

Vibrational spectra of *trans*-N-benzylideneaniline and its isotopomers

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Abstract - Solid state and solution infrared and Raman spectra of *trans*-N-benzylideneaniline and its 15 isotopomers have been analyzed on the basis of a nonplanar molecular model. The normal vibrations are rationalized in terms of local symmetry coordinates of the two phenyl rings and the imine group. The most characteristic modes are discussed in detail. From the analysis of the spectra of a number of isotopomers it was possible to distinguish between aniline and benzylidene ring modes. A comparison with the structurally related *trans*-stilbene molecule has shown very similar mechanism of mixing of central group and ring vibrations.

INTRODUCTION

Schiff bases represent an interesting class of compounds due to their importance in biology. On the other hand, derivatives of aromatic imines possess properties of liquid crystals in nematic phase even at room temperature (ref. 1). Schiff bases of the general formula R-CH=N-R' take usually the *trans* form. In his review article Bulkin (ref. 2) stresses the importance of interpreting vibrational spectra of liquid crystals, which are very complex due to low symmetry of constituting molecules. *trans*-N-Benzylideneaniline or *trans*-benzalaniline (tBA) is a model aromatic Schiff base, which is otherwise isoelectronic with *trans*-stilbene (tSB) and *trans*-azobenzene (tAB). Contrary to *trans*-stilbene, for which a rather extensive amount of vibrational data exist (ref. 3), there are only several papers on vibrational spectrum of *trans*-N-benzylideneaniline (refs. 4-6). Ostrowska and Tramer (ref. 4) have assigned fundamental vibrations of tBA from infrared spectra of *trans*-N-benzylideneaniline, pentadeutero-(A)-*trans*-N-benzylideneaniline and benzylidene-*p*-toluidine, suggesting some important structural features before an x-ray analysis has been available. Vergoten and Fleury (ref. 6) performed a normal coordinate calculation applying a modified Urey-Bradley force field to assign the complete vibrational spectrum of tBA, but using only Raman spectra of the light isotopomer. The assignments were not quite in agreement and both missed some important features.

For some time the structure of binuclear aromatic compounds is the subject of our research (refs. 7-9), including a detailed vibrational analysis of tSB (ref. 3). An extension to an elaborate vibrational analysis of tBA is straightforward, particularly when we have in hand a variety of specifically deuterated isotopomers (ref. 10) and additionally the ¹⁵N-labelled species. In this paper we discuss main features of infrared and Raman spectra of the parent molecule, its 13 partially and perdeuterated isotopomer and ¹⁵N-labelled species of tBA, in order to ensure a sound basis for a detailed normal coordinate analysis.

EXPERIMENTAL PART

Substances

All the isotopomers studied here have been prepared from corresponding freshly distilled anilines and benzaldehydes by the standard condensation procedure (ref. 11). The details of the preparation of deuterated precursors or the origins of commercial reactants were reported in the recent paper (ref. 10). The new isotopomer is *trans*-¹⁵N-benzylideneaniline, which was prepared using ¹⁵N-aniline (Isocommerz, Berlin, DDR, 95% ¹⁵N). All the compounds were identified by NMR spectroscopy and deuterium contents determined by mass spectrometry (ref. 10). The mass spectrum of ¹⁵N-tBA gave 95% ¹⁵N. The melting points for all the isotopomers were in the range 50.0 - 52.0°C.

Fig. 1 shows the numeration of heavy atoms in *trans*-N-benzylideneaniline (D₀-tBA, 1), as well as 15 isotopomers used in this study: *trans*-∞-deutero- (∞-D-tBA, 2), *trans*-4-deutero- (4-D-tBA, 3), *trans*-4'-deutero- (4'-D-tBA, 4), *trans*-∞,4'-dideutero- (∞,4'-D₂-tBA, 5), *trans*-4,4'-dideutero- (4,4'-D₂-tBA, 6), *trans*-2,3,4,5,6-pentadeutero- (D₅(B)-tBA, 7),

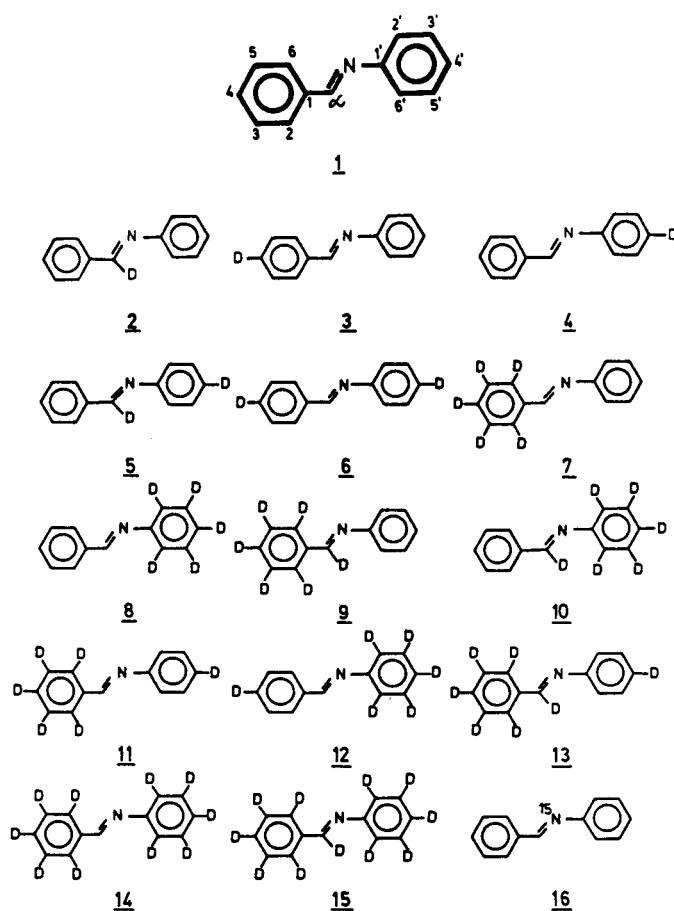


Fig. 1. Isotopomers of trans-N-benzylideneaniline (tBA) and numeration of heavy atoms in the tBA molecule.

trans-2',3',4',5',6'-pentadeutero- ($D_5(A)$ -tBA, 8), trans-2,3,4,5,6, α -hexadeutero- ($D_5(B)$, α -D-tBA, 9), trans- α ,2',3',4',5',6'-hexadeutero- (α -D, $D_5(A)$ -tBA, 10), trans-2,3,4,5,6,4'-hexadeutero- ($D_5(B)$,4'-D-tBA, 11), trans-4,2',3',4',5',6'-hexadeutero- (4-D, $D_5(A)$ -tBA, 12), trans-2,3,4,5,6, α ,4'-heptadeutero- ($D_5(B)$, α -D,4'-D-tBA, 13), trans-2,3,4,5,6,2',3',4',5',6'-decadeutero- (D_{10} -tBA, 14), trans-perdeutero- (D_{11} -tBA, 15) and trans- ^{15}N -benzylideneaniline (^{15}N -tBA, 16).

Spectra

The infrared spectra were recorded in the range from 4000-400 cm^{-1} on a Digilab 20C interferometer equipped with a TGS detector and a NOVA-3 computer. Solid state spectra were taken from KBr pellets and solution spectra from carbon tetrachloride, methylene chloride and carbon disulfide solutions in 1 mm cells with 200 scans at a 2 cm^{-1} resolution. Solvent subtraction and other Digilab routines have been used. Far infrared spectra were recorded in the range 400 - 40 cm^{-1} from polyethylene pellets and benzene solutions.

The Raman spectra were measured from 3500 - 50 cm^{-1} with a Dilor Z24 spectrometer equipped with a triple monochromator and an IBM AT03 computer. Polycrystalline samples in capillary tubes, and carbon tetrachloride and benzene solutions were excited with the 514.5 nm line of a Coherent INNOVA-165 argon ion laser. Spectra were recorded in the sequential mode with a 2 cm^{-1} resolution. All the routines were performed by the Dilor software.

MOLECULAR MODEL

Many structural studies confirm the nonplanar conformation of the tBA molecule in all phases. Thus Bürgi and Dunitz (ref. 12) have determined the geometry of tBA from x-ray diffraction patterns of the crystal, quoting the dihedral angles between the azomethine plane and phenyl rings of 55.2 and 10.3 degrees for the aniline (A) and benzylidene (B) moieties, respectively. In this respect tBA differs from its isoelectronic counterparts trans-stilbene (ref. 13) and trans-azobenzene (ref. 14) which are essentially planar in the crystals.

The conformation of tBA is nonplanar also in fluid phases, as evidenced by UV (ref. 15) and NMR spectroscopy (ref. 16), where again spectra differ markedly from those of tSB and tAB. For a free tBA molecule both photoelectron spectra (ref. 17) and theoretical calculations (ref. 18) give best fits for a nonplanar model, differing however in values of dihedral angles. An approach combining electron diffraction and molecular mechanics suggested the coplanarity of the CH=N and B-ring planes, and the A-ring being rotated by ca. 52° about the Ph-N bond (ref. 19). For a nonplanar tBA molecule the corresponding point group is C_1 with all 69 normal vibrations (a species) being both infrared and Raman active. However, for the sake of easier calculations a planar model of the C_s molecular symmetry may be assumed (ref. 20), while the spectral activities of the C_1 point group are preserved.

In any case three planes are present in the tBA molecule (Fig. 2): two phenyl and the imine plane. The normal vibrations are then grouped accordingly into two times 30 modes for the phenyl groups and 9 modes for the azomethine moiety. Within each of the three groups in-plane and out-of-plane modes can be treated separately in terms of the local symmetry

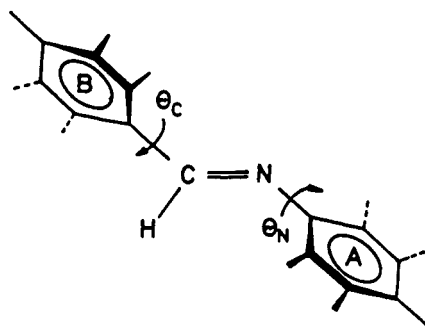


Fig. 2. Molecular model of trans-N-benzylideneaniline. A and B denote aniline and benzylidene ring, respectively. θ_N and θ_C are rotational dihedral angles about N-Ph and C-Ph bond, respectively.

coordinates: 21 in-plane and 9 out-of-plane for each phenyl group, and 5 in-plane and 4 out-of-plane for azomethine. It is assumed that within one group there is no mixing between in-plane and out-of-plane vibrations, according to selection rules for the particular local symmetry (C_{2v} for phenyls, C_s for imine). However, couplings between e.g. in-plane phenyl and out-of-plane azomethine coordinates are now possible. Such an approach makes it possible to compare characteristic local modes of tBA with those of tSB, which are analyzed in detail (ref. 3). For the sake of consistency, solution vibrational spectra of both compounds will be taken for comparison. In the normal coordinate analysis of tSB (ref. 8) a planar model of the C_{2h} symmetry was successfully applied, although there is an evidence that tSB may be nonplanar in solution (ref. 21).

RESULTS AND DISCUSSION

Solid state and solution infrared spectra have been recorded for all sixteen isotopomers (Fig. 1). It is still not possible to assign all vibrations of an individual isotopomer from only infrared spectra, because of too many band overlaps and accidental degeneracies. Due to different band-widths and intensities, Raman spectra have been used to clear up regions in infrared spectra where either frequencies are too close to each other or bands are too intensive, and vice versa.

Another approach was to compare solid state and solution spectra of a particular isotopomer within the same spectroscopy. Fig. 3 illustrates differences in infrared solid and carbon disulfide solution spectra of D_{10} -tBA (14).

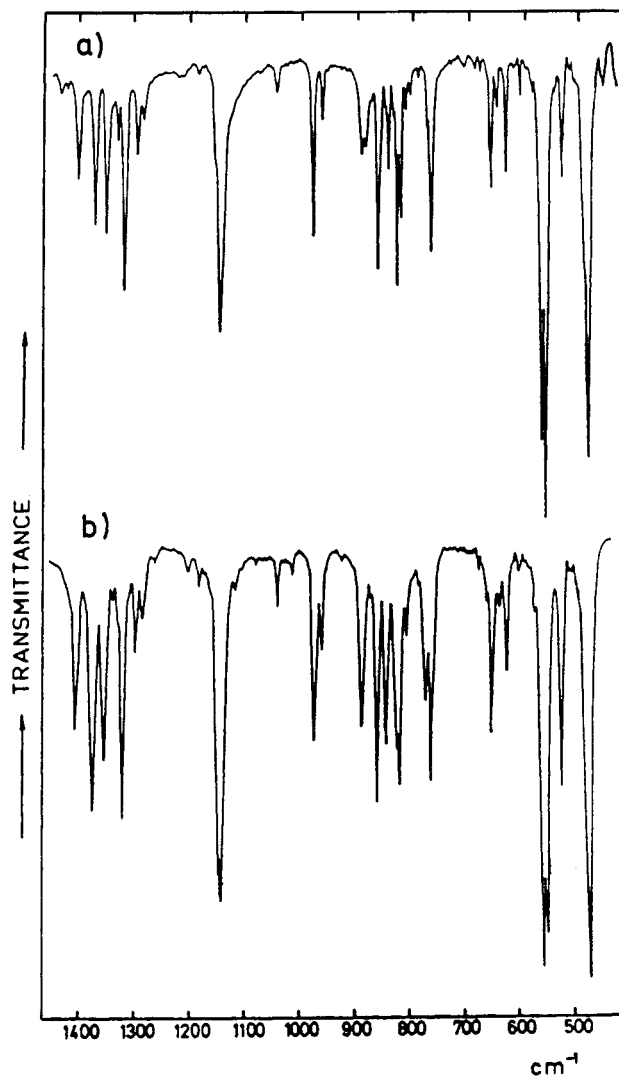


Fig. 3. Solid state (a) and solution (b) infrared spectra of trans-2,3,4,5,6, 2',3',4',5',6'-D₁₀-N-benzylideneaniline in the range 1400 - 400 cm⁻¹.

The most reasonable approach to start an assignment of vibrational spectrum of tBA seems to be a comparison with existing assignments (refs. 4-6). It is, however, necessary to examine critically both proposed assignments, which do not agree completely. This holds primarily for vibrational modes of the rings. Although phenyl group modes do not vary markedly for different substituents, the differences between N-phenyl (A) and C-phenyl (B) modes are here very important due to expected differences in couplings with the central imine group. Previous authors have claimed that there were hardly any differences in frequencies between equivalent modes of the two rings, or even that there were no characteristic vibrations for the tBA molecule (ref. 6). This seems very improbable, because we have found out, that in spite of extensive vibrational mixing and coupling in the tSB molecule (ref. 3), characteristic local modes still exist. These characteristic vibrations can be followed systematically by selective isotopic substitution. Thereby it is of great practical value to choose particular pairs of isotopomers to avoid too many simultaneous changes, both frequency shifts and band intensity variations, in vibration spectra of several isotopomers. Moreover, it is possible to deduce qualitatively the significance of particular couplings between vibrational coordinates, which give hints for selecting interaction force constants in normal coordinate calculations. In return the results obtained enable correcting of spectral assignments, until consistency between calculated and observed spectra is achieved.

In order to simplify the empirical assignment as much as possible, it is necessary to clarify characteristic group vibrations. Three groups of characteristic local modes will be

discussed: a) CH stretching, b) CH=N and c) phenyl vibrations. Within groups b) and c) we shall treat fundamental vibrations in terms of in-plane and out-of-plane modes with respect to the plane of the particular atomic group (A-ring, B-ring and imine).

a) CH stretching vibrations

All ten aromatic CH stretching frequencies of D_0 -tBA (1) appear between 3085 and 3005 cm^{-1} and cannot be assigned unambiguously even on complete deuteration of one of the rings. However, the imine CH stretching was assigned by means of the CH/CD shifts. For this purpose following pairs of tBA isotopomers have been chosen: 1 and 2, 4 and 5, 7 and 9, 8 and 10, 11 and 13, and 14 and 15. The members of any pair differ only in the isotopic contents of the imine group. For each pair the infrared band at 2872 cm^{-1} (mean value) is shifted to 2158 cm^{-1} (also mean value) upon deuteration, irrespective of the degree of deuteration in aromatic ring(s). Furthermore, for isotopomers without a deuterated counterpart (3, 6, and 12) a band at the mean value of 2878 cm^{-1} was observed, supporting thus our assignment. This extremely low imine CH stretching frequency is in contrast with the previous assignment where it was calculated to be above 3000 cm^{-1} (ref. 6). An additional evidence for our assignment is the decrease of this band by 10 cm^{-1} in ^{15}N -tBA (16). Fig. 4 shows a comparison of two pairs of isotopomers in the CH/CD stretching regions.

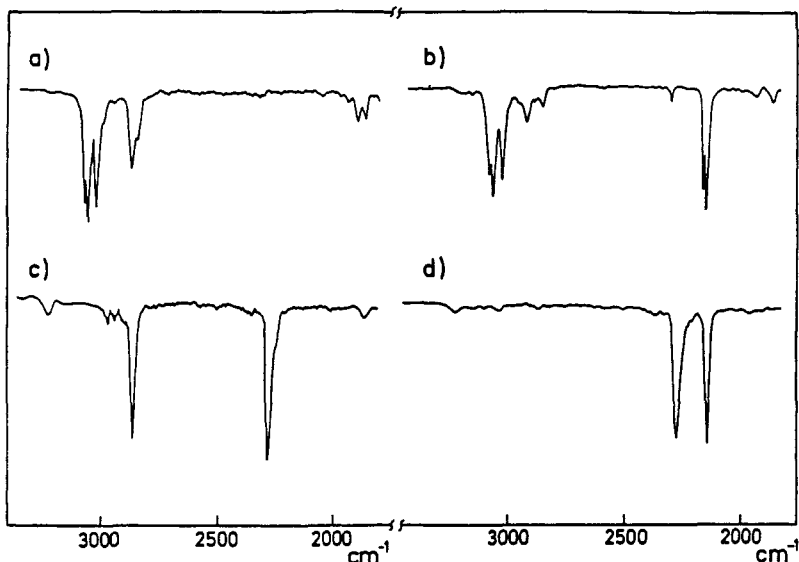


Fig. 4. CH/CD stretching regions (infrared spectra of carbon tetrachloride solutions) for two typical pairs of tBA isotopomers: 1 (a) and 2 (b), viz. 14 (c) and 15 (d).

In addition to this characteristic $C_{\alpha}H$ or $C_{\alpha}D$ stretching band, another one was observed at 2852 cm^{-1} or 2176 cm^{-1} , respectively, for isotopomers 1 through 8 and 12. The doublet was observed if the B-ring contained none or only one deuterium and/or the A-ring was perdeuterated. A possible explanation would be the presence of two long-living conformers of tBA in solution, but this hypothesis needs to be further elaborated.

b) CH=N group vibrations

The imine CH stretching mode was discussed in the previous section, where it was shown that it is a very specific vibration characteristic of this group. However, the real probe for a reactive site of Schiff bases is the C=N stretching vibration (ref. 22). For tBA it was assigned to the infrared band at 1627 cm^{-1} (ref. 4) and the Raman band at 1630 cm^{-1} (ref. 5). In the normal coordinate analysis the C=N stretching coordinate was distributed among modes at 1680 and 1592 cm^{-1} (ref. 6). With the series of specifically labelled compounds it was possible to assign this mode by following its shifts upon consecutive isotopic substitution. In the parent compound it is assigned to the very strong infrared band at 1627 cm^{-1} in solid and 1629 cm^{-1} in solution, and to the strong Raman band at the same position. It is shifted to 1615 cm^{-1} in the solution infrared spectrum of α -D-tBA (2), while the ring modes

around 1600 cm^{-1} (8a and 8b after Wilson notation) are hardly affected (Section c). On the other hand, the deuteration of either B-ring (7) or A-ring (8) decreases the C=N stretching frequency by just a few wavenumbers (Table 1). If both rings are deuterated (14) the shift is still of the same magnitude. In perdeuterated tBA (15) the frequency is 1612 cm^{-1} (Table 1). In other words, the intrinsic C=N stretching frequency is decreased by approximately 15 cm^{-1} upon deuteration of the imine group, as seen from the comparison of the pairs 1/2 and 14/15. This fact indicates a rather strong coupling between the C=N stretching and $C_{\infty}H$

Table 1. Selected values of CH=N group frequencies (cm^{-1}) for trans-N-benzylideneanilines 1, 2, 7, 8, 14, 15 and 16 (infrared spectra of solutions)

| Description of the mode | <u>1</u> | <u>2</u> | <u>7</u> | <u>8</u> | <u>14</u> | <u>15</u> | <u>16</u> |
|-------------------------|----------|----------|----------|----------|-----------|-----------|-----------|
| C=N str. | 1629 | 1615 | 1626 | 1629 | 1626 | 1612 | 1613 |
| $C_{\infty}H$ ip def. | 1367 | 1021 | 1363 | 1350 | 1352 | 1021 | 1359 |
| $C_{\infty}H$ op def. | 972 | 735 | 970 | 971 | 971 | 744 | 971 |

in plane deformation. The shift in frequency is practically the same as in the case of the ^{15}N -isotopomer (16) (where ^{15}N belongs to the C=N coordinate). On the other hand, a partial or total deuteration of one or both rings does not affect appreciably the C=N stretching, indicating a weak mixing between this particular mode and ring stretching vibrations. Both, a strong coupling with $C_{\infty}H$ in-plane deformation and a weak coupling with ring modes, have been observed also for the central C=C bond in undeuterated and α -deuterated trans-stilbene (ref. 3).

Both the single bond stretches between imine and phenyl groups, i.e. the C-Ph and N-Ph stretching modes, are shared between the two moieties, but will be discussed here with imine group vibrations. The former mode was assigned to the infrared band at 1233 cm^{-1} , and the latter to one at 1193 cm^{-1} (ref. 4). The assignment of Raman frequencies (ref. 5) is the same: 1240 cm^{-1} for C-Ph and 1190 cm^{-1} for N-Ph stretching. However, in the normal coordinate analysis (ref. 6) no contributions of the corresponding coordinates have been attributed to these frequencies. There is a contribution in potential energy distribution (PED) of the N-Ph coordinate to the mode at 1352 cm^{-1} , and of C-Ph coordinate to several modes around 1000 cm^{-1} .

In the case of trans-stilbene both C-Ph stretching vibrations, the anti-mode at 1266 cm^{-1} and syn-mode at 1197 cm^{-1} , are mixed (ref. 3) with significant contributions of ring coordinates. It is reasonable to assume that similar situation appears also in trans-N-benzylideneaniline (D_0 -tBA, 1). Indeed, it was not possible to make here a straightforward assignment of either C-Ph or N-Ph stretching mode. Neither the deuteration of the imine group or ring(s) gave any firm support, since a number of neighbouring bands were shifted as well. Moreover, the introduction of ^{15}N into the imine group did not induce a significant frequency shift of any band in the range $1350\text{--}1150\text{ cm}^{-1}$, where the N-Ph stretching should be expected. Only few frequencies around 1200 cm^{-1} were decreased by three or four cm^{-1} . This feature indicates that these two particular vibrations are rather phenyl than imine group modes, like in trans-stilbene (ref. 3). It is obvious that only normal coordinate calculations can distinguish between these two and the neighbouring ring modes (Wilson modes 14, 3 9a and 15, see Section c).

Two deformation vibrations should also be discussed: imine CH bendings in-plane and out-of-plane. The in-plane mode is assigned to the medium infrared band at 1370 cm^{-1} for D_0 -tBA (1), which is in agreement with previous proposals (refs. 4-6). It is shifted to 1021 cm^{-1} in the spectrum of α -D-tBA (2) in accordance with related systems (ref. 3). This mode for the light species (1) is at an appreciably higher frequency than two subsequent ring vibrations (Wilson modes 14 and 3) and is not mixed with them, unlike the $a_g C_eH$ in-plane deformation in trans-stilbene (ref. 3). However, it is coupled with some other ring modes, because it decreases by 4 cm^{-1} when the B-ring is deuterated ($D_5(B)$ -tBA, 7), and even by

17 cm⁻¹ in the case of the deuterated A-ring (D₅(A)-tBA, 8). If both rings are deuterated (D₁₀-tBA, 14) the shift is approximately the superposition of the two effects (Table 1). Taking into account the molecular geometry determined by the x-ray analysis (ref. 12) and assuming both angles, C₁C_∞H and NC_∞H being equal, the distances have been calculated from imine hydrogen to the proximate ortho hydrogen atoms in the rings: 2.543 Å to the A- and 2.494 Å to the B-ring. For a hypothetical planar model with equal angles around imine carbon (C_∞) the distances would be 1.667 Å and 2.480 Å, respectively. A stronger coupling of the imine CH deformation mode with the A-ring could indicate a conformation in solution which is different from that in crystal (ref. 12) or gas (ref. 19). Besides, from solution ¹³C NMR spectra the dihedral angle θ_N was deduced with values between 35° and 41° (ref. 9) which is less than in crystal (55.2°, ref. 12).

The out-of-plane imine CH deformation is assigned to the infrared band at 870 cm⁻¹ (ref. 4) and 875 cm⁻¹ (refs. 5, 6) in Raman. However, we believe that it should be assigned to the strong solution infrared band at 972 cm⁻¹ for D₀-tBA (1), which shifts upon deuteration to 735 cm⁻¹ for α-D-tBA (2). In appearance and isotope shift the band is similar to that of the b_u infrared active mode in *trans*-stilbene, where it is insensitive to the degree and position of deuteration in the ring(s). In *trans-N-benzylideneaniline* too, the deuteration of either one or both rings does not change its position (Table 1). The assignment of this mode was possible by taking the pairs with CH=N and CD=N groups and the equivalent rest of the molecule, like 1/2, 7/9, 8/10 and 14/15, and following the frequency shifts in several analogous cases.

c) Phenyl group vibrations

It is interesting to know if there is a possibility to distinguish here between A-ring and B-ring modes taking into account different interactions with the imine group. Although it is well established, that in monosubstituted benzenes the fundamental vibrations are practically unaffected by a substituent, except for six substituent-sensitive modes (ref. 23), the approach with selective isotopic substitution enables distinctions of equivalent modes of two closely related moieties. Among numerous examples only several most characteristic ring modes will be discussed.

According to our research of vibrational spectra of binuclear aromatic compounds (ref. 24), the local symmetry coordinates of the C_{2v} point group are natural vibrational coordinates whenever the phenyl group is a part of a molecule. The use of Wilson notation for phenyl modes is appropriate as well. In the particular case of the tBA molecule syn- and anti-modes exist no more, unlike in tSB (refs. 3, 7) or tolane (ref. 25). Besides, due to different polarities in the aniline (A) and benzylidene (B) moieties band intensities in infrared and Raman spectra of the vibrations of the particular pair of equivalent vibrations can help in distinguishing between A- and B-ring modes.

In previous reports (refs. 4-6) in general the same frequencies for a particular pair of fundamentals, e.g. 19a(A) and 19a(B), 19b(A) and 19b(B), etc. have been assigned to both A- and B-ring modes. By using selective deuteration of rings, it was possible to distinguish in nearly all cases between A- and B-modes. In cases where some doubts existed, instead of one perdeuterated (D₅) and one non-deuterated (D₀) ring, a pairwise combination of a D₅- and a p-deuterated-ring, e.g. 7/11 or 8/12, was applied to clarify any ambiguity.

In the infrared spectrum of the methylene chloride solution of D₀-tBA (1) two strong bands appear at 1593 and 1582 cm⁻¹ for four vibrations: 8a(A), 8a(B), 8b(A) and 8b(B). The two bands were previously assigned (refs. 4-6) to 8a(A) and 8a(B). Since for these two modes there is practically no coupling between the rings, they can be distinguished by comparison of 1 and 7, viz. 1 and 8. In this way the assignment of 8a(A) and 8a(B) is confirmed (Table 2), but with alternative deuteration of B-ring (7) or A-ring (8) it was possible to assign modes 8b(A) and 8b(B) which are overlapped in the spectrum of D₀-tBA (1). For compounds with both deuterated rings (14 and 15) it was even possible to assign all the four modes by combining solution and KBr Infrared spectra.

The next four ring modes, 19a(A), 19a(B), 19b(A) and 19b(B), were assigned using the same technique of comparing pairs of nondeuterated and deuterated moieties. Thus it was found out, that 19a(B) appears at slightly higher frequency than 19a(A). On the other hand, 19b(A) and 19b(B) are practically degenerate (Table 2) and differ only in band intensities if both rings are nondeuterated (1, 2, 16), but can be clearly distinguished for perdeuterated rings (14, 15).

Table 2. Selected values of phenyl group frequencies (cm^{-1}) for *trans*-N-benzylideneanilines 1, 2, 7, 8, 14, 15 and 16 (infrared spectra of solutions, if not otherwise stated)

| Description of the mode | <u>1</u> | <u>2</u> | <u>7</u> | <u>8</u> | <u>14</u> | <u>15</u> | <u>16</u> |
|-------------------------|-------------------|-------------------|-------------------|----------|-------------------|-------------------|------------------|
| 8a(A) | 1593 | 1592 | 1592 | 1562 | 1558 | 1558 | 1591 |
| 8b(A) | 1582 | 1580 | 1581 | 1544 | 1544 ^a | 1541 ^a | 1577 |
| 8a(B) | 1581 ^b | 1580 ^b | 1565 ^a | 1581 | 1552 ^a | 1552 ^a | 1580sh |
| 8b(B) | 1570 ^b | 1570 ^b | 1544 ^a | 1570sh | 1540sh | 1540sh | 1570sh |
| 19a(B) | 1495 | 1493 | 1394 | 1493 | 1404 | 1399 | 1491 |
| 19a(A) | 1486 | 1485 | 1486 | 1389 | 1379 | 1370 | 1484 |
| 19b(B) | 1453 | 1451 | 1339 | 1453 | 1337 | 1339 | 1449 |
| 19b(A) | 1450 ^b | 1450 ^b | 1450 | 1326 | 1319 | 1329 | 1445sh |
| 11(A) | 765 | 763 | 752 | 650 | 649 | 649 | 764 |
| 11(B) | 749 | 746 ^b | 638 | 747 | 622 | 619 | 748 |
| 4(A) | 692 ^c | 692 ^c | 694 | 553 | 553 | 553 | 697 ^a |
| 4(B) | 692 ^c | 692 ^c | 549 | 691 | 547 | 547 | 691 ^a |

^aKBr pellet.

^bOverlapped band.

^cAccidentally degenerate vibrations.

The following two pairs of ring vibrations (Wilson modes 14 and 3) appear in the same region as Ph-N or Ph-C stretching modes, and besides are mixed with the 19b mode of a deuterated ring in cases where there is a nondeuterated or a p-deuterated ring left. Thus it will be possible to solve this problem only by means of a normal coordinate analysis. Similar considerations hold also for Wilson modes 9a, 9b, 15, 18a and 18b, which appear in the range 1200 - 1000 cm^{-1} , although for some of them bands can be observed in pairs, corresponding to A- and B-ring vibrations.

Out-of-plane ring vibrations have frequencies below 1000 cm^{-1} for both the light and heavy phenyl group. It is difficult here to distinguish between A-ring and B-ring vibrations. The replacement of hydrogen with deuterium in the imine group causes many changes of both band positions and intensities due to strong couplings with out-of-plane ring modes. Fig. 5 illustrates changes in infrared spectra upon deuteration of the imine group for two typical pairs of tBA isotopomers: 1/2 and 14/15. Many bands in the fingerprint region change their positions, but also their relative intensities and widths.

There are two phenyl out-of-plane vibrations which give very strong absorptions in infrared spectra of all monosubstituted benzenes - Wilson modes 11 and 4. The former band appears at 750 cm^{-1} and the latter one at 690 cm^{-1} , which is also the case for *trans*-N-benzylideneaniline. For D_0 -tBA (1) vibration mode 4 has been assigned to the strongest infrared band at 692 cm^{-1} for both rings (ref. 4), which is in perfect agreement with our result (Fig. 5a). The deuteration of the imine group does not affect this band at all (Fig. 5b), but in the spectrum of solid ^{15}N -tBA (16) two peaks were observed at 697 and 691 cm^{-1} (Table 2). If both rings are perdeuterated (tBA's 14 and 15), two bands in solution spectra were clearly resolved, at 553 and 547 cm^{-1} for the A- and B-ring, respectively (Table 2 and Fig. 5c-d). For the mode 11 two infrared bands of different intensities appear for all tBA isotopomers. While 11(A) band has the constant position for either nondeuterated or deuterated ring, 11(B) vibration is sensitive to the deuteration of the imine group (Table 2). This latter fact indicates coupling of out-of-plane ring modes with imine modes, giving in this way hints for assuming initial values of on- and off-diagonal local symmetry force constants.

CONCLUSION

Due to non-planarity of the *trans*-N-benzylideneaniline molecule all the 69 normal vibrations are both infrared and Raman active. However, a division of normal modes into three groups, belonging to two phenyl and one imine moiety, is experimentally well founded for the cases

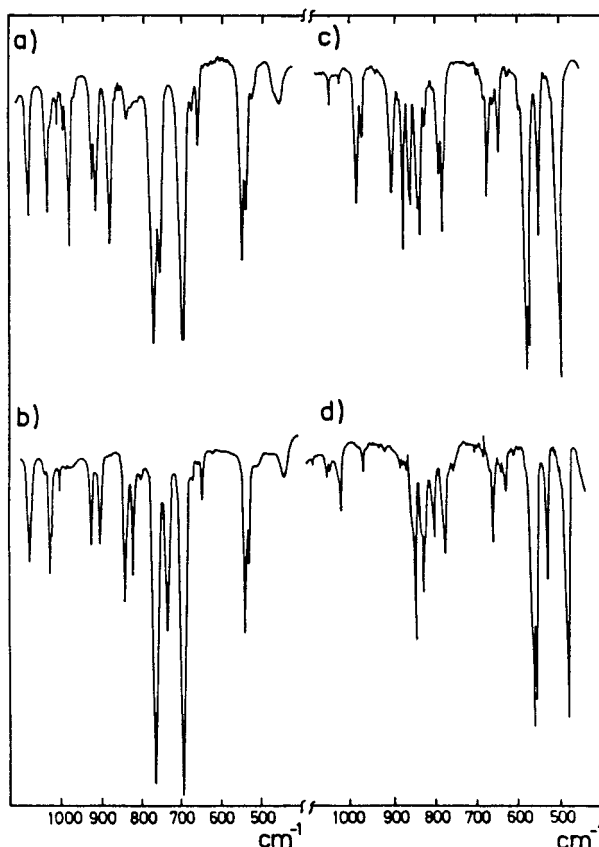


Fig. 5. Solution infrared spectra of *trans-N-benzylideneanilines* 1 (a), 2 (b), 14 (c) and 15 (d) in the fingerprint region.

discussed here and is thus justified for an introductory empirical assignment of infrared and Raman spectra. Using a number of isotopomers it was possible to assign the most characteristic vibrations for the A-phenyl, B-phenyl and imine group in terms of local symmetry vibrational coordinates. The assignment presented differs in some important points from Vergoten's (refs. 5, 6), which is understandable due to use of just one isotopic species. The normal modes of *trans-N-benzylideneaniline* are similar to those of *trans-stilbene* (ref. 3) not only concerning mixing of the bridging group and phenyl vibrations, but also because of the surprising similarity between the CH=N and CH=CD vibrational modes. The results of the assignment of vibrational spectra of sixteen isotopomers of tBA is a necessary prerequisite for the calculation of a force field and a detailed normal coordinate analysis of a non-planar model. The important question to be addressed is the transferability of the phenyl force field previously obtained (refs. 3 and 8) on a series of tSB isotopomers.

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