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52. Concerning the Conformation of Isolated Benzylideneaniline¹⁾

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Summary. From PE.-spectroscopical studies the torsional angle φ of the N-phenyl ring in isolated benzylideneaniline **1** has been found to be definitely smaller than $\varphi = 90^\circ$. An approximate value $\varphi = 36^\circ$ has been estimated which is even smaller than the one observed in the crystal ($\varphi = 55^\circ$) and suggested to prevail also in solutions of **1**. A reevaluation of the gas phase optical spectrum of isolated **1** supports a torsional angle similar to that found in the other phases.

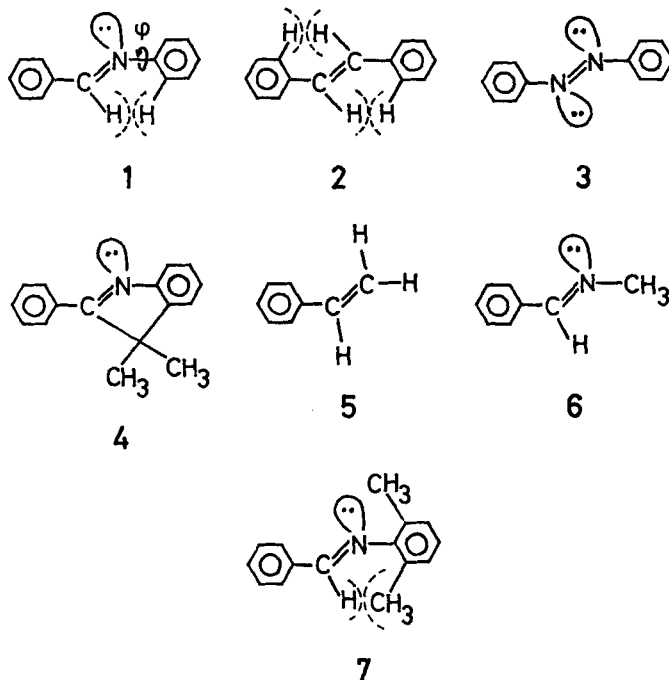
Calculations of the most stable conformation of **1** as well as of stilbene and azobenzene by the MINDO/3-technique lead to torsional angles $\varphi = 90^\circ$ for both phenyl rings in all cases. These results are at variance with the experimental results and suggest that MINDO/3-like its less advanced precursor MINDO/2 or like CNDO/2-is unreliable for low energy processes involving rotation of π -systems connected by essential single bonds.

It is concluded that the π -energy of benzylideneaniline, like that of stilbene or azobenzene, would favor a planar conformation. The increased torsional angle in **1** as compared to the other two *iso*-conjugate systems arises from a larger steric interaction between phenyl- and bridge-protons.

Introduction. – Crystalline benzylideneaniline (**1**) exhibits – in contrast to its *iso*-electronic and essentially planar analogues *trans*-stilbene (**2**) [2] and *trans*-azobenzene (**3**) [3] – an angle of twist $\varphi = 55^\circ$ of the N-phenyl-ring about the C–N essential single bond [4]. This deviation from planarity was already postulated on the basis of the marked differences between the optical spectra of **1** and **2** or **3** [5] and by the resemblance of the optical absorption spectrum of **4**, where planarity is enforced by bridging, to those of **2** and **3** [6]. That the angle of twist for **1** in solution is not too different from that in the solid is suggested by the similarity between its solution and its crystal reflectance spectrum [7]. A recent illuminating study employing derivatives of **1** and of the planar reference system **4** has indicated that the angle of twist varies markedly for different substituents in the *p, p'*-positions, $\varphi \approx 0^\circ$ being presumably realized for 'push-pull' substitution which increases the bond order of the relevant $C_{sp^2}-N_{sp^2}$ bond [8].

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Theoretical studies have suggested that the driving force for the out-of-plane twist of the N-phenyl ring in **1** essentially arises from steric hindrance due to the contact of the *ortho*-H-atoms of the N-phenyl ring and the H-atom attached at the imino C-atom [9]. This idea implies that the out-of-plane motion is associated with an increase in π -energy which is, however, overcompensated by a decrease in steric hindrance up to $\varphi = 55^\circ$.



Using *Allen's* nomenclature [10] the non-planarity of **1** is thus the result of a 'repulsive-dominant' process. This mechanism seems certainly reasonable in view of the actual planarity of the *iso*-electronic system **3** where a similar steric contact is absent. It should be added here that **3** seems to be at least *peri*-planar in the gas phase as well, since its vapour phase optical spectrum is remarkably similar to those obtained from solutions or from the crystal [11].

For **2** a recent electron diffraction study indicates a torsional angle $\varphi = 30^\circ$ for the phenyl rings about the essential single bonds [12]. Of course, **2** exhibits a similar steric contact between H-atoms as present in **1**. The non-planarity of **2** is, however, not so large as to seriously influence its resonance energy [12].

The idea of **1** being twisted by a 'repulsive dominant' driving force is, however, implicitly challenged by the conclusions delivered in [13] where the gas phase optical spectrum of **1** has been measured. Indeed, this spectrum is sufficiently different from those obtained from solutions or from the crystal of **1** and sufficiently similar to that expected from a superposition of the spectra of aniline, benzaldehyde and N-benzylidenemethylamine to spontaneously support these author's conclusion that the twist angle of **1** in the gas phase is about 90° .

If, however, this angle is indeed realized in isolated **1**, the out-of-plane twist of the N-phenyl ring could hardly be rationalized on the basis of a 'steric hindrance driving force'. It would then seem that the π -energy (E_π) of **1**⁹⁰, with two orthogonal π -systems *iso*-conjugate to styrene and benzyl-anion is more favourable than E_π for a stilbene-like planar **1**⁰. Likewise the non-planarity of **1** would then be the result of an 'attractive dominant' driving force for the process **1**⁰ \rightarrow **1**⁹⁰. The smaller twist angle found for **1** in condensed phases could then be thought of as a medium effect, since the polarizability of the molecule will increase with decreasing φ , allowing greater *Van der Waals* interaction between substrate and surroundings.

A clear assessment of the gas phase molecular conformation of **1** is therefore highly desirable since it would settle questions other than simple structural ones. It would, for example, delimit the widely used concept of '*iso*-conjugatedness' which allows to predict qualitatively properties of unknown systems from known *iso*-electronic ones. Is **1** really '*iso*-conjugate' to **2** or **3**, or not?

To our knowledge no direct gas phase structure determination of **1** has as yet been published. The questions indicated above seemed to warrant at least a semi-quantitative investigation of the conformation of **1** in the gas phase by means of photoelectron spectroscopy (PES.), using **4** as a planar reference system. In the following discussion the validity of *Koopmans'* theorem [14] is implicitly assumed.

Orbital structure of 4 and 6. – The highest occupied orbital (HOMO) π_1 in styrene (**5**) is found to be at $\varepsilon(\pi_1) = -8.50$ eV [15]. For **6**, which is *iso*- π -electronic to **5**, we take $\varepsilon(\pi_1) = -8.77$ eV, the shift towards lower energies with respect to **5** being due to the azasubstitution (Fig. 1). On this basis $\varepsilon(\pi_1) = -8.10$ eV (Fig. 1) for **4** follows in view of $\varepsilon(\pi_1) = -8.00$ eV found for **2** [15].

For **5** $\varepsilon(\pi_2) = -9.30$ eV, for **2** $\varepsilon(\pi_2) = \varepsilon(\pi_3) = -9.25$ eV [15] and for **3** $\varepsilon(\pi_2) = \varepsilon(\pi_3) = -9.30$ eV [16] are found⁵⁾. This near equality of energies, reminiscent of the HOMO-energies of benzene [17], is, of course, expected since in all these compounds the corresponding MO's have a node at the *ipso*-C-atoms of the benzene rings. It is therefore reasonable to expect similar IP's also for **4** and for **6**. Hence IP₂ = 9.38 eV for **6** is associated with $\varepsilon(\pi_2)$. Similarly, the band system peaking at 9.32 eV for **4** contains the bands corresponding to ejection of electrons from π_2 and π_3 , which leads to $\varepsilon(\pi_2) = \varepsilon(\pi_3) \approx -9.4$ eV.

Inspection of the low energy region of the PE. spectrum of styrene and stilbene [15] shows that the areas of the band systems are to a good approximation proportional to the number of orbitals from which electrons are ejected with that particular energy. Application of this rule to the present aza-analogues shows that the band system at 9.38 eV for **6** involves in addition to electron-ejection from π_2 that from another orbital. For the N_{sp²}-lone-pair orbital energy of pyridine $\varepsilon(n) = -9.59$ eV has been found [18]. On this basis we conclude that for **6** $\varepsilon(n) \approx -9.6$ eV. In order to establish $\varepsilon(n)$ for **4** the question arises concerning the inductive effect on $\varepsilon(n)$ on replacing the methyl- by a phenyl-substituent. A comparison between the PE. spectra of alkyl- and phenyl-halides shows that the IP's of those halogen-*n*-orbitals which are orthogonal to the phenyl π -MO's, are nearly identical [19]. This suggests that $\varepsilon(n) \approx -9.6$ eV is also valid for **4**.

⁵⁾ Note that the orbitals π_2 and π_3 for **2** and **3** are accidentally degenerate in HMO-theory.

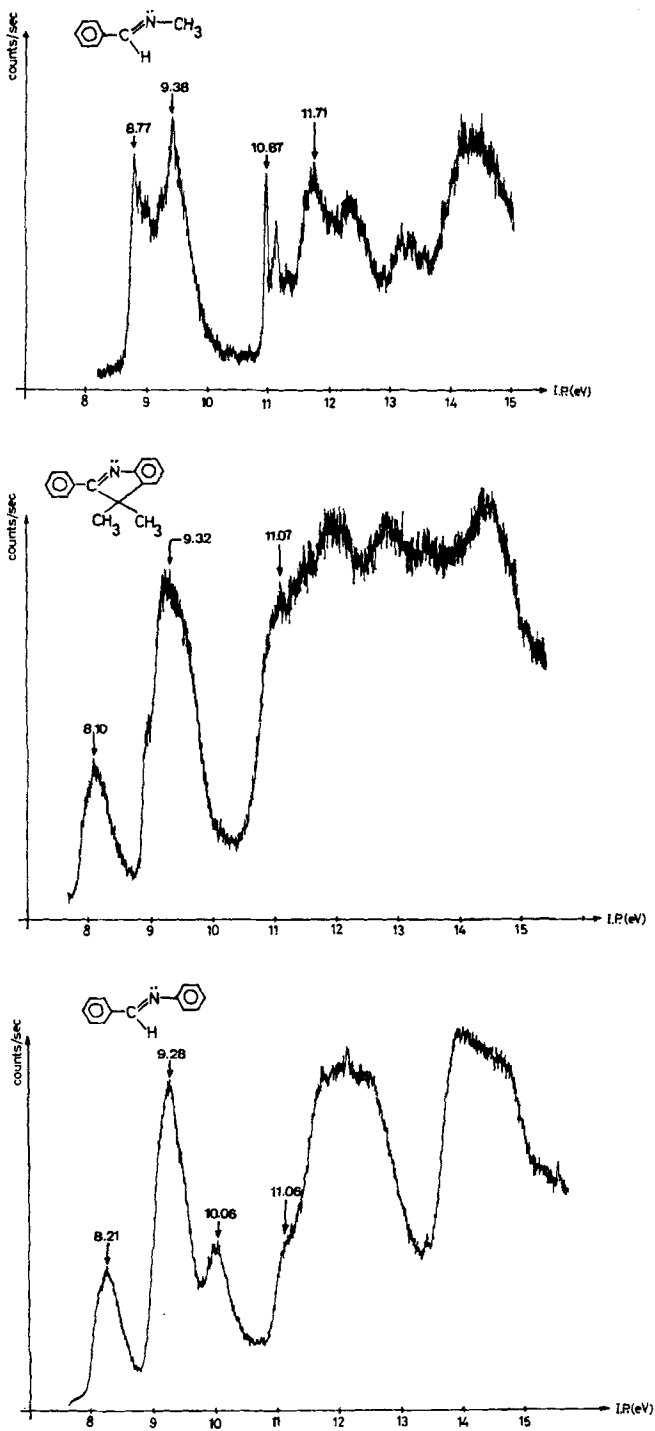


Fig. 1. Photoelectron spectra of *N*-benzylidenemethylamine (6), 3,3-dimethyl-2-phenylindolenine (4) and benzylideneaniline (1)

Application of the proportionality rule to the broad band system at 9.32 eV indicates that a fourth IP is hidden under this band. $\epsilon(\pi_4) = -9.55$ eV was found for [15]. The π_4 -orbital has small coefficients in the bridge but large ones at the *ipso*-C atoms. Hence it is not surprising to find $\epsilon(\pi_4) = -9.77$ eV in **3** [16], since aza-substitution in the bridge will not greatly affect the π_4 -orbital energy. Taking the mean between the above two values we set $\epsilon(\pi_4) = -9.66$ eV for **4**.

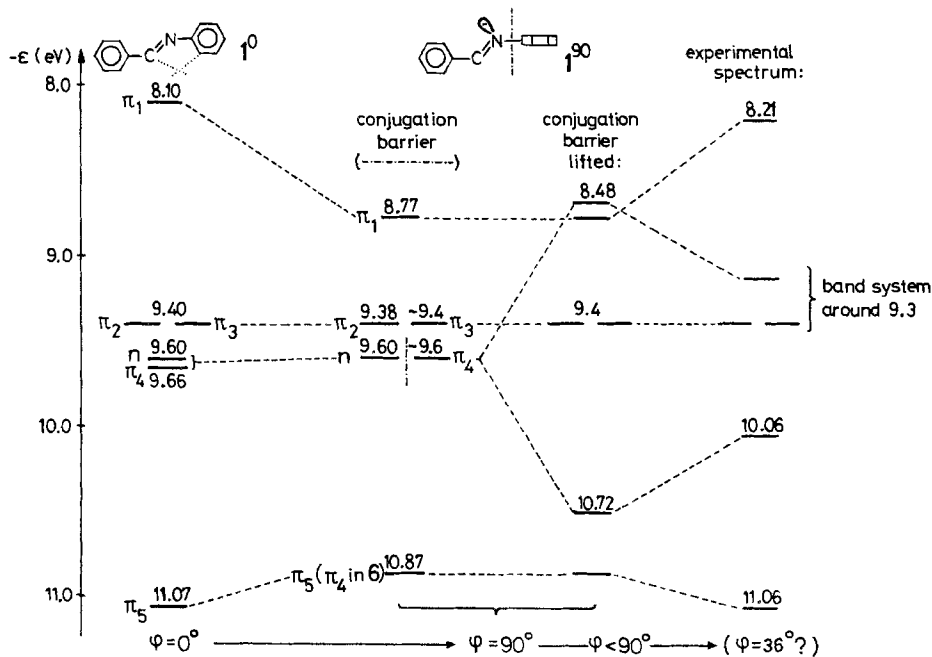
Nearly identical orbital energies $\epsilon(\pi_3) = -10.55$ eV for **5** and $\epsilon(\pi_5) = -10.60$ eV for **2** have been deduced [15]. If this finding for the two topologically similar orbitals which are strongly localized in the bridge [20] [21], is carried over to **6** and **4** we arrive at $\epsilon(\pi_3) = -10.87$ eV for **6** and $\epsilon(\pi_5) = -11.07$ eV for **4**. The shifts toward lower energies with respect to the analogous hydrocarbons is again due to the aza substitution.

Orbital structure and molecular conformation of **1** in the gas phase.

We are now in a position to discuss the orbital structure of **1** as a function of the torsional angle φ . For the limiting value $\varphi = 0^\circ$ the orbital energies observed for **4** are expected.

On this basis $\varphi = 0^\circ$ for **1** can already be excluded in view of the well resolved additional band at 10.06 eV in **1** (Fig. 1) which is not present in the planar reference system **4**⁶⁾. For $\varphi = 90^\circ$ the orbital energies of **6** and benzene should be found. They will, however, be modified by the additional interaction between the N-lone pair and

Fig. 2. Correlation diagram between the orbitals of **1**⁰, **1**⁹⁰ and **1**³⁶ and comparison with experimental PE. spectrum (cf. text)



⁶⁾ The PE. spectrum of **1** has been recorded in [16] and in [22]. It is reproduced for convenience.

the rotated N-phenyl ring. Therefore, while the former possibility can be judged on an unambiguous basis the expected values for $\varphi = 90^\circ$ require a further thought.

In the correlation diagram of Fig. 2, left part, the expected change in orbital energies for **1** in going from $\varphi = 0^\circ$ (**10**) – realized in **4** – to $\varphi = 90^\circ$ (**1⁹⁰**) – approximated by the orbital energies of **6** and those of an orthogonal phenyl ring – are drawn with the assumption that there is no interaction between the N-lone pair and the N-phenyl ring. For the additional π -orbitals π_3 and π_4 localized in the rotated phenyl ring, the orbital energies follow from the fact that π_3 has a node at the *ipso*-C-atom whereas the corresponding coefficient a_{ipso} (**1⁹⁰**) in π_4 is $\sqrt{1/3}$. Therefore π_4 will be lowered relative to π_3 by the inductive effect of the sp^2 -hybridized N-atom. HMO-results [20] show that π_4 in **4** is also largely localized in the benzene rings; its orbital energy lowering with respect to π_2 or π_3 will thus also be strongly determined by the inductive effect of the imino bridge.

Turning now to the question of n - π interaction in **1⁹⁰** we note that for reasons of symmetry we have to consider only the n - π_4 interaction. For $0^\circ < \varphi < 90^\circ$, however, π_1 and π_5 can also admix to n . From these three candidates π_4 engages predominantly in this interaction for all values of φ for the following two reasons:

(i) π_4 is always localized in the benzene ring(s). On the other hand π_1 and π_5 are mainly localized in the imino part of the system, resulting in a small coupling parameter to the n -orbital due to a small C_{ipso} -coefficient;

(ii) π_4 is almost degenerate with the n -lone-pair, the corresponding interaction being thus essentially first order. On the other hand the gaps between n and π_1 or π_5 are significantly larger for all values of φ .

As a corollary of this we can already settle the question raised earlier about the position of 'the n -IP' in the PE. spectrum of **1**. In [22] the 10.06 eV band was assigned to 'the n -IP'. This finding was disputed in [16] where a shoulder at 9.47 eV was proposed as arising from n -electron ejection. This latter result was deduced on the basis of the PE. spectrum of **3** which, as mentioned earlier, is *peri*-planar in the gas phase. It thus seems that in [16] no proper attention was given to possible n - π -interaction in **1** as a result of the non-planarity of the N-phenyl ring. At any rate both suggestions are superfluous since according to (ii) there is essentially first order interaction between n and π_4 . Hence the question as to where 'the n -lone-pair' is located energetically is meaningless.

A crucial question concerns the expected magnitude of the n - π_4 splitting in **1⁹⁰**. For anilines [23] and naphthylamines [24] the interaction parameter $B(sp^3(N)-p_z(C)) = -2.4$ eV, equivalent to $\beta(p_z(N)-p_z(C)) = -2.94$ eV has been established. The following arguments lead to an estimate of the effective coupling parameter $B(n-\pi_4)$ applicable to **1⁹⁰**:

- The n -orbital in **1⁹⁰** is of sp^2 -type, the p_z -contribution to it being associated with a mixing coefficient of $\sqrt{2/3} \cdot \sin 120^\circ$.
- The coupling coefficient at C_{ipso} of the π_4 -orbital is $\sqrt{1/3}$.
- The C-N bondlength in aromatic amines is around 1.43 Å [25], whereas it is 1.467 Å in **1** [4]. For the corresponding reduction of the one electron resonance integral β we assume the *Mulliken* approximation [26] $\beta \propto S$ to hold,

where S denotes the overlap integral between the basis AO's $p_z(C)$ and $p_z(N)$. Hence

$$\beta(1.467 \text{ \AA}) = \beta(1.43 \text{ \AA}) \times \frac{S(1.467 \text{ \AA})}{S(1.43 \text{ \AA})}.$$

For the two overlap integrals, the values 0.1677 and 0.1802, respectively are calculated using standard procedures.

Combining these points we arrive at the following expression for the effective interaction parameter B in $\mathbf{1}^{90}$:

$$B = -2.98 \text{ eV} \cdot \sqrt{\frac{2}{3}} \cdot \sin 120^\circ \cdot \sqrt{\frac{1}{3}} \cdot \frac{0.1677}{0.1802} = -1.12 \text{ eV}.$$

In view of the near degeneracy of the basis functions n and π_4 (*cf.* Fig. 2) first order interaction leads to two expected bands for $\mathbf{1}^{90}$ at 8.48 eV and 10.72 eV (*cf.* Fig. 2).

Inspection of the experimental spectrum of $\mathbf{1}$ shows that neither of the two postulated additional bands for $\mathbf{1}^{90}$ are observed; in fact the high energy one should show up where the spectrum displays a clear intensity minimum. We conclude on this basis that $\varphi = 90^\circ$ is *not* realized in gaseous $\mathbf{1}$ at 65° , the temperature at which the PE. spectrum was recorded.

Let us now postulate that the band at 10.06 eV arises from electron ejection out of the $(n + \pi_4)$ -component orbital. Using -9.6 eV for the energy of the n - and π_4 -basis orbitals leads to the prediction that the $(n - \pi_4)$ -component is associated with an IP of 9.14 eV. This band could indeed be hidden under the 9.28 eV band system, the area of which indicates a third band besides the bands corresponding to IP(π_2) and IP(π_3). For this assignment a coupling parameter $B = -0.46$ eV results, leading to a torsional angle φ much smaller than 90° .

An analytical expression for $B = B(\varphi)$ cannot be obtained in a straightforward way. To a first approximation $B(\varphi) = B(\varphi = 90^\circ) \cdot \cos(90^\circ - \varphi)$ will hold as a result of decreasing overlap between n and π_4 . The resulting φ would be 24° , which is much too small. However, an additional reduction factor enters $B = B(\varphi)$ due to the decrease of the C_{1pso} -coefficient in π_4 with decreasing φ . For the *iso*-conjugated system $\mathbf{2}$ this reduction amounts to 50% in going from $\varphi = 90^\circ$ to $\varphi = 0^\circ$. Adopting this limiting value also for $\mathbf{1}$ and – in the absence of a better choice – assuming proportionality between this factor and φ , we obtain the value $\varphi = 36^\circ$. This crudely estimated angle is still somewhat smaller than that observed for solid $\mathbf{1}$ ($\varphi = 55^\circ$ [4] and proposed to prevail also in solution [7]). For $\mathbf{1}^{36}$ $\varepsilon(\pi_1) = -8.33$ eV results, given $\varepsilon(\pi_1) = -8.10$ eV for $\mathbf{1}^0$, $\varepsilon(\pi_1) = -8.77$ eV for $\mathbf{1}^{90}$ and a \cos^2 -dependence between orbital energy and torsional angle. This value is in acceptable agreement with IP $_1 = 8.21$ eV observed in the PE. spectrum of $\mathbf{1}$. One might argue that $\varepsilon(\pi_1) = -8.77$ eV for $\mathbf{1}^{90}$ is presumably a lower bound, since in establishing it, we have neglected any interaction between the π -system of the aza-styrene moiety with the high lying σ -MO's of the rotated phenyl ring. If such interaction were taken into account, the expectation value for $\varepsilon(\pi_1)$ for $\mathbf{1}^{36}$ would even improve (*cf.* Fig. 2, right part).

To conclude we wish to stress that we do not insist on the crudely estimated angle $\varphi = 36^\circ$. Of greater importance is the fact that the results of our PE. analysis

are incompatible with $\varphi = 90^\circ$ for gaseous **1**. We suggest furthermore that the actual angle is such as to render **1** still 'iso-conjugate' to **1⁰** (e.g. **4**) as evidenced for example by their similar HMO-energies which determine largely chemical behaviour [27]. Finally we wish to point out that the present work adds to the few already known [38] (and certainly limited) applications of PE. spectroscopy to questions of molecular conformation.

Re-evaluation of the gas phase optical spectrum of 1. - Our conclusions stated above are in apparent disagreement with those presented in [13] on the basis of the gas phase optical spectrum of **1** (cf. introduction to this paper). It was therefore decided to register this spectrum once again. Highly purified **1** was inserted into a 10-cm quartz cell which then was evacuated to 10^{-5} Torr. The cell was heated to approximately 100° and the spectrum taken on a Unicam SP.800D spectrometer. It is displayed (spectrum a) together with the solution spectrum obtained after redissolving this sample in pentane (spectrum C) in Fig. 3. It can be seen that according to our spectra (Fig. 3) there is no qualitative difference between solution and gas phase

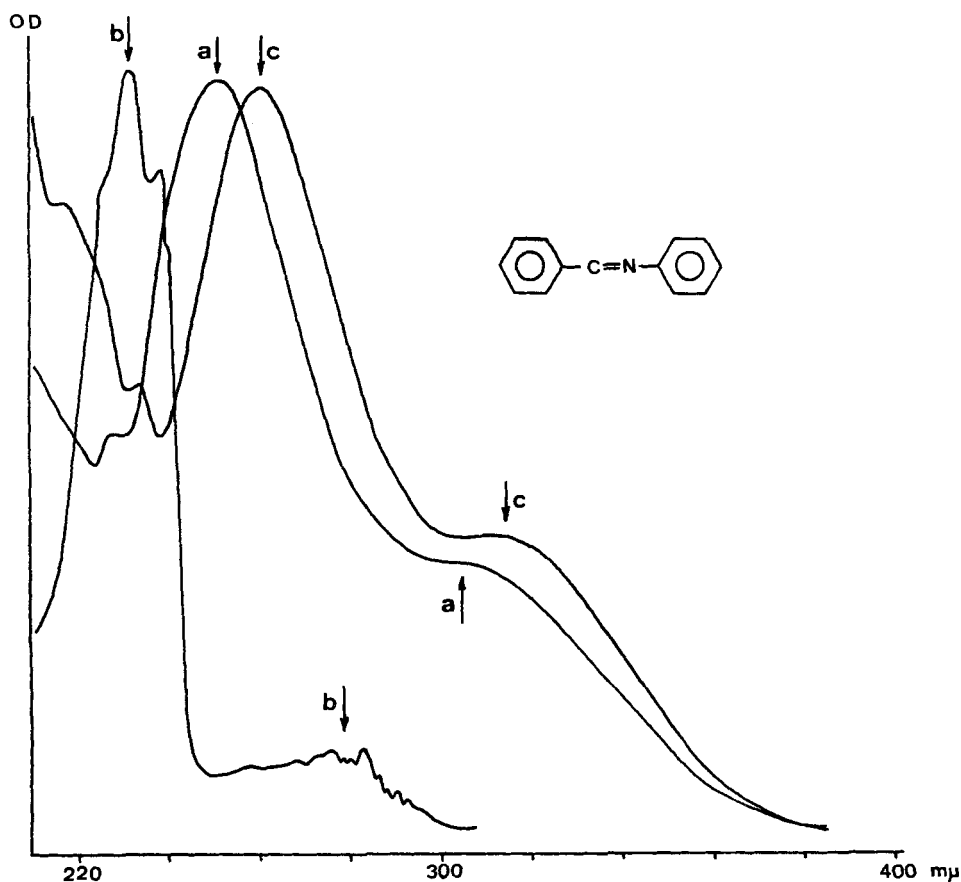


Fig. 3. Optical spectra of: benzylidenaniline in gas phase (a); same sample with trace of water (b); (a) (or (b)!) after dissolution in pentane (c)

absorption of **1**. (The bathochromic displacement of the former with respect to the latter is a well known solvation effect). In particular, the intensity ratio between the long wavelength shoulder and the peak of the band in the 260 nm region is roughly the same for both phases. This intensity ratio has been qualitatively shown to depend strongly on the torsional angle of the N-phenyl ring [8] [28]. Hence we conclude from the optical spectrum of isolated **1** that its molecular conformation is

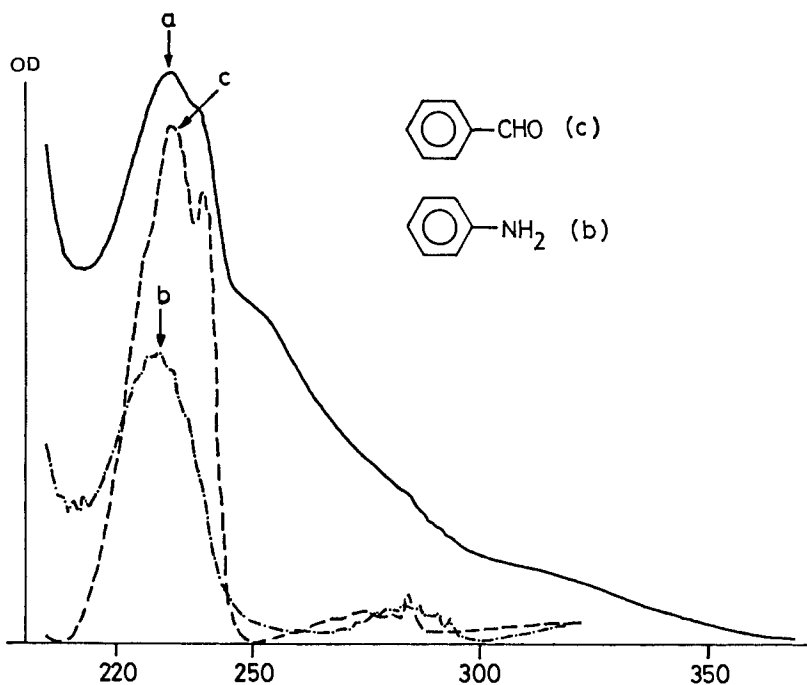


Fig. 4. Optical spectra reported in [13]: alleged gas phase spectrum of benzylidenaniline (a); gas phase spectra of aniline (b) and benzaldehyde (c)

about the same as that in solution or in the solid, *e.g.* the torsional angle being around 50° in all phases. This conclusion is qualitatively in agreement with that obtained from the PE.-work above.

The spurious results reported in [13] (reproduced in Fig. 4a) can be accounted for by considering Fig. 3b. This gas phase spectrum was obtained after adding a very small amount of water to **1**, cooling the cell to liquid nitrogen temperature, evacuating it again to 10^{-5} Torr and recording the spectrum as before after heating. Its long wavelength pattern corresponds to a superposition of the spectra of the hydrolysis products aniline and benzaldehyde (Fig. 4b, c) which are of course more volatile than **1**. The band system around 230–240 nm is almost exactly that of pure benzaldehyde which under equal gas phase conditions absorbs twice as much as aniline in this region. After dissolution of the entire sample in pentane the spectrum of **1** (Fig. 3c) could be remeasured. This is not surprising, given the large difference in vapour pressure of **1** and its hydrolysis products. Thus, it cannot be proved this way 'that the sample has not undergone chemical changes during the (gas phase) experiment'

[13]. The spectrum reported there corresponds to a superposition of spectrum b and the true gas phase spectrum a of **1** (Fig. 3): all its prominent features have their analogue in either of these component spectra. Note that even the vibrational fine structures of aniline and benzaldehyde show up in the 275–295 nm-region. Apparently slight hydrolysis of **1** has occurred under the experimental conditions employed by these authors.

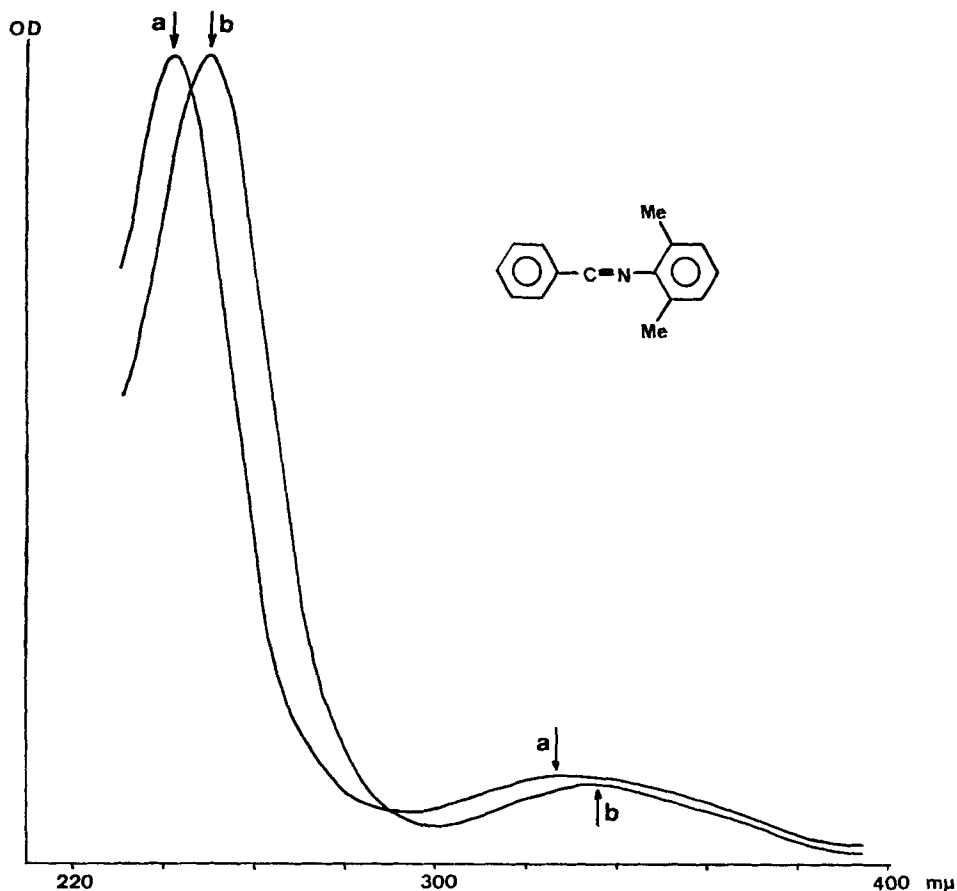


Fig. 5. Optical spectra of *N*-benzylidene-2,6-xylidine in gas phase (a) and in pentane solution (b)

In Fig. 5 we display the gas- and solution-phase spectra of *N*-benzylidene-2,6-xylidine (**7**). Molecular models suggest that **7** is strongly non-planar, the torsional angle φ approaching 90° . Such a large angle is further evidenced by the much smaller intensity ratio between the long- and the short-wavelength band systems, a diagnostic tool first established in [28]. Hence there is less degree of freedom for any conformational changes on change of phases, both spectra therefore arising from substrates with about equal conformations.

The relative appearance of the two spectra in Fig. 5 is about the same as for **1** (Fig. 3) with a similar bathochromic shift of the solution spectrum due to solvation.

We conclude on this basis and in support of what was said above that the two spectra for **1** displayed in Fig. 3 also involve molecules with about equal conformations, *e.g.* with $\varphi \approx 50^\circ$ – 60° .

Theoretical calculation of the conformation of (isolated) stilbene (2), benzal-aniline (1) and azobenzene (3) – In recent years *semi*-empirical quantum-chemical calculations have become feasible for molecular systems of this size. Before applying such procedures for predictive purposes their scope and limitations have to be rigorously established in advance by checking against known experimental facts. Clearly the right of existence of a particular theoretical model is directly proportional to its rate of success.

In retrospective then CNDO/2- [29] or MINDO/2- [30] calculations of the conformation of the three title compounds appear to have badly failed, yielding torsional angles $\varphi = 90^\circ$ for both phenyl rings in all cases [31]. This statement is justified in view of the presently available structural indications for the three isolated systems which were in the case of **2** and **3** cited and for **1** are found in the present paper. As a further warning sign a series of disturbing CNDO/2-failures for related systems such as benzaldehyde, biphenyl, butadiene *etc.* were listed in [32]. In summary, one is forced to conclude that the CNDO/2 – as well as the MINDO/2 – method are completely unreliable for predicting the relative conformation of π -systems connected by an essential single bond. A closer look at the calculated energetics using energy partitioning techniques revealed that the MINDO/2-method overestimates σ - π -interactions [33]. This is not unexpected, since the energies of σ -orbitals usually turn out too high.

Recently a new version of the MINDO-procedure, MINDO/3 has been introduced [34]. This method undoubtedly has met with impressive success in the prediction of a great variety of observables [35]. Accordingly we set out to apply MINDO/3 to the present issue. To keep the costs of computation within tolerable limits, the geometry search routine was subjected to the following constraints:

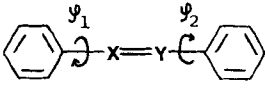
(i) Local D_{6h} -symmetry was imposed on the phenyl rings, this apart from the external C–C (or C–N) bonds and the external C=C–C (or C=C–N)-angles, which were allowed to vary.

(ii) For **2** and **3**, C_2 -symmetry was imposed.

In order to visualize tendencies, heats of formation are not only given for the completely optimized structures but also for fixed torsional angles of $\varphi = 0^\circ$, 30° , 60° and 90° (Table 1). For each angle the rest of the geometry was optimized observing (i) and (ii).

Apparently also MINDO/3 predicts – at variance with the experimental indications – torsional angles of $\varphi = 90^\circ$ for both phenyl rings in the equilibrium conformation of all three systems. In addition the results listed in Table 1 indicate a monotonic increase of the energy in going to the planar structures ($\varphi = 0^\circ$). The lowest-energy structures were found to lie higher by 2.1 kcal/mol for **2**, 3.4 kcal/mol for **1** and 5.4 kcal/mol for **3**. This sequence suggests that the basic problem with MINDO/3 is again an overestimation of σ - π -interaction which increases for the $\varphi = 90^\circ$ conformations on successive replacement of the CH-moieties by N-atoms carrying

Table 1. Heats of formation (ΔH_f° , kcal/mol) for various conformations of stilbene, benzylideneaniline and azobenzene (torsional angles of the phenyl rings φ_1 and φ_2 in degrees), calculated by the MINDO/3-method (see text)

	$\varphi_1 = 0^\circ$ $\varphi_2 = 0^\circ$	$\varphi_1 = 30^\circ$ $\varphi_2 = 30^\circ$	$\varphi_1 = 60^\circ$ $\varphi_2 = 60^\circ$	$\varphi_1 = 0^\circ$ $\varphi_2 = 60^\circ$	$\varphi_1 = 90^\circ$ $\varphi_2 = 90^\circ$
Stilbene (X=Y=C)	82.1	81.2*	80.0		79.5
Benzylideneaniline (X=C, Y=N)	90.8			90.2*	87.4
Azobenzene (X=Y=N)	75.9*	74.4	71.6		70.5

*) Values calculated for the (approximate) experimental conformations.

high lying lone pairs. Judged on the basis of known rotational barriers for related systems such as benzaldehyde [36], butadiene [37] *etc.* there is no doubt that the actual barriers for rotation of the phenyl rings in the present systems are at most 5 kcal/mol. The data displayed here suggest that MINDO/3-results for processes involving rotation of π -systems around essential single bonds accompanied by energetical changes of this magnitude are to be looked at with due caution.

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