

Structure and Conformation of Asymmetrically 4,5-Substituted
1-(α -Aroyloxyarylideneamino)-1,2,3-triazoles (1)

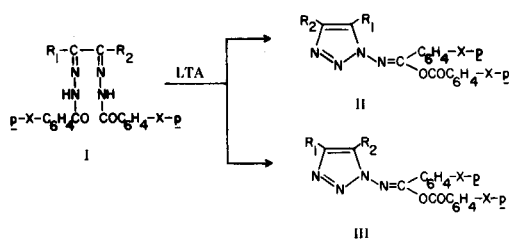
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The dipole moments of several asymmetrically 4,5-substituted 1-(α -aroyloxyarylideneamino)-1,2,3-triazoles, produced by oxidation of bis-aroylhydrazones of α -dicarbonyl compounds, were measured in benzene solution. The structure and the probable conformation of each of these compounds was determined by comparing their experimental and theoretical dipole moments. It has been found that when one of the substituents R_1 or R_2 is an aryl group, it is located at the 4-position of the triazole ring. Considering the conformation of the ester-imino function, it has been found to be the same as that of symmetrically substituted derivatives.

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From the oxidation with lead tetraacetate (LTA) (3) of bis-aroylhydrazones of asymmetrically substituted α -dicarbonyl compounds (I), two possible 1-(α -aroyloxyarylideneamino)-1,2,3-triazoles can be formed, II or III. In cases where the substituents R_1 , R_2 are methyl and hydrogen or methyl and ethyl, both isomers II and III are formed (4), but in all other cases studied, only one isomer is isolated, which has been proved by this work to be III. In cases where one of the substituents R_1 , R_2 is a methyl group, the isomer which is formed can be identified by means of benzene induced shifts (ASIS) in nmr spectra (5). In this respect, we have found that dipole moment measurements can be used as a more general and



- A $R_1 = C_6H_5$, $R_2 = H$, $X = H$;
 B $R_1 = C_6H_5$, $R_2 = H$, $X = Cl$;
 C $R_1 = C_6H_5$, $R_2 = H$, $X = OCH_3$;
 D $R_1 = p\text{-ClC}_6\text{H}_4$, $R_2 = H$, $X = H$;
 E $R_1 = p\text{-ClC}_6\text{H}_4$, $R_2 = H$, $X = Cl$;
 F $R_1 = p\text{-ClC}_6\text{H}_4$, $R_2 = H$, $X = OCH_3$;
 G $R_1 = p\text{-O}_2\text{NC}_6\text{H}_4$, $R_2 = H$, $X = H$;
 H $R_1 = p\text{-O}_2\text{NC}_6\text{H}_4$, $R_2 = H$, $X = OCH_3$;
 J $R_1 = C_6H_5$, $R_2 = CH_3$, $X = H$;
 K $R_1 = C_6H_5$, $R_2 = CH_3$, $X = Cl$;
 L $R_1 = C_6H_5$, $R_2 = CH_3$, $X = OCH_3$;
 M $R_1 = p\text{-BrC}_6\text{H}_4$, $R_2 = CH_3$, $X = H$;
 N $R_1 = p\text{-BrC}_6\text{H}_4$, $R_2 = CH_3$, $X = OCH_3$;
 O $R_1 = p\text{-CH}_3\text{OC}_6\text{H}_4$, $R_2 = CH_3$, $X = H$;
 P $R_1 = p\text{-CH}_3\text{OC}_6\text{H}_4$, $R_2 = CH_3$, $X = Cl$.

conclusive method for the characterization of the isomers II or III. This method is more applicable when one of the substituents R_1 , R_2 is an aryl group, bearing a polar group in the p -position.

In our previous work (1) we have used dipole moments to reveal the conformation of the ester-imino function and the configuration with respect to the $C=N$ bond of some 4,5-dimethyl-1-(α -aroyloxyarylideneamino)-1,2,3-triazoles in benzene solution. It has been found after theoretical calculations of the dipole moments, that the compounds in question adopt the Z -configuration and that the overall conformations of these molecules are like those given in Figure 1.

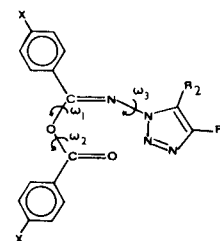


Figure 1. Structure of the Z -isomer of compounds (III). The most probable conformation corresponds to $\omega_1 = 60\text{--}80^\circ$, $\omega_2 = 0\text{--}20^\circ$ and $\omega_3 = 0\text{--}40^\circ$. The angles are considered with respect to the planar structure, where $\omega_1 = \omega_2 = \omega_3 = 0^\circ$ and in the direction of the arrows.

On the basis of the structure shown in Figure 1, which was reconfirmed for the compounds under investigation, it is possible to determine the structure of asymmetrically 4,5-substituted triazolyl-isoimides of the type II or III, comparing experimental and theoretical values of dipole moments calculated separately for each isomer. Theoretical moments were obtained by vector addition of all bond moments and by using the comparative graphical method of Exner and Jehlička (6) for several possible conformations. It was assumed that a change of the substituents from methyl to aryl groups in the 4,5-positions of the triazole ring does not affect the overall conformation of the molecule, especially that of the ester-imino function. This assumption was, however, confirmed by computing the total moment for all possible conformations and

Table II
Analytical Data for the Asymmetrically 4,5-Substituted 1-(α -Aroyloxyarylideneamino)-
1,2,3-triazoles (III) Obtained by Oxidation of bis-Aroylhydrazones of α -Dicarbonyl Compounds (I)

Compound	M.p. °C	Ir ν C=O C=N, Cm ⁻¹ (Nujol)	Nmr δ (Deuteriochloroform)	Ms <i>m/e</i> (R.I. %)	Formula (Molecular Weight)	C	H	N
IIIA	169-171 (13)							
IIIB	161-163 (10)							
IIIC	147-149 (13)							
IIID	161-163 (a)	1745 1620	7.21 (m), 8.11 (s) 8.21 (m)	M ⁺ 404 (0.1), 402 (0.4) 374 (5), 136 (36) 105 (100)	C ₂₂ H ₁₅ ClN ₄ O ₂ (402.82)	65.59 65.57	3.75 3.87	13.90 14.04
IIIE	174-175 (a)	1745 1630	7.5 (m), 7.85 (d) 8.13 (m), 8.10 (s)	M ⁺ 472 (n), 470 (n) 442 (3), 305 (2) 139 (100)	C ₂₂ H ₁₃ Cl ₃ N ₄ O ₂ (471.68)	56.01 56.12	2.78 2.75	11.88 11.99
IIIF	151-153 (a)	1730 1630	3.95 (s), 7.01 (d) 7.40 (d), 7.75 (d) 8.03 (s), 8.08 (m)	M ⁺ 464 (n), 462 (n) 434 (4), 407 (3) 297 (2), 135 (100)	C ₂₄ H ₁₉ ClN ₄ O ₄ (462.87)	62.27 61.87	4.14 4.13	12.11 12.09
IIIG	183-185 (a)	1755 1610	7.65 (m), 8.20(m)	M ⁺ 413 (0.4), 385 (3.5) 358 (4), 147 (16) 105 (100)	C ₂₂ H ₁₅ N ₅ O ₄ (413.39)	63.92 63.43	3.66 3.73	16.94 16.88
IIIH	177-179 (a)	1720 1620	3.94 (s), 7.05 (d) 8.18 (s), 8.20 (m)	M ⁺ 473 (0.1), 445 (0.4) 418 (1), 297 (1) 147 (4), 135 (100)	C ₂₄ H ₁₉ N ₅ O ₆ (473.44)	60.88 60.77	4.05 4.10	14.79 14.82
IIIJ	166-168 (14)							
IIIK	175-176 (a)	1745 1640	2.66 (s), 7.6 (m) 8.15 (m)	M ⁺ 452 (n), 450 (n) 422 (2), 381 (2) 139 (100)	C ₂₃ H ₁₆ Cl ₂ N ₄ O ₂ (451.27)	61.21 61.13	3.57 3.61	12.41 12.41
IIIL	150-151 (b)	1740 1630	2.65 (s), 3.91 (s) 7.03 (d), 7.43 (m) 7.76 (m), 8.14 (m)	M ⁺ 442 (0.4), 414 (8) 373 (7), 311 (5) 135 (100)	C ₂₅ H ₂₂ N ₄ O ₄ (442.47)	67.86 67.98	5.01 4.95	12.66 12.38
IIIM	176-178 (a)	1730 1630	2.66 (s), 7.58 (m) 7.66 (m), 8.21 (m)	M ⁺ 462 (0.3), 460 (0.3) 432 (2), 391 (2) 194 (16), 105 (100)	C ₂₃ H ₁₇ BrN ₄ O ₂ (461.32)	59.90 59.88	3.72 3.73	12.14 12.29
IIIN	178-179 (a)	1745 1630	2.63 (s), 3.91 (s) 7.02 (d), 7.61 (s) 8.11 (m)	M ⁺ 522 (n), 520 (n) 492 (1), 451 (2) 194 (11), 135 (100)	C ₂₅ H ₂₁ BrN ₄ O ₂ (521.37)	57.59 57.28	4.06 4.03	10.74 10.65

Table II (continued)
 Analytical Data for the Asymmetrically 4,5-Substituted 1-(α -Aroyloxyarylidenearmino)-
 1,2,3-triazoles (III) Obtained by Oxidation of bis-Aroylhydrazones of α -Dicarbonyl Compounds (I)

Compound	M.p. °C	Ir ν C=O C=N, Cm ⁻¹ (Nujol)	Nmr δ (Deuteriochloroform)	Ms m/e (R.I. %)	Formula (Molecular Weight)	Analysis % Calcd./Found	C	H	N
III O	173-175 (c)	1755 1640	2.61 (s), 3.82 (s)	M ⁺ 412 (1), 384 (7)	C ₂₄ H ₂₀ N ₄ O ₃ (412.44)	4.89	69.89	4.89	13.59
			6.98 (d), 7.60 (m)	343 (7), 251 (5)		4.94	69.47	4.94	13.95
			8.17 (m)	146 (27), 105 (100)					
III P	182-183 (b)	1745 1640	2.61 (s), 3.83 (s)	M ⁺ 482 (0.1), 480 (0.2)	C ₂₄ H ₁₈ Cl ₂ N ₄ O ₃ (481.30)	3.77	59.80	3.77	11.64
			6.97 (d), 7.50 (d)	452 (2), 319 (1)		3.74	59.00	3.74	11.75
			7.63 (d), 8.07 (m)	146 (23), 139 (100)					

(a) Recrystallized from a mixture of dichloromethane-methanol. (b) Recrystallized from a mixture of dichloromethane-ether. (c) Recrystallized from a mixture of dichloromethane-benzene. (n) Negligible intensity.

comparing the values obtained with those experimentally determined.

The dipole moments, (μ), were measured in benzene solution at 25° by the method of Guggenheim and Smith (7), using the equation:

$$\mu^2 = \frac{27kTM(\alpha_\epsilon - \alpha_n)}{4\pi Nd_1 (\epsilon_1 + 2)^2}$$

where k = Boltzmann's constant, N = Avogadro's number, T = absolute temperature, d_1 = density of the solvent, ϵ_1 = dielectric constant of the solvent, α_ϵ = slope of the line obtained by plotting $(\epsilon_{12} - \epsilon_1)$ against w , where ϵ_{12} is the dielectric constant of a solution and w is the weight fraction of that solution, α_n = slope of the line obtained by plotting $(n_{12}^2 - n_1^2)$ against w , where n_{12} is the refractive index of a solution and n_1 is the refractive index of the solvent, and M = molecular weight of the solute. The values α_ϵ and α_n were determined by the least-squares method. The dipole moments of the asymmetrically substituted triazolylisoimides which actually must be considered as III are given in Table I.

Table I

Dipole Moments of Compounds (III) at 25° in Benzene Solution

Compound	α_ϵ	α_n	$\mu/D (\pm 0.06)$
IIIa	3.51	0.44	3.23
IIIb	2.37	0.39	2.82
IIIc	5.81	0.30	4.66 (1)
IIId	5.60	0.49	4.36
IIIe	2.84	0.34	3.29
IIIf	7.53	0.46	5.49
IIIg	11.90	0.69	6.53 (2)
IIIh	13.41	0.34	7.55
IIIj	3.35	0.37	3.24
IIIk	2.16	0.39	2.71
IIIl	5.51	0.37	4.58
IIIm	4.75	0.38	4.31
IIIn	7.41	0.58	5.73
IIIo	2.84	0.44	3.02
IIIp	2.18	0.37	2.84

(1) $\Delta\mu = \pm 0.12$ D. (2) $\Delta\mu = \pm 0.17$ D.

For the theoretical calculation of the dipole moments of the compounds under investigation, we have divided the total moment into two components, one arising from the triazole ring and the other from the aroyloxyarylidenearmino-group; we have calculated the moments of each isomer II or III for all possible conformations and configurations. The values of the bond and group moments as well as their orientation in the molecule were the same with those previously used (1). The moment for C₆H₅-C_{tr} was taken equal to 0.35 D. On the other

hand, all the angles in the molecule were taken from X-ray data given by Katritzky and co-workers (8) for 1-(α -benzoyloxybenzylideneamino)-4,5-dimethyl-1,2,3-triazole. It should be noticed that other possible sets of bond angles and bond moments were also tried in these calculations, without any significant change in our results. Vector addition was carried out by analyzing the group or bond moments in their components in the three co-ordinate axes arbitrarily chosen (1). Since there are rotating polar groups, their components for a given conformation were calculated using Gilman's equations (9). The conformation of the ester-imino group is expressed by means of the angles ω_1 , ω_2 , whereas the coplanarity of the triazole ring with respect to the C=N bond is expressed by means of the angle ω_3 (Figure 1). The calculations for the methoxy derivatives were made assuming that the methoxy groups are freely rotating. Since it is possible to have incidental coincidence between experimental and theoretical values of the dipole moments for more than one conformer, we used the graphical method proposed by Exner and Jehlička (6). In this method, a comparative study of the theoretical values relative to the possible conformations and configurations in several pairs of compounds is made.

Theoretical calculations carried out on the derivatives bearing a *p*-substituted phenyl group (D-H, M-P) in the triazole ring have shown that if these derivatives are considered as having the structure II (aryl in the 5-position of the triazole ring) it is not possible to have coincidence between theoretical and experimental dipole

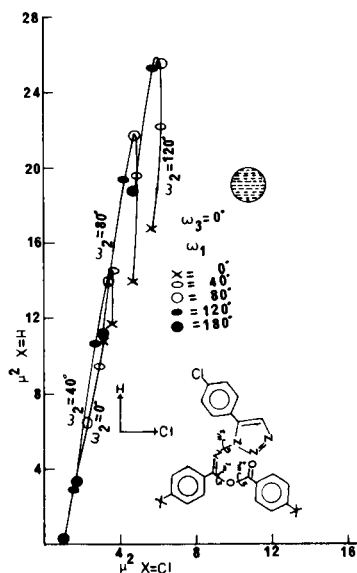


Figure 2. Comparison of theoretical dipole moments squared $\mu^2 X = H$ versus $\mu^2 X = Cl$ for the Z-isomers of compounds (IID and IIE) for $\omega_1 = 0-180^\circ$, $\omega_2 = 0-120^\circ$ and $\omega_3 = 0^\circ$. Hatched circles refer to the experimental dipole moments.

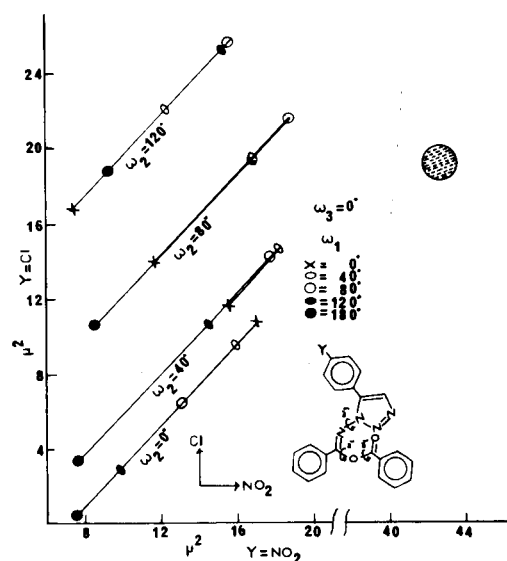


Figure 3. Comparison of theoretical dipole moments squared $\mu^2 Y = Cl$ versus $\mu^2 Y = NO_2$, for the Z-isomers of compounds (IIG and IIG) for $\omega_1 = 0-180^\circ$, $\omega_2 = 0-120^\circ$ and $\omega_3 = 0^\circ$. Hatched circles refer to the experimental dipole moments.

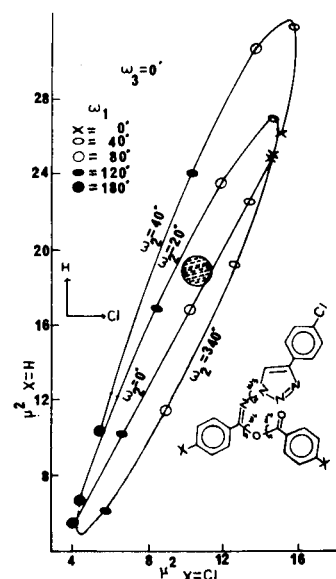


Figure 4. Comparison of theoretical dipole moments squared $\mu^2 X = H$ versus $\mu^2 X = Cl$ for the Z-isomers of compounds (IIID and IIIE) for $\omega_1 = 0-180^\circ$, $\omega_2 = 0-340^\circ$ and $\omega_3 = 0^\circ$. Hatched circles refer to experimental dipole moments. Curves for other values of ω_1 and ω_2 are omitted for reasons of simplicity.

moment values. This can be seen in Figures 2 and 3, where two representative pairs of compounds, IID, IIE and IID, IIG, are given. However, assuming that the aryl group is located in the 4-position of the triazole ring, a good agreement between theoretical and experimental dipole

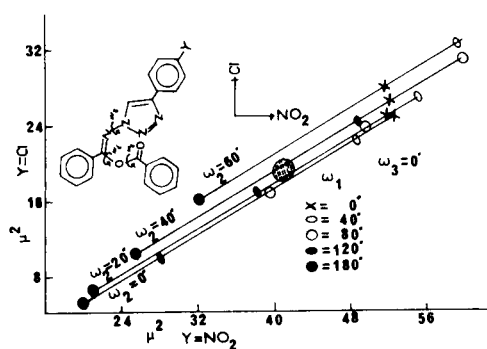


Figure 5. Comparison of theoretical dipole moments squared μ^2 $Y = \text{Cl}$ versus μ^2 $Y = \text{NO}_2$ for the Z-isomers of compounds (IID and IIIG) for $\omega_1 = 0-180^\circ$, $\omega_2 = 0-60^\circ$ and $\omega_3 = 0^\circ$. Hatched circles refer to experimental dipole moments. Curves for other values of ω_1 and ω_2 are omitted for reasons of simplicity.

moments is found, as is shown in Figures 4 and 5 for the pairs of compounds IID, IIE and IID, IIIG, respectively.

For the theoretical calculations, the previously reported configuration and conformation of the molecule for the symmetrically 4,5-substituted derivatives (1) were considered. Thus, the configuration of the molecule was assigned as the Z-one with respect to the C=N bond, and the conformation was assigned as that given in Figure 1 with $\omega_1 = 60-80^\circ$, $\omega_2 = 0-20^\circ$ and $\omega_3 = 0-40^\circ$. Furthermore, the above data were also reconfirmed from a comparative study between several pairs of compounds under present investigation, as can be seen in Figures 4 and 5.

The conclusion from this study is that in the compounds where one of the substituents R_1 , R_2 is a *p*-substituted aryl group, it is located at the 4-position of the triazole ring and that the corresponding triazolyliisoimides should be considered as III. In the case where one of the substituents R_1 , R_2 is an unsubstituted aryl group (A-C, J-L), it is not possible to find its position on the triazole ring, since the difference in dipole moments between the 4- or 5-phenyl substituted derivatives (II or III) is in the range of experimental error, even in the case of *p*-substituted aryl groups in the ester-imino group. These derivatives can be considered as structure III only by analogy. However, in the case of phenyl and methyl substituted derivatives (J-L), the general conclusion that the phenyl group is found in the 4-position (III) is supported by nmr spectral data (5).

EXPERIMENTAL

All melting points are uncorrected and they were obtained with a Kofler hot stage apparatus. Ir spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer, whereas nmr spectra, reported in δ units, were obtained with a Varian Associates A-60A

spectrometer with TMS as internal reference. The mass spectra were measured with a Hitachi-Perkin-Elmer Model RMU-6L spectrometer, with an ionization energy of 70 eV. Analyses were performed with a Perkin-Elmer Model 240 Analyzer.

Dipole Moment Measurements.

Dielectric constants were measured with a WTW type DM-01 dipolmeter using a DFL-2 cell (8 ml. volume). The refractive index of each solution was measured using an Abbé high precision refractometer (Bausch and Lomb, type 3L). Benzene (May and Baker, Pronalys, b.p. 80.5° , n_D^{25} 1.4980) was used as the solvent in all measurements, whereas the temperature in all experiments was maintained at $20 \pm 0.05^\circ$.

Details of the method and technique used for dipole moment measurements were described previously (1). Theoretical dipole moments have been computed (by vector addition of all bond and group moments) by means of a computer program using a Univac 1106 computer.

Bis-arylhyazones of α -dicarbonyl compounds (I) were prepared by standard procedures (10,11,12).

The asymmetrically 4,5-substituted 1-(α -aryloxyarylidene-amino)-1,2,3-triazoles were generally prepared by oxidation with lead tetraacetate (LTA) of the corresponding bis-arylhyazones of α -dicarbonyl compounds by a known procedure (1,10) in yields of 50-75%. The samples used for dipole moment measurements after recrystallization and washing with ether were carefully dried in vacuum. Their analytical and spectral data are given in Table II.

Acknowledgement.

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REFERENCES AND NOTES

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