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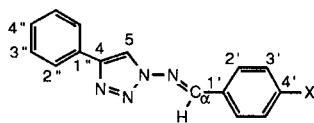
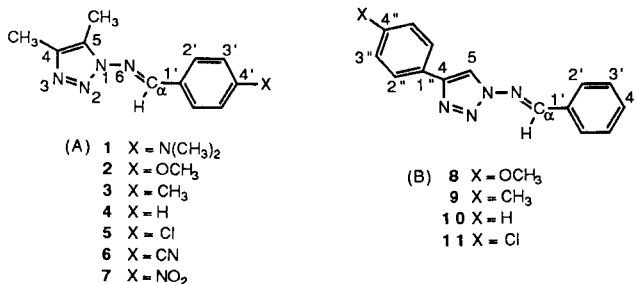
The ¹³C nmr spectra of several 1-(*N*-arylidene)amino-1,2,3-triazoles were determined. The long range influence of substituents on ¹³C resonances of triazole and C=N carbon atoms was examined and a correlation of their chemical shifts with net charge densities ($q_{\pi} + \rho$) calculated by the CNDO/2 method was made. It was also shown that the dependence of the coupling constants ¹J(CH) for C=N carbon on the substituents is better correlated using electrons in bond values instead of charge densities.

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Introduction.

The ¹³C nmr spectroscopy has been extensively used for the investigation of *N*-benzylideneanilines [1-6] and similar compounds [7-11], but there is no other relevant study on Schiff bases with a heterocyclic system in imino nitrogen. This, in connection to the low reactivity of N(6)=C(α) bond of the compounds in question in 1,3-dipolar or [2 + 2] cycloadditions [12] prompted us to examine their ¹³C nmr spectra as well as the substituent effects in relation to some electronic parameters for atoms and bonds (net charge, electrons in bond and π bond order) derived by CNDO/2 calculations and to compare these data to those of benzylideneaniline.

The compounds **1-16** are divided into three groups (A-C): (A) with a *para*-substituent in arylidene function and two methyl groups in 4- and 5-positions of the triazole ring (**1-7**), (B) with a *para*-substituent in the 4-aryl group (**8-11**) and (C) with a phenyl in 4-position of the triazole ring and analogously substituted, as in (A), in arylidene group (**12-16**).



- (C) 12 X = N(CH₃)₂
13 X = OCH₃
14 X = CH₃
15 X = Cl
16 X = NO₂

The compounds **1-16** show the presence of only one isomer to which the less hindered and more stable (*E*)-configuration was attributed on the basis of an existing X-ray [13] and dipole moments data [14] for aryloxyarylidene-amino-1,2,3-triazoles, as well as literature data [7,15,16] for many other Schiff bases.

EXPERIMENTAL

The arylideneamino-1,2,3-triazoles **1-16** were prepared by condensation of the appropriately substituted benzaldehydes and 1-amino-1,2,3-triazoles in refluxing toluene [12]. The mp of the compounds used for spectral study were as follows: **1**, 157-159°; **2**, 133-135°; **3**, 112-114°; **4**, 76-78°; **5**, 143-145°; **6**, 218-220°; **7**, 225-227°; **8**, 152-154°; **9**, 158-160°; **10**, 134-135°; **11**, 194-196°; **12**, 188-190°; **13**, 157-158°; **14**, 186-187°; **15**, 207-208°; **16**, 257-259°.

All ¹³C nmr spectra were obtained at ca 40° with a FT Varian CFT-20 spectrometer at 20 MHz in deuteriochloroform solutions with TMS as internal standard ($\delta = 0$ ppm) using complete proton decoupling, off-resonance decoupling and proton coupling techniques. Depending on the sample concentration accumulations up to 80,000 transients were obtained with a pulse width of 10-12 μs (flip angle 50-60°).

The theoretical calculations of carbon net charge densities ($q_{\pi} + \rho$) as well as π bond orders and electrons in bond [17] (B_{AB}) were carried out by the CNDO/2 method (141 QCPE program after appropriate modification) using a Univac 1106 computer. The geometry used for the triazole ring was obtained by X-ray analysis [13a] of 4,5-dimethyl-1-(α-benzoyloxybenzylideneamino)-1,2,3-triazole whereas for the geometry of benzylidene function the X-ray data [18] of benzylideneanilines was used. The calculations were made for several conformations in respect to N(1)-N(6) bond, but as a most probable conformation that with the triazole ring forming a torsional angle of 15° with the N=C-α phenyl group was considered [13a]. In the compounds of group (B) and (C) the torsional angle between 4-phenyl and triazole ring was taken equal [13b] to 21.5°.

Results and Discussion.

Chemical Shifts.

The chemical shifts of all carbons and the coupling constants ¹J(CH) for the compounds **1-16** are given in Table 1, whereas Table 2 contains the calculated charge densities for some critical atoms (C-4, C-5, C-α) and bond orders for N(6)=C(α) bond and electrons in C(α)-H bond (B_{AB} values).

Table 1

¹³C NMR Chemical Shifts [δ, deuterochloroform, ppm from TMS, and coupling constants J(CH) in Hz, values in parenthesis for the compounds 1-16

Compound	C-4	C-5	CH ₃ -4	CH ₃ -5	C-α	C-1'	C-2'	Carbon Atoms				C-X		
								C-3'	C-4'	C-1''	C-2''		C-3''	C-4''
1	140.35	127.93	10.55 (127.9)	7.52 (129.8)	154.68 (164.0)	120.04	130.60	111.61	152.92				40.04 (136.0)	
2	140.53	128.50	10.48 (128.0)	7.46 (129.9)	153.79 (166.1)	125.24	130.65	114.44	162.84				55.45 (144.5)	
3	140.63	128.68	10.51 (127.7)	7.48 (130.0)	154.14 (166.6)	129.94	128.84	129.70	142.81				21.68 (126.9)	
4	140.66	128.80 [a]	10.44 (127.9)	7.42 (129.9)	153.94 (166.7)	132.53	128.76 [b]	128.89 [b]	132.03					
5	140.85	128.96	10.49 (127.8)	7.47 (130.1)	152.64 (168.2)	131.11	129.97 [b]	129.35 [b]	138.24					
6	141.12	129.40	10.47 (128.0)	7.48 (130.0)	151.52 (170.3)	136.64	129.10	132.70	115.18				118.11	
7	141.21	~129.5 [a]	10.48 (128.0)	7.51 (130.2)	151.06 (170.8)	138.25	129.49	123.91	149.71					
8	147.41	118.04 (196.8)			155.66 (167.0)	132.11	129.05	129.05	132.47	123.04	126.99	114.34	159.85	55.32
9	147.60	118.32 (196.6)			155.66 (167.2)	132.12	129.08	129.08	132.51	127.53	125.58	129.59	138.52	21.31 (126.6)
10	147.52	118.85 (197.0)			155.79 (167.1)	132.03	129.07	129.07	132.54	130.31	125.65	128.89	128.42	
11	147.17	118.94 (196.7)			156.06 (166.8)	131.97	129.13	129.13	132.66	128.85	126.89	129.13	134.26	
12	147.12	118.01 (196.0)			156.21 (163.9)	119.36	130.92	111.71	153.17	130.78	125.62	128.84	128.16	40.05 (136.4)
13	147.37	118.56 (196.5)			155.53 (166.0)	124.71	131.01	114.64	163.25	130.46	125.67	128.91	128.37	55.53 (144.5)
14	147.85	118.69 (196.8)			155.89 (166.5)	129.37	129.09 [c]	129.84	143.40	130.41	125.67	128.89 [c]	128.37	21.72 (126.7)
15	147.94 [c]	118.98 (197.3)			154.48 (168.0)	131.06 [b]	130.25	129.56	138.84	130.50 [b]	125.72	128.98	128.56	
16	~148.0 [c]	119.05 (-)			152.58 (-)	139.44	129.91	124.10	(-)	129.91	125.60	128.88	128.25	

[a] Masked under the C-2' peak; from the coupled spectrum. [b] Assignments may be interchanged. [c] Peaks of very low intensities because of low solubility; assignments not certain.

Table 2

Net Charge Densities ($q_{\pi+\sigma}$) of C-4, C-5, C- α Atoms,
 π Bond Orders of N(6)=C(α) Bond and Electrons in
 Bond (B_{AB}) of C(α)-H Bond for the Compounds **1-16**

Compound	C-4	$q_{\pi+\sigma}$ (electrons) C-5	C- α	π Bond order N(6)=C(α)	Electrons in bond C(α)-H
1	0.0158	0.0635	0.1035	0.8400	0.9465
2	0.0163	0.0642	0.1015	0.8409	0.9467
3	0.0163	0.0644	0.0989	0.8412	0.9468
4	0.0166	0.0649	0.0965	0.8422	0.9470
5	0.0177	0.0662	0.0929	0.8419	0.9473
6	0.0174	0.0659	0.0937	0.8418	0.9472
7	0.0191	0.0680	0.0866	0.8417	0.9478
8	0.0369	0.0124	0.1032	0.8416	0.9471
9	0.0343	0.0148	0.1030	0.8416	0.9471
10	0.0321	0.0169	0.1034	0.8416	0.9471
11	0.0296	0.0205	0.1056	0.8413	0.9471
12	0.0309	0.0159	0.1104	0.8391	0.9466
13	0.0315	0.0163	0.1085	0.8401	0.9468
14	0.0316	0.0165	0.1058	0.8405	0.9469
15	0.0336	0.0176	0.0997	0.8415	0.9474
16	0.0355	0.0186	0.0935	0.8415	0.9479

In the compounds of group (A) the C-5 methyl carbons always resonate at higher field than the C-4 methyl carbons, the corresponding chemical shifts being in the range of 7.4-7.5 and 10.4-10.55 ppm respectively. An analogous situation also holds for the triazole carbons, the C-5 atoms resonating in the range of 127.9-129.5, whereas those of C-4 between 140.4-141.2 ppm, in agreement with our previous observations [19,20]. In the compounds of groups (B) and (C) the chemical shifts of C-5 atoms are again found in much higher field than C-4, the corresponding values being for C-5, 118-119 ppm [$^1J(\text{CH}) = 196-197$ Hz] and for C-4, 147-148 ppm.

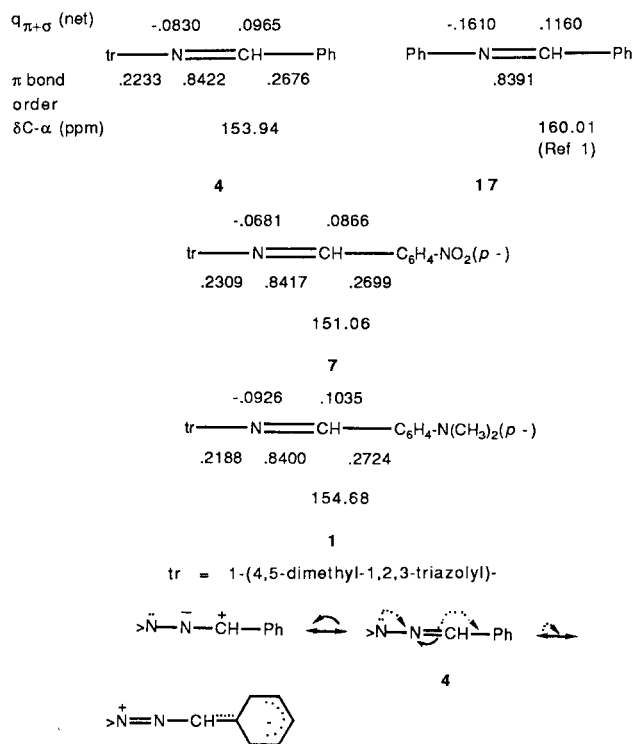
For the compounds of group (A) there is a good correlation between the chemical shifts of C(4)-CH₃ and C(5)-CH₃ and carbon methyl charge densities, the electron density for C(5)-CH₃ being always higher than the corresponding electron density of C(4)-CH₃ [$q_{\pi+\sigma}$ C(4)-CH₃ ca -0.0135 and $q_{\pi+\sigma}$ C(5)-CH₃ ca -0.0230] in agreement with their chemical shifts (Table 1). On the other hand, although C-5 undoubtedly shows upfield shifts in respect to C-4 (Table 1), their electron densities are opposite (Table 2), a fact suggesting the operation of some anisotropic effects, as it was observed in several other cases [21], where there is a poor correlation between chemical shifts and charge densities calculated with CNDO or *ab initio* methods [22]. It is mentioned that the triazole ring atoms charge densities presented in this work are similar to those given previously for some other triazole derivatives [23,24].

In all compounds **1-16** the chemical shift of C- α carbon is found between 151-156 ppm [$^1J(\text{CH}) = 164-170$ Hz] (Table 1) and it is subjected to a more pronounced influence from the substituents X than the corresponding shifts for triazole carbon atoms C-4, C-5. These C- α shift values are close to that reported for C=N carbons (147-154 ppm) in aryloxyarylideneamino-1,2,3-triazoles [20], whereas the C=N carbon shifts in analogously to compounds of group (A) substituted benzylideneanilines [1,2] are found between 157-160 ppm.

The observed C- α shifts of the compounds **1-16** could be more related to (*E*)-benzaldoximes [10], which show C=N signals between 148-151 ppm. On the other hand, this carbon resonates in phenylhydrazones [10] at 135-139 ppm, indicating that the sp³-hybridized heterocyclic nitrogen plays a different electronic effect than that of the same hybridization nitrogen in phenyl hydrazones, although part of this effect might be due to a paramagnetic shift caused by the triazole ring.

Comparing some electronic parameters as they are obtained by CNDO/2 method for the compound **4** and benzylideneaniline (**17**) (Scheme 1) it is noticed that the electron net charge ($q_{\pi+\sigma}$) on C- α in **4** is higher (less positive charge) than the corresponding charge in **17**, in agreement with the observed C- α chemical shifts. On the other hand, the negative charge on N-6 atom is much higher in **17** than in **4** and the π bond order value for the bond N(6)=C(α) is higher in **4** than in **17**. All these data provide

Scheme 1



evidence in favor of the aspect, previously proposed as a speculation [3], that an inverse conjugative interaction is operative and the resonance form **18** should be more important in the compounds under study than in benzyldeneanilines.

This effect is more pronounced in *para*-nitro-derivative (**7**), where the C- α atom resonates at 151.1 ppm, its net charge being 0.0866. Another factor which supports the previous aspect is the π bond order indexes for $>\dot{N}(1) \cdots N(6)$ bond, which are increased from dimethylamino-**(1)** to nitro-derivative (**7**), their values being 0.2188 and 0.2309 respectively.

Substituent Effects.

In respect to the substituent effects on the chemical shifts of triazole and imino carbons (C-4, C-5 and C- α) there is a very small but characteristic influence depending on the electronic effect of the substituent X.

Thus, in the compounds of group (A) the electron-withdrawing substituents cause a very small paramagnetic shift on both C-4 and C-5, the chemical shift difference $\Delta = \delta NO_2 - \delta N(CH_3)_2$ between nitro- **7** and dimethylamino-derivative **1** being +0.9 and +1.6 ppm respectively. More pronounced is, however, the influence of substituents on C- α resonances but with opposite sign, the chemical shift difference between the compounds **7** and **1** being in this

case -3.6 ppm. Analogous, in sign and magnitude, is also the electronic substituent effect on C- α shifts in benzyldeneanilines [1], where the difference in chemical shift for the same substituents is -3.6 ppm. Exactly the same behavior concerning the long range influence of the substituent X on C-4, C-5 and C- α resonances was also found in compounds of group (C). Less important substituent effects are observed in compounds of group (B), where the difference in chemical shifts even for C-4 atom is less than 1 ppm. This could be explained assuming a steric inhibition of resonance, the 4-aryl group being out of coplanarity in respect to the triazole ring, but this aspect is not supported by crystal structure [13b] of 4,5-diphenyl-1-(α -benzoyloxybenzyldeneamino)-1,2,3-triazole, where the 4-phenyl group forms with triazole ring a dihedral angle equal to 21.5°. It is therefore more likely to suggest a compensation in the transmission of the electronic substituent effect, which was also proposed in benzyldeneanilines [1] with a *para*-nitro-group in aniline function.

The substituent effects on the chemical shifts of C=N carbon in several benzyldeneanilines has been extensively studied [1-7] by means of their σ Hammett or σ_t and σ_p values. In this work the substituent effects are considered using the net charge densities of the carbon atoms and in several other cases very good linear correlations between carbon chemical shifts and charge densities were reported [19,21,22,25].

The various carbon resonances, δC , in an analogously substituted system can be expressed in relation to the calculated carbon net charge densities, $q_{\pi+\sigma}$, with the following simple expression (1):

$$\delta C \text{ (ppm)} = a \cdot q_{\pi+\sigma} + b \quad (1)$$

where a and b are constants. Thus, by plotting the C- α resonances against the net charges of this carbon in the compounds **1-16**, a reasonable linear correlation is found (Figure 1) with a correlation coefficient $r = 0.933$, the corresponding a and b constants being equal to 241.9 and 130.05 respectively. It is mentioned that by changing the conformation of the system the influence on C- α chemical shift is rather unimportant. Thus, in the case of the *para*-nitro-derivative **7** the net charge density of C- α carbon is changed from 0.0866 to 0.0880 when the nitro-group turns from the phenyl coplanar conformation to one forming a torsional angle of 30° with the phenyl group. These charge densities give, according to equation (1), for the C- α chemical shifts the values of 151.0 and 151.3, respectively, whereas the experimental value is 151.06 ppm, indicating that several anomalies previously reported [1] and connected to a poor correlation between C- α chemical shifts and σ Hammett values in benzyldeneanilines cannot solely be attributed to a change of conformation.

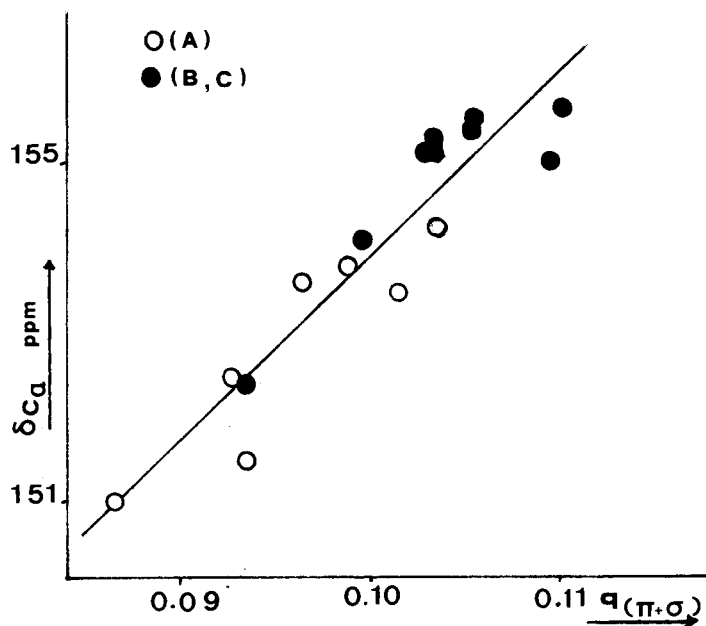


Figure 1. Plot of δC_{α} chemical shifts versus the net charge densities ($q_{\pi+\sigma}$) for the compounds of groups (A,B,C).

Similar linear correlations (Figure 2) are also held for C-4 and C-5 chemical shifts in relation to their charge densities in the compounds of group (A), the corresponding r values being 0.912 and 0.896 respectively.

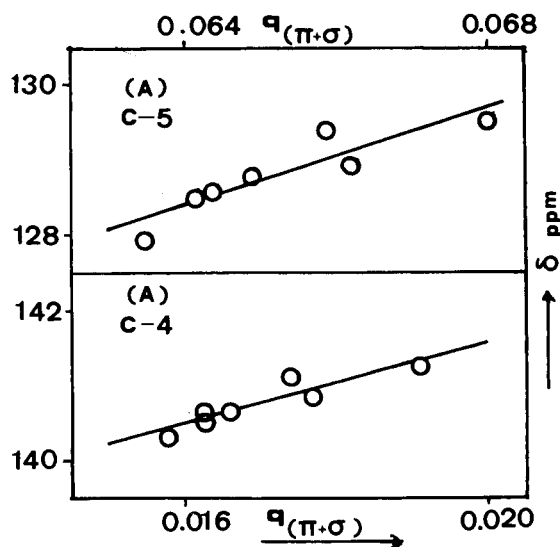


Figure 2. Plot of $\delta C-4$ and $\delta C-5$ chemical shifts versus the net charge densities ($q_{\pi+\sigma}$) for the compounds of group (A).

In the compounds of groups (B) and (C) the correlation for C-4 and C-5 is very poor, probably because the substituent effect is very small.

By plotting the C- α chemical shifts versus σ Hammett values [26] for the compounds of group (A) a better linear correlation is found ($r = 0.949$) than the one obtained by plotting $\delta C-\alpha$ values against C- α charge densities ($r = 0.912$). The latter method, however, has a more general application giving reasonable linear correlation with all compounds **1-16** ($r = 0.933$).

Coupling Constants.

In respect to the C- α -H coupling constants, $^1J(\text{CH})$, we have found, on the contrary to the chemical shifts, that the $^1J(\text{CH})$ values are increased as the C- α positive net charge decreased, in analogy to previous observations [1] concerning some benzylideneanilines which give a negative ρ Hammett between $^1J(\text{CH})$ coupling constants and σ values. Thus, the $^1J(\text{CH})$ values in *para*-dimethylamino-**1** and *para*-nitro-derivative **7** are equal to 164.0 and 170.3 Hz, respectively, whereas the corresponding C- α net charge densities are 0.1035 and 0.0866. However, the coupling constants $^1J(\text{CH})$ are increased as the electrons in bond values for C- α -H bond increase and moreover by plotting (Figure 3) the last two parameters for the compounds **1-15** a reasonable linear correlation is found, the r value being equal to 0.898. This correlation is improved ($r = 0.958$) by omitting the cyano-derivative **6**. The correlation of $^1J(\text{CH})$ values with C- α charge densities, a method which is usually used in analogous studies [1] is less accurate ($r = -0.814$), whereas there is a very poor correlation using π

bond order or electrons in bond values for N(6)=C(α) bond.

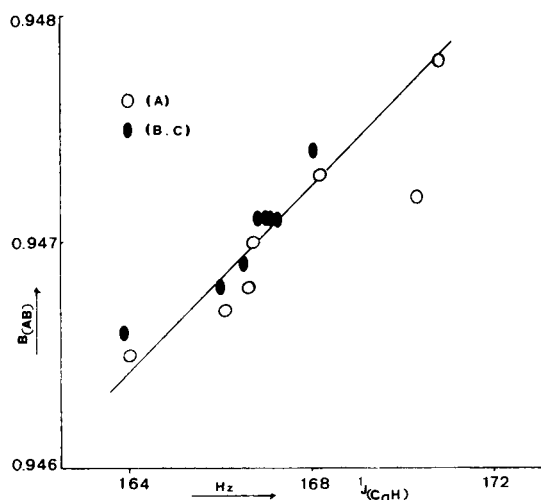


Figure 3. Plot of $^1J(\text{C}\alpha\text{H})$ coupling constants versus the electrons in C(α)-H bond for the compounds of groups (A,B,C).

This paper is dedicated to Professor David Y. Curtin on his 67th birthday.

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