shielding effects on H^{α} (p.p.m.) for several model *trans* ⟶ *cis* processes. Isomer models denoted as in Table 4

cis	*trans*	Δ (model) (p.p.m.)
III	I	−0.40
III	II	0.20
V	IV	0.30
V	II	0.30

U.v. spectroscopic studies of *trans*-(11) in solution suggest a planar conformation,[15] while a 1-α twisted conformation is indicated for the *cis*-isomer.[15] Going from the planar *trans*- to the 1-α twisted *cis*-isomer (Table 2) H^{α} undergoes a high-field shift [as in (15)], the result of the deshielding effect of ring A on H^{α} in the *trans*-isomer. Compound (11) can thus serve as model for molecules of group b, and as such enables the shielding effects of the nitrogen lone pair on H^{α} to be separated from other shielding effects. That Δ^{α} in (11) [and (12)] and in the group b molecules are of the same sign (negative) indicates that the nitrogen lone pair shielding effects should not significantly affect the present conclusions.

Comparison of Deshielding Effects on H^{α} *in the* trans-*Isomers*.—Tables 2 and 3 reveal marked differences in the H^{α} chemical shifts of the *trans*-isomers. On the one hand in (1), (7), (9), (15), and (17) H^{α} falls between δ 8.41 and 8.65. On the other, in the compounds with *ortho*-methyl substituents on ring A, such as (3) and (16), H^{α} fall at *ca.* 8.1: in these two molecules ring A is clearly not coplanar with the H^{α}–C^{α}–$N^{\alpha'}$ plane as no deshielding influence on H^{α} is exerted here. For similar effects in other *trans*- benzylideneanilines with *ortho*-methyl groups on ring A, see ref. 16.

Up to this point we were concerned only with the diamagnetic shielding effects of ring A on H^{α} or CH_3^{α} and with the way these effects depend on θ_N in the *trans*- or *cis*-isomers as function of substituents. Substitution at the 2 and 6 position of ring B requires the inclusion of another magnetic interaction as can be judged from the low field at which H^{α} appears in *trans*-(6) [δ 8.56 compared with δ 8.1 for H^{α} in *trans*-(3) or *trans*-(16)].

This low field shift is probably due to a *loss of shielding by ring* B as a result of the decrease of overlap across the 1-α bond and the accompanying decrease in electron density on the α-carbon and on H^{α}. Similar deshielding effects of ring B on H^{α} were described recently in *trans*-benzylideneanilines substituted at the 2 position with methyl, methoxy-, bromo-, and nitro-groups.[16]

Shielding Effects on Ring Protons and Ring Methyl Protons.—All these nuclei show a qualitatively similar behaviour though with varying quantitative aspects. The chemical shift differences Δ are mostly negative (Tables 2 and 3) because, due to the shielding effect, the signal of a given nucleus occurs in the *trans*-isomer at a lower field than in the *cis*-isomer. The important factor for understanding such effects is the mutual shielding of one ring on the protons of the other. In the *css*-isomers, due to the shorter inter-ring distance and to the favourable tilting with respect to the 1-α-α′-1′ plane, a relative shielding effect ensues. The effects are the most prominent on the *ortho*-groups, slightly lower on the *meta* protons, and smallest on the *para*-groups as required by considerations of proximity to the shielding region of the opposite ring.

Electronic Spectra.—Methyl substitution at the α and at the four *ortho*-ring positions as well as the *trans–cis* isomerization process give rise to increased intramolecular steric hindrance which would result in molecular strain were a planar conformation maintained. This strain is minimized by distortions to new conformations. The most effective distortion (energywise) for lowering this strain in the benzylideneanilines as well as in the related 1,2-diarylethylene series [17] is the torsion about the 1′-α′ and the 1-α single bonds. Thus comparing the intensity of an electronic transition of an undistorted molecule with the intensity in a molecule distorted by either methyl substitution or *trans–cis* isomerization allows the determination of the effects of a particular distortion (in this case torsion about a single bond) on a given electronic transition. The lack of a sizeable effect would mean that the molecular orbitals of the upper and lower state have only small coefficients at the 1,1′, α, and α′ atoms. The contrary conclusion would be reached if a considerable effect was observed. The present discussion is concerned only with ground-state distortion (*cf.* ref. 17 for effects of distortions on excited-state geometry.

The results are summarized in Figure 2 and in Table 6.

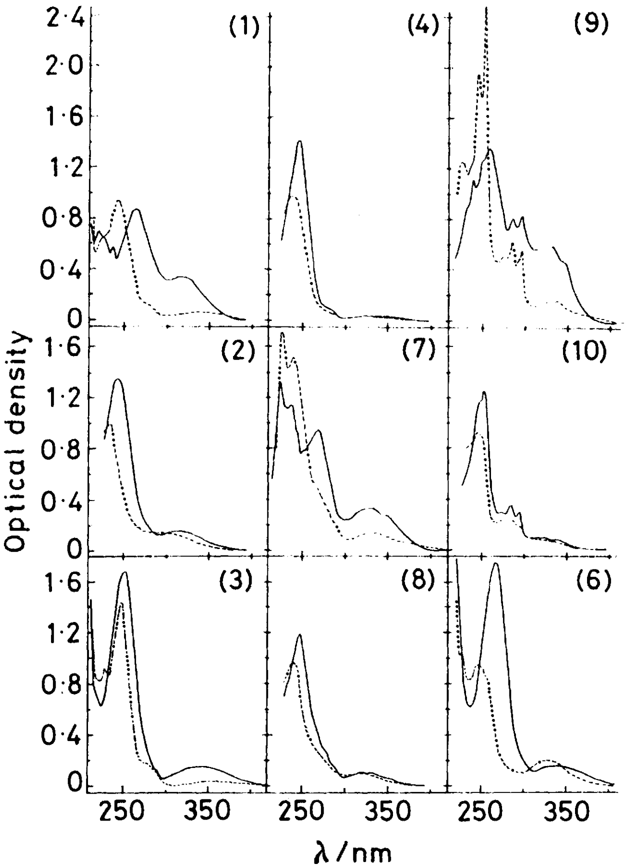

Figure 2 Low temperature absorption spectra of *trans*- (——) and *cis*-isomers (– – – –, extrapolated) of benzylideneanilines (1)—(4) and (6)—(10). The conditions used are as follows: (1) 3.7×10^{-5}M, −100°, MCH–2-MP; (2) 5.7×10^{-5}M, −70°, CH_2Cl_2; (3) 5.8×10^{-5}M, −100°, MCH–2-MP; (4) 4.2×10^{-5}M, −70°, CH_2Cl_2; (6) 6.5×10^{-5}M, −100°, MCH–2-MP; (7) 2.9×10^{-5}M, −100°, MCH; (8) 2.2×10^{-5}M, −60°, CH_2Cl_2; (9) 3.6×10^{-5}M, −100°, MCH; (10) 1.8×10^{-5}M, −60°, CH_2Cl_2

The solvents used were methylcyclohexane (MCH) and its mixture with 2-methylpentane (2-MP). In the following discussion we shall limit ourselves to the first transition.

Unsubstituted Molecules (1), (7), *and* (9).—The extinction coefficients for the first transition in the *trans*-molecules vary between 9 600 and 16 500 indicating a not unduly twisted conformation. This conclusion is supported by the large effect of *trans–cis* isomerization which reduces the extinction coefficients by a factor of *ca.* 7.

α-Methyl-substituted Molecules (2), (8), *and* (10).—These molecules differ from (1), (7), and (9) by a methyl group at the central unit. This methyl group exerts a pronounced effect on the intensity of the first transition in the *trans*-isomers: going from (1) to (2) we observe a three-fold reduction in the intensity and similar effects in (8) and (10). These results strongly suggest an intermediate deviation from planarity in these molecules, and a similar situation in the *cis*-molecules (in which however both θ_N and θ_C would be larger).

TABLE 6

Absorption maxima λ (nm) and ε values ($\times 10^{-4}$, in parentheses) at −100 °C in MCH solution

Compound												
(1)	*trans*	218 (1.9)	226 (sh)	237 (1.6)	264 (2.4)				318 (0.96)			
	cis		225 (sh)	235 (sh)	243 (2.6)	285 (sh)			343 (0.13)			
(2)	*trans*				248 (2.6)				323 (0.27)			
	cis				237 (2.0)				314 (0.24)			
(3)	*trans*	220 (sh)	230 (sh)		254 (2.9)		288 (0.20)		344 (0.26)			
	cis	222 (sh)	230 (1.6)		250 (2.5)	278 (0.31)	285 (0.21)		380 (0.045)			
(4) *	*trans*				245 (3.36)	276 (sh)	285 (sh)		330 (0.092)			
	cis			236 (2.32)	242 (sh)	276 (sh)	285 (sh)		324 (0.087)			
(5) *	*trans*				244 (3.75)				322 (0.087)			
	cis				237.5 (2.75)				315 (0.079)			
(6)	*trans*	224 (sh)			267 (2.7)				304 (sh)	337 (0.25)		
	cis	227 (1.6)			247 (1.4)	257 (sh)				327 (0.30)		
(7)	*trans*	225 (4.52)	232 (sh)	238 (3.90)	245 (3.17)	252 (2.67)	269 (3.22)		330 (1.14)	348 (0.95)		
	cis	228 (0.59)		240 (0.52)	245 (sh)		267 (sh)		333 (0.47)	370 (sh)		
(8) *	*trans*			247 (5.34)			278 (sh)	288 (sh)	321 (0.45)	332 (0.45)		
	cis			242 (4.31)					320 (0.39)	332 (sh)		
(9)	*trans*	233 (sh)	240 (3.10)	249 (sh)	258 (3.79)	285 (2.25)	297 (2.31)		318 (1.59)	332 (1.65)	346 (1.44)	
	cis	226 (3.49)	244 (5.42)	253 (6.99)	280 (1.44)	285 (1.73)	292 (1.33)	297 (1.55)	326 (0.43)	332 (0.44)	339 (0.45)	360 (0.22)
(10) *	*trans*	248 (sh)	254 (6.84)	274 (1.65)	284 (1.96)	295 (1.65)	324 (0.55)	337.5 (0.47)				
	cis	245 (5.1)	250 (4.9)	276 (1.3)	285 (1.3)		329 (0.49)					

* In CH_2Cl_2 solution at −70 °C. (sh) = shoulder.

Molecules with Methyl Groups on the Aniline Ring. (3), (4), (5), *and* (6).—The *ca.* 4-fold reduction in intensity of the first transition in *trans*-(3) [compared with (1)] again suggests an *intermediate* extent of twist about the 1′-α′ C–N bond in *trans*-(3). The further intensity reduction going to *cis*-(3) would indicate that only in this case is ring A nearly perpendicular to the 1′-α′-α plane. The same holds for the α-methyl substituted (4) and (5): here in both *trans*- and *cis*-isomers ring A is expected to be nearly perpendicular to the 1′-α′-α plane. *trans* and *cis*-(6) seem to resemble strongly *cis*-(1), *cis*- and *trans*-(2), and *trans*-(3), probably involving some intermediate torsion about both 1-α and 1′-α′ bonds.

Conclusions.—The above analysis suggests two conclusions which differ, however, from those of earlier authors.

(a) The first transition in benzylideneanilines clearly extends over the whole molecule as it is drastically influenced by torsion about the 1′-α′ and the 1-α bonds and thus closely resembles the first transition of stilbene.

(b) Ring A is definitely not perpendicular to the 1′-α′-α plane in *trans*-benzylideneaniline (1), in *trans*-(7), and in *trans*-(9) and even in the not too highly sterically hindered derivatives such as *cis*-(1), *cis*-(7), *cis*-(9), *cis*- and *trans*-(2), *trans*-(3), *trans*-(6), *trans*-(8), and *trans*-(10). An angle θ_N close to 90° is likely only in *cis*-(3) and *cis*- and *trans*-(4) and -(5). On the other hand *trans*-benzylideneaniline probably deviates to some extent from true planarity as deduced by Skrabal *et al.*[9] by comparing the intensity of the first transition in *trans*-benzylideneaniline and in the necessarily planar 3*H*-indole. That this deviation is still far away from perfect perpendicularity of ring A is shown however by the n.m.r. results and the electronic transition intensity effects reported here.

EXPERIMENTAL

The spectrophotometric and photochemical techniques are described in ref. 1. N.m.r. experiments were performed at 90 MHz on a Bruker HFX-10 spectrometer in the Fourier-transform mode. The *in situ* optical-irradiation technique is described elsewhere.[18] The compounds used were prepared according to the original literature.[19]

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