

Valence Force Constants of N-Benzylideneanilines

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Valence force constants for N-benzylideneaniline and for two *p,p'*-disubstituted derivatives were estimated by means of a point-charge model using CNDO data. A vibrational assignment of bands which are sensitive to the electron donor-acceptor characteristic of substituents is proposed. The conformational changes are interpreted in terms of an intramolecular energy transfer between substituents.

Introduction

Within the family of organic compounds with π -systems, N-benzylideneaniline (NBA) is interesting because of the nature of the phenyl-N, N=C and C-phenyl bonds, and the influence of the *p,p'*-substituents on the molecular conformation (see Fig. 1). As a consequence of the electron donor and acceptor ability of the substituents, N-benzylideneanilines adopt different conformations. Although several papers dealing with this subject have been published [1], to our knowledge, there is no information about vibrational studies on N-benzylideneaniline (**1**), *p*-methylbenzylidene-*p*-nitroaniline (**2**) and *p*-dimethylaminobenzylidene-*p*-nitroaniline (**3**) compounds. The aim of the present paper is to perform a normal coordinate analysis of **1** by calculating the valence force constants in the series and then, to interpretate the influence of the substituents on the molecular conformation.

In order to analyze the substituent effects on the conformation of N-benzylideneanilines **1** to **3** we used a point-charge model proposed by Kosmus [2]. This formulas which consist in a simple method to discuss bond properties at the equilibrium position, allows us to estimate the electronic contributions to the force constants. These valence force constants have been shown to be appropriate to describe several molecular systems [3].

Experimental

All compounds, synthesized by standard methods [4], were purified by recrystallization before measurements. Infrared spectra (IR) were recorded on a Perkin-Elmer 621 spectrophotometer for the crystal dispersed in KBr pellets. Raman spectra were recorded on a Coderg T800 spectrophotometer using the 647.1 nm exciting line of an Spectra Physics Kr⁺ laser. The spectra are displayed in Fig. 2.

Computational Method

A CNDO/2 computational programme [5] was employed and experimental geometries were obtained from the literature [6, 7]. X-ray structure determinations of compounds **1** to **3** indicate that the aniline and benzylidene rings are twisted out of the C₁–N₂=C₃–C₅ plane by varying angles in opposite directions (see Fig. 1). The torsion angles are defined as $\theta = \text{C}_3\text{N}_2\text{C}_1\text{C}_{20}$ and $\varphi = \text{N}_2\text{C}_3\text{C}_5\text{C}_6$.

Results and Discussion

The CNDO calculations can give some insight into the electron distributions and σ and π polarities of bonds. Using the Wiberg bond index (W) criterium, we have a pure covalent bond if W equals 1 and a

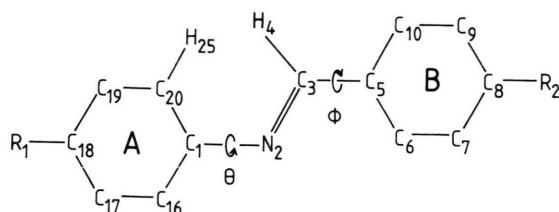


Fig. 1. *p,p'*-Substituted N-benzylideneanilines.

1: R₁ = R₂ = H, $\theta = 55^\circ$, $\varphi = 10^\circ$.
2: R₁ = NO₂, R₂ = CH₃, $\theta = 52^\circ$, $\varphi = 8^\circ$.
3: R₁ = NO₂, R₂ = N(CH₃)₂, $\theta = 49^\circ$, $\varphi = 7.1^\circ$.
 A: aniline ring; B: benzylidene ring.

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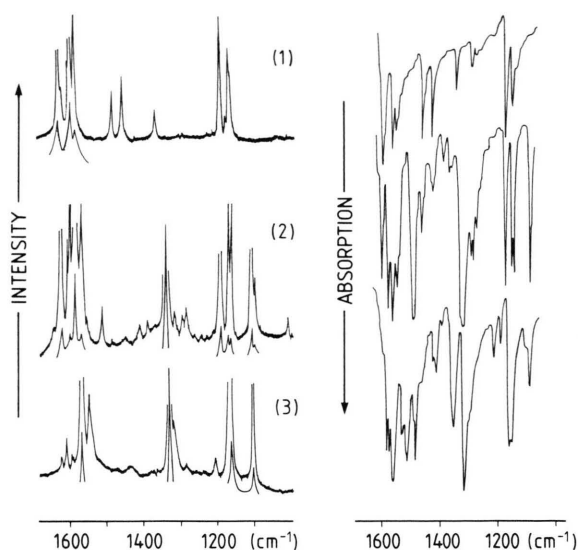


Fig. 2. Raman and Infrared spectra of N-benzylideneaniline (**1**), *p*-methylbenzylidene-*p*-nitroaniline (**2**) and *p*-dimethylaminobenzylidene-*p*-nitroaniline (**3**) in the region 1650–1100 cm^{-1} .

partial polarized bond if W is less than 1 [8]. Thus, we have two figures to characterize a bond: the bond index which represents the occupation of the covalent part of a bond and the atomic net charges (Q) which show the polarities within the whole molecule. The pure covalent bonds are highly directional, or rigid, with a large force constant, in comparison to polar or ionic bonds which become more flexible with increasing ionicity.

Chemical bonds with a large force constant value are characterized by a relatively high vibrational frequency and can be regarded as rigid chemical bonds [9]. The force constants (f) for the most relevant bonds in compounds **1**, **2** and **3** are displayed in Table I. The range of the calculated constants agrees with collected approximated numerical values for stretching forces [10]. In general, for N–C and C–C bonds treated as pseudodiatomics, three characteristically distinct potential wells are commonly found and may be identified with a) single bonds with f close to 5.3 and 4.5 $\text{mdyn } \text{\AA}^{-1}$, b) double bonds with

Table I. Length (R) (\AA), atomic net changes (Q), Wiberg indices (W), and valence force constants (f) ($\text{mdyn } \text{\AA}^{-1}$) for different bonds in N-benzylideneaniline (**1**), *p*-methylbenzylidene-*p*-nitroaniline (**2**) and *p*-dimethylaminobenzylidene-*p*-nitroaniline (**3**).

Comp.	Acceptor	Donor	R	Q_i	Q_j	W	f	R	Q_i	Q_j	W	f
			$\text{N}_{2(i)}\text{C}_{3(j)}$					$\text{C}_{16}\text{C}_{17}$				
1	H	H	1.237	–0.153	0.119	1.922	8.71	1.403	–0.029	0.021	1.428	7.28
2	NO_2	CH_3	1.269	–0.156	0.120	1.869	7.91	1.379	–0.026	0.029	1.472	7.71
3	NO_2	$\text{N}(\text{CH}_3)_2$	1.279	–0.178	0.139	1.836	7.57	1.382	–0.035	0.032	1.482	7.71
			C_1N_2					$\text{C}_{17}\text{C}_{18}$				
1	H	H	1.460	–0.153	0.114	0.993	5.28	1.371	0.021	–0.006	1.466	7.61
2	NO_2	CH_3	1.400	–0.156	0.143	1.038	6.29	1.378	0.029	0.019	1.401	7.52
3	NO_2	$\text{N}(\text{CH}_3)_2$	1.400	–0.178	0.142	1.048	6.52	1.384	0.032	0.016	1.394	7.51
			C_3C_5					C_5C_6				
1	H	H	1.496	0.119	0.014	1.035	4.41	1.391	0.014	0.006	1.392	7.20
2	NO_2	CH_3	1.474	0.120	0.003	1.057	4.71	1.387	0.003	0.018	1.376	7.14
3	NO_2	$\text{N}(\text{CH}_3)_2$	1.447	0.139	–0.036	1.086	5.16	1.405	–0.036	0.044	1.334	6.58
			C_3H_4					C_6C_7				
1	H	H	1.080	0.119	–0.042	0.942	5.37	1.405	0.006	0.004	1.459	7.30
2	NO_2	CH_3	1.080	0.120	–0.032	0.949	5.40	1.379	0.018	–0.009	1.480	7.87
3	NO_2	$\text{N}(\text{CH}_3)_2$	1.080	0.139	–0.038	0.947	5.42	1.367	0.044	–0.068	1.530	8.45
			$\text{C}_{20}\text{H}_{25}$					C_7C_8				
1	H	H	1.080	–0.029	–0.002	0.958	5.24	1.380	0.004	0.013	1.433	7.56
2	NO_2	CH_3	1.080	–0.032	0.008	0.957	5.22	1.383	–0.009	0.051	1.392	7.25
3	NO_2	$\text{N}(\text{CH}_3)_2$	1.080	–0.038	0.009	0.958	5.22	1.426	–0.068	0.164	1.323	6.13
			C_1C_{16}									
1	H	H	1.386	0.114	–0.029	1.424	7.68					
2	NO_2	CH_3	1.378	0.143	–0.026	1.381	7.58					
3	NO_2	$\text{N}(\text{CH}_3)_2$	1.400	0.142	–0.035	1.372	7.30					

$f \approx 10.5$ and $11.0 \text{ mdyn } \text{\AA}^{-1}$ and c) triple bonds with $f \approx 17.0$ and $15.0 \text{ mdyn } \text{\AA}^{-1}$, respectively. The force constants are consistent with the conventional idea of single, double and triple CN and CC bonds and such bonds are always found to be associated with potential wells with force constants close to those given above. However, any observed intermediate value of f may also be identified with a bond of intermediate character.

N_2C_3 bonds

Polarity changes observed in N_2C_3 bonds may be explained on the basis of both the bond lengths and the net charges of atoms directly involved (see Table I). In fact, as expected, the longer the bond distance the bigger is the resulting dipole moment of the bond. The Wiberg values suggest that the π overlapping on these bonds decreases when increasing the relative electron donor and acceptor ability of substituents. Therefore, we should expect a similar effect on the N_2C_3 force constants (see Table I), or a frequency shifting of the corresponding stretching mode toward lower energies. In fact, this trend is verified in the IR and Raman spectra where the observed band at 1625 cm^{-1} in NBA is shifted to 1620 and 1575 cm^{-1} in compounds **2** and **3**, respectively (see Fig. 2). This assignment is in agreement with reported data on Schiff's bases [11].

C_1N_2 bonds

In Table I it may be seen that the C_1N_2 bond distances decreases when increasing only the acceptor property of *p*-substituents, but the bond polarity increases in the same order. In such a case it seems that the charge redistribution has a bigger influence than the variation of bond lengths. That is, the charge distribution induced by the variation of the distance makes that overall an increasing of the dipole moment is observed.

As suggested by the Wiberg indices analysis, the C_1N_2 bonds are nearly covalent single bonds. However, their covalency degree is reinforced when going from compound **1** to **2** (see Table I). $f(C_1N_2)$ increases by increasing only the electron donating ability (case **2** and **3**); it is worth noticing that the corresponding bond lengths are identical. The force constant values in the series (5.28 to $6.52 \text{ mdyn } \text{\AA}^{-1}$) suggest a trend to localize the π electrons between the $-N=CH-$ double bond and the aniline phenyl

ring. The interaction of the bridge nitrogen lone pair and the aromatic π system should be essentially zero for a planar conformation. As a consequence, we expect the stretching mode $\nu(C_1N_2)$ to be shifted to higher frequencies. This effect is verified for the absorption band at 1310 cm^{-1} in NBA which is observed at 1320 cm^{-1} and 1370 cm^{-1} in compounds **2** and **3**, respectively (see Fig. 2). This result is in agreement with the observed frequencies and assignments proposed for *p*-aminoazobenzene derivatives [12], *p*-hydroxiazobenzene [13] and related compounds [14]. We should also expect to observe an increasing of the relative intensity of $\nu(C_1N_2)$ bonds when increasing the bond polarity. Unfortunately the spectra are nearly impossible to analyse because of a significant coupling of $\nu(C_1N_2)$ with other vibrational modes.

C_3C_5 bonds

Table I shows that the C_3C_5 single bond distance decreases by increasing the electron donating property of substituents. The polarity increasing in the same sense suggests an important charge redistribution effect. The observed trend of Wiberg indices allow us to predict a π -delocalization between the $-N=CH-$ double bond and the benzyldiene ring which should be essentially maximum for a planar conformation but decreases when increasing the twisting angle φ (see Fig. 1). Therefore, $f(C_3C_5)$ values are expected to increase with electron donor characteristics. The values indicate that a shifting to higher frequencies must be observed for the corresponding vibrational bands. We propose the absorptions at 1190 , 1190 and 1205 cm^{-1} of compounds **1**, **2** and **3**, respectively, to be attributed to the stretching C_3C_5 vibration; the corresponding Raman intensity decreases in the same order (see Fig. 2). This assignment is in agreement with others proposed for *p*-methylbenzonitrile [15] and stilbene [16].

CH bonds

From an *ab initio* study [1] it has been proposed that one of the factors determining conformation of N-benzylideneaniline involves the interaction of the *ortho* hydrogen on the aniline ring (H_{25}) and the azomethine proton (H_4). This interaction is repulsive in the planar conformation but is relieved by a twisting of the N-phenyl bond (see Fig. 1). Nevertheless our results do not permit any vibrational interpreta-

tion of that effect: the Wiberg indices and the resulting force constants are practically identical in the three molecules (see Table I). The $\nu(\text{CH})$ modes are expected to be observed beyond 2900 cm^{-1} .

A-ring CC bonds

The Wiberg indices values for CC bonds in the aniline ring are characteristics of an intermediate single-double bond (see Table I). A more detailed analysis of these values allow us to infer that the π -electrons will be preferentially localized on the $\text{C}_{16}\text{C}_{17}(\text{C}_{20}\text{C}_{19})$ bond when increasing electron donor and acceptor strengths. However, its acquired covalency degree remains almost invariant by changing only the electron donor groups. On the adjacent bonds a similar trend is verified. The resulting force constants are quite similar in the whole A-ring group. $f(\text{C}_1\text{C}_{16})$ decreases by increasing electron donor and acceptor abilities. Nevertheless the force constant for the central bond $\text{C}_{16}\text{C}_{17}(\text{C}_{20}\text{C}_{19})$ increases exclusively when increasing the electron withdrawing characteristics; $f(\text{C}_{17}\text{C}_{18})$ decreases in the same manner. Thus, it can be inferred that the $f(\text{C}_1\text{C}_{16})$ variations are mainly due to the influence of electron donating groups.

B-ring CC bonds

Table I shows that the Wiberg indices values for the $\text{C}_6\text{C}_7(\text{C}_{10}\text{C}_9)$ bond increase with the electron donor strength. In the same sense the adjacent bonds become electron deficient. This result is well interpreted by the corresponding force constants: within the series of molecules $f(\text{C}_6\text{C}_7)$ value increases by increasing the electron donating properties. Because of the difference between $f(\text{C}_5\text{C}_6)$ or $f(\text{C}_7\text{C}_8)$ and $f(\text{C}_6\text{C}_7)$ with $f(\text{CC})$ values in the A-ring, we propose to assign the higher frequency to the $\nu(\text{C}_6\text{C}_7)$ mode in compound **3**; this band is observed at 1600 cm^{-1} in absorption and at 1612 cm^{-1} in Raman (see Fig. 2). This assignment is consistent with the proposed ones for stilbene (1594 cm^{-1}) [16] and anisole (1588 cm^{-1}) [17]. The lowest frequency at 1320 cm^{-1} in the spectra of compound **3** could be ascribed to the $\nu(\text{C}_7\text{C}_8)$ mode (see Fig. 2). The same assignments have been proposed in stilbene (1339 cm^{-1}) [16] and anisole (1332 cm^{-1}) [17].

Infrared and Raman frequencies of the most relevant stretching vibrations in compounds **1**, **2** and **3** are summarized in Table II.

Tab. II. Infrared (IR) and Raman frequencies (cm^{-1}) and proposed assignment for stretching modes in N-benzylideneaniline (**1**), *p*-methylbenzylidene-*p*-nitroaniline (**2**) and *p*-dimethylaminobenzylidene-*p*-nitroaniline (**3**).

Compound	$\nu(\text{N}_2\text{C}_3)$	$\nu(\text{C}_1\text{N}_2)$	$\nu(\text{C}_3\text{C}_5)$	
1	1625	1310	1190	IR
	1627	—	1193	Raman
2	1620	1320	1190	IR
	1622	1318	1195	Raman
3	1575	1370	1205	IR
	1577	—	1209	Raman

Conclusions

The calculated force constants, which are in good agreement with reported data [10], allowed us to propose a vibrational assignment of the most relevant stretching modes of three *p,p'*-disubstituted N-benzylideneanilines. The observed frequency shifting explains quite well the experimental conformational structure of these compounds. The trend to the planarity when increasing mainly the electron donor property could be explained on the basis of an intramolecular electron transfer between substituents. In fact, besides the stabilization of a non-planar structure due to both an interaction of the bridge nitrogen lone pair and the aromatic π -system and a repulsion between the azomethine hydrogen and one of the *ortho* hydrogen on the aniline ring [1], delocalization of π -electrons between benzylidene and aniline rings through the $-\text{N}=\text{CH}-$ double bond plays an important role in stabilizing a less non-planar structure. Similar conclusions have been obtained from a crystal structure analysis of two isomeric benzylideneaniline derivatives [7].

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