

# Dipole Moments and Conformation of 1-(*N,N*-Diaroyl)amino-1,2,3-triazoles [1]

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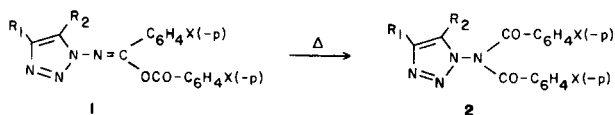
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Experimental dipole moments of a number of the title compounds are given and theoretical dipole moments have been calculated by vector addition for all possible conformations. The graphical method has been used to correlate experimental and calculated dipole moments. The more probable conformation in solution of the title compounds and especially of the imide group is proposed.

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1-(*N,N*-Diaroyl)amino-1,2,3-triazoles, (*N*-triazolyl-*N,N*-diaroylamides), **2** are obtained [2] by thermal rearrangement of the corresponding triazolyl isoimides **1**. The mechanism of this reaction has been studied by other authors [2b,3].

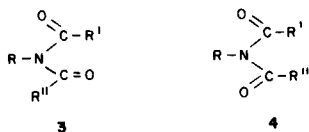


- a)  $R_1 = R_2 = \text{CH}_3$ ,  $X = \text{H}$     b)  $R_1 = R_2 = \text{CH}_3$ ,  $X = \text{CH}_3$   
 c)  $R_1 = R_2 = \text{CH}_3$ ,  $X = \text{OCH}_3$     d)  $R_1 = R_2 = \text{CH}_3$ ,  $X = \text{Cl}$   
 e)  $R_1 = R_2 = \text{CH}_3$ ,  $X = \text{NO}_2$

Although there are many studies on the conformation of unsubstituted and *N*-substituted acylimides [4], there is no systematic study on analogous aroylimides and especially on those of *N*-substituted with a heterocyclic system.

In the course of our further work [5,6] on the structure determination and conformation of 1,2,3-triazole derivatives, we have undertaken the study on the conformation of the above mentioned compounds **2** in solution, using dipole moment measurements.

Conformation of the imide group in solution has been studied mostly by dipole moments [7,8]. Other methods, such as ir [7,9], <sup>1</sup>H- and <sup>13</sup>C-nmr [4,8] and microwave spectroscopy [10] have been also used. Thus, in acetimide and its derivatives [4,7,9] (**3**,  $R = R' = R'' = \text{CH}_3$ ) the molecule has been found to be planar, the two acyl groups having a *s-cis-s-trans* (*EZ*) conformation in respect to the bonds C-N (**3**). The same (*EZ*) conformation adopts formimide [7,10] (**3**,  $R = R' = R'' = \text{H}$ ), for which however in



low temperatures the (*EE*) form **4** has been also found [4] to be present in solution. On the other hand, *N,N*-dipivaloyl anilide, (**3**,  $R = \text{Ph}$ ,  $R' = R'' = \text{C}(\text{CH}_3)_3$ ), has been found [8] to be nonplanar, whereas the imide group appeared in two conformations in solution, one near the

*s-cis-s-trans* (*EZ*) form **3**, and another one, less populated, near the *s-trans-s-trans* (*EE*) form **4**.

Experimental dipole moments of compounds **2** which were determined by the Guggenheim-Smith method [11] are given in Table 1.

Table 1  
Experimental Dipole Moments of Compounds **2** at 25° C  
in Benzene Solution

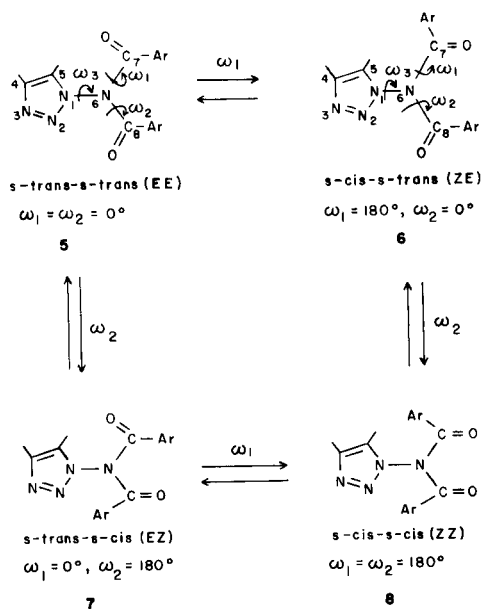
Compound	$\alpha_\epsilon$ [a]	$\alpha_\eta$ [a]	$\mu/D$ ( $\pm 0.05$ )
<b>2a</b>	7.56	0.25	4.64
<b>2b</b>	7.55	0.32	4.83
<b>2c</b>	7.69	0.23	5.11
<b>2d</b>	4.21	0.24	3.77
<b>2e</b>	4.53	0.36	3.97

[a]  $\alpha_\epsilon$  and  $\alpha_\eta$  are slopes of the plots ( $\epsilon_{1,2} - \epsilon_1$ ) vs.  $w_2$  and ( $\eta_{1,2}^2 - \eta_1^2$ ) vs.  $w_2$  respectively [5,6,11].

Theoretical dipole moment values of various conformers were calculated by vector addition using Gilman's equations [12] as described previously [5,6]. The moment of the bond C-N was taken [13] equal to 0.45 D. All the other bond moments have been taken equal to those used previously [5]. The angles of the triazole ring have been taken from the data extracted in the X-ray analysis of the 4,5-diphenyl-1-(*N,N*-*p*-chlorobenzoyl)amino-1,2,3-triazole [14], whereas for the bond angles the following values have been used:  $\widehat{N_1 N_6 C_7} = \widehat{N_1 N_6 C_8} = 116^\circ$ ,  $\widehat{N_6 C=O} = 115^\circ$  and  $\widehat{C_{ar} C=O} = 130^\circ$  (**5**).

Conformation of the imide group is expressed by means of the angle  $\omega_1$  and  $\omega_2$ . Orientation of the plane of the triazole ring in respect to the plane of the atoms  $C_7 N_6 C_8$  is expressed by means of the angle  $\omega_3$  (**5**).

Four extreme conformations can be distinguished (**5-8**), considering planarity of the molecule, *i.e.* *s-trans-s-trans* (*EE*), (**5**), *s-cis-s-trans* (*ZE*), (**6**), *s-trans-s-cis* (*EZ*), (**7**) and *s-cis-s-cis* (*ZZ*), (**8**). By rotation of the triazole ring around the bond  $N_1-N_6$  by  $90^\circ$ ,  $\omega_3 = 90^\circ$ , conformations **6** and **7** become equivalent. Except for these extremes, several other non-planar conformations can be formed by rotation



of the aroyl groups and/or the triazole ring around the bonds  $C_7-N_6$ ,  $C_8-N_6$  and  $N_1-N_6$  respectively.

Theoretical calculations were carried out for all possible conformations of the imide group, that can be derived by rotating the aroyl groups around the bonds  $C_7-N_6$  and  $C_8-N_6$  at angles  $\omega_1$  and  $\omega_2$  from  $0^\circ$  to  $360^\circ$ . In respect to the triazole ring, four extreme orientations were considered, *i.e.*  $\omega_3 = 0^\circ, 90^\circ, 180^\circ$  and  $270^\circ$ , as well as the case of its free rotation around the bond  $N_1-N_6$ . Calculations for the methoxy derivative **2c** were made assuming free rotation of the methoxy group.

From the computed data it is seen that in more than one

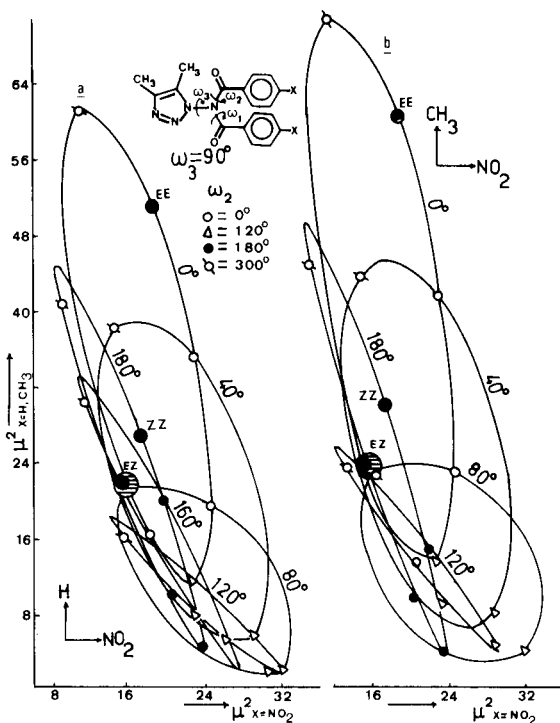


Figure 1. Comparison (a) of squared dipole moments of compounds **4a** and **4e** and (b) **4b** and **4e** for  $\omega_3 = 90^\circ$ ,  $\omega_1 = 0-180^\circ$  and  $\omega_2 = 0-360^\circ$ . Hatched circles refer to experimental dipole moments. Curves for other values of  $\omega_1$  and  $\omega_2$  are omitted for reasons of simplicity.

conformer of each compound under investigation the calculated dipole moment is similar to the experimental value.

Table 2  
Spectroscopic Data, IR and  $^1\text{H-NMR}$  of Compounds **2**

	IR (Nujol, $\text{cm}^{-1}$ ) $\nu$ C=O	$^1\text{H-NMR}$ (Deuteriochloroform, $\delta$ , TMS)				
		$\text{CH}_3$ -4	$\text{CH}_3$ -5	2,6	3,(4),5	X
<b>2a</b>	1720	2.23 (s)	2.17 (s)	7.95 (m)	7.57 (m)	
<b>2b</b>	1710	2.23 (s)	2.14 (s)	7.80 (d) [a] ( $J = 8.0$ Hz)	7.37 (d) [a] ( $J = 8.0$ Hz)	2.38 (s)
<b>2c</b>	1700	2.22 (s)	2.15 (s)	7.83 (d) [a] ( $J = 8.6$ Hz)	6.87 (d) [a] ( $J = 8.6$ Hz)	3.81 (s)
<b>2d</b>	1725	2.23 (s)	2.10 (s)	7.84 (d) [a] ( $J = 8.4$ Hz)	7.43 (d) [a] ( $J = 8.4$ Hz)	
<b>2e</b>	1720	2.23 (s)	2.15 (s)	7.97 (d) [a] ( $J = 8.6$ Hz)	8.30 (d) [a] ( $J = 8.6$ Hz)	

[a] AA'BB' spin system, as J-value is given the separation between the two main peaks of each AA' or BB' part of the spectrum.

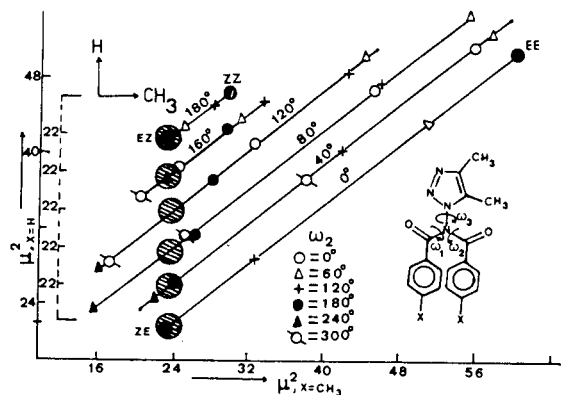


Figure 2

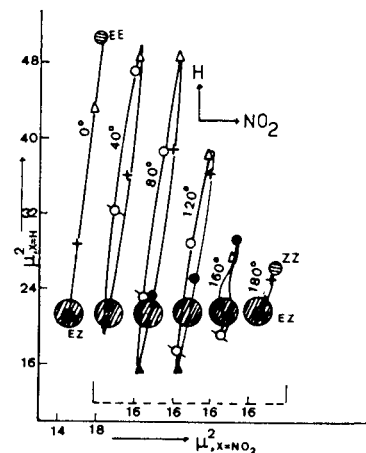


Figure 3

Figures 2 and 3. Comparison of squared dipole moments of compounds **4a** and **4b**, (Figure 2), and **4a** and **4e** (Figure 3), for free rotation of the triazole ring and for  $\omega_1 = 0-180^\circ$  and  $\omega_2 = 0-360^\circ$ . Hatched circles refer to experimental dipole moments. Actually all the curves coincide, but for better presentation and evaluation of the results, those corresponding to values of  $\omega_1$  from  $40-180^\circ$  are given separately. Curves for other values of  $\omega_1$  and  $\omega_2$  are omitted for reasons of simplicity.

Table 3

$^{13}\text{C}$ -NMR Shift Data [16] of Compounds **2** in ppm, Taken in Deuteriochloroform Solution With TMS as Internal Reference

	C-4 <sub>tr</sub>	C-5 <sub>tr</sub>	CH <sub>3</sub> -4	CH <sub>3</sub> -5	C-1	Aromatic Carbons [a]				
						C-2	C-3	C-4	C=O	X
<b>2a</b>	140.30	131.42	10.76	7.26	131.86	129.32	128.91	133.76	169.50	
<b>2b</b>	140.09	131.50	10.69	7.18	128.58	129.49	129.49	144.49	169.49	21.68
<b>2c</b>	140.08	131.80	10.70	7.21	123.85	131.87	114.23	164.04	168.92	55.54
<b>2d</b>	—	131.50	10.67	7.13	129.78	130.61	129.31	140.48	168.41	
<b>2e</b>	141.04	131.32	10.70	7.19	136.45	130.09	124.14	150.66	167.51	

[a] For numbering see Scheme in Table 2.

In order to avoid any incidental coincidence between experimental and theoretical values and to have reliable results about the true conformation in solution, we used the previously reported [5,6] graphical method proposed by Exner [15] (Figures 1-3).

From this comparison (Figures 1-3) it comes out that the planar conformations, *EZ* and *ZE*,  $\omega_1 = 0^\circ$ ,  $\omega_2 = 180^\circ$ , or  $\omega_1 = 180^\circ$ ,  $\omega_2 = 0^\circ$ , as well as other non-planar conformations of the imide group have calculated dipole moments similar to the experimental. Such conformations of the imide group are e.g. for the case of free rotation of the triazole ring (Figures 2-3):  $\omega_1 = 40^\circ$ ,  $\omega_2 = 200^\circ$  or  $240^\circ$ ;  $\omega_1 = 80^\circ$ ,  $\omega_2 = 200^\circ$  or  $280^\circ$ ;  $\omega_1 = 120^\circ$ ,  $\omega_2 = 200^\circ$  or  $330^\circ$ ;  $\omega_1 = 160^\circ$ ,  $\omega_2 = 240^\circ$  or  $340^\circ$ . Similar are the conformations coming out when  $\omega_3 = 90^\circ$  (Figure 1). It should be noted that in all the above conformations the phenyls of the two aryl groups lie at opposite sides of the plane determined by the atoms  $\text{C}_7\text{N}_6\text{C}_8$ .

The above data could be explained considering the presence of more than one conformation for the imide group in solution, which interchange rapidly.

Concerning the orientation of the triazole ring, the experimental data can be explained equally well if its plane is perpendicular to the plane  $\text{C}_7\text{N}_6\text{C}_8$ ,  $\omega_3 = 90^\circ$ , or if it rotates freely around the bond  $\text{N}_1\text{-N}_6$ .

In agreement to the above suggestion are found to be both the  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectra of the compounds **2**. Thus, in  $^1\text{H}$ -nmr the aromatic protons of the imide group show exactly the same shift values at room temperatures for the two phenyls, e.g. one AA'BB' spin system for the *p*-substituted derivatives (Table 2). Similarly, in  $^{13}\text{C}$ -nmr the twelve aromatic carbons give rise to four peaks in the aromatic region of the spectrum, according to the four kinds of carbon atoms of each phenyl, whereas the two carbonyl carbons resonate both at  $\sim 169$  ppm (Table 3). It is mentioned here that in the  $^1\text{H}$ -nmr spectrum of com-

pound **2c** taken at  $-60^\circ$  in toluene- $d_8$ , the aromatic protons of the two phenyl groups did not show any differentiation in their chemical shifts.

On the contrary to the above, the dipivaloyl-anilide showed three signals in its  $^1\text{H-nmr}$  spectrum for the two *t*-butyl groups [8], a fact suggesting the presence of two different non-planar conformations in solution (see above). Here, the more crowded *t*-butyl groups do not probably allow a rapid interchange between the conformers at room temperatures.

It should also be noted that in an X-ray study of the 4,5-diphenyl-1-(*N,N*-di-*p*-chlorobenzoyl)amino-1,2,3-triazole, (**2**,  $R_1 = R_2 = \text{C}_6\text{H}_5$ ,  $X = \text{Cl}$ ), it has been found [14] that, in the crystalline state, the triazole ring is perpendicular oriented to the plane  $\text{C}_7\text{N}_6\text{C}_8$ , whereas the imide group adopts an asymmetric, *ZE*, conformation. In this form the planarity is distorted by rotation of the aroyl groups around the bond  $\text{C}_8\text{-N}_6$  at an angle of  $50^\circ$ , (**6**,  $\omega_1 = 180^\circ$ ,  $\omega_2 = 50^\circ$ ,  $\omega_3 = 90^\circ$ ).

#### EXPERIMENTAL

Melting points were obtained with a Kofler hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer 257 spectrophotometer, whereas the  $^1\text{H-nmr}$  spectra, reported in  $\delta$  units, were obtained in a Varian A-60A spectrometer. The  $^{13}\text{C-nmr}$  spectra were recorded in a Varian CFT-20 spectrometer in deuteriochloroform solutions and concentrations of 5% w/v, with TMS as internal standard.

Experimental dipole moments were determined by the Guggenheim-Smith method [11]. Dielectric constants were measured with a WTW type DM-01 dipolmeter using a DFL-2 cell. The refractive index of each solution was measured using an Abbe high precision refractometer, (Baush and Lomb, type 3L). Benzene (May and Baker, Pronalys, bp  $80.5^\circ$ ,  $n_D^{25}$  1.4980) was used in all measurements, whereas the temperature in all experiments was maintained at  $25 \pm 0.05^\circ$ .

Details of the method and technique used for dipole moment measurements have been described previously [5,6].

1-(*N,N*-Diaroyl)amino-1,2,3-triazoles **2** have been prepared by thermal [2] isomerization of the corresponding triazolylisoimides **1**. Their spec-

tral data, (ir,  $^1\text{H-nmr}$  and mass), were identical to that previously reported [2b,3], and are given (ir,  $^1\text{H-nmr}$ ) in Table 2. The  $^{13}\text{C-nmr}$  shifts [16] are given in Table 3. Uncorrected mp of the samples used for the dipole moments were as follows: **2a**  $97\text{-}99^\circ$  (lit [2a]  $94\text{-}96^\circ$ ); **2b**  $182\text{-}184^\circ$  (lit [2b]  $184\text{-}186$ ); **2c**  $112\text{-}115^\circ$  (lit [2b]  $112\text{-}114^\circ$ ); **2d**  $148\text{-}150^\circ$  (lit [2b]  $144\text{-}146^\circ$ ); **2e**  $188\text{-}191^\circ$  (lit [2b]  $187\text{-}190^\circ$ ).

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#### REFERENCES AND NOTES

- [1] Preliminary Communication, N. A. Rodios and A. G. Coutsolelos, 5th Congress of Greek Chemist Association, Abstracts of papers, Athens, Greece, 1980, p 161.
- [2a] D. Y. Curtin and N. E. Alexandrou, *Tetrahedron*, **19**, 1697 (1963); [b] N. E. Alexandrou and C. P. Hadjiantoniou, *J. Heterocyclic Chem.*, **14**, 269 (1977).
- [3] C. P. Hadjiantoniou, Ph. D. Thesis, University of Thessaloniki, (1975).
- [4] E. A. Noe and M. Raban, *J. Am. Chem. Soc.*, **97**, 5811 (1975), and references cited therein.
- [5] N. A. Rodios and N. E. Alexandrou, *J. Chem. Soc., Perkin Trans. II*, 1779 (1977).
- [6] N. A. Rodios and N. E. Alexandrou, *J. Heterocyclic Chem.*, **16**, 571 (1979).
- [7] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **84**, 571 (1962); *ibid.*, **84**, 565 (1962); *ibid.*, **83**, 4586 (1961).
- [8] A. Laurent, E. Laurent and N. Pellisier, *Tetrahedron Letters*, 2955 (1970).
- [9] T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **34**, 545 (1961); *ibid.*, **35**, 1226 (1962); *ibid.*, **36**, 427 (1963).
- [10] W. E. Steinmetz, *J. Am. Chem. Soc.*, **95**, 2777 (1973).
- [11] E. A. Guggenheim, *Trans. Faraday Soc.*, **47**, 573 (1951); J. W. Smith, *ibid.*, **46**, 394 (1950).
- [12] T. L. Gilman, *J. Am. Chem. Soc.*, **88**, 1861 (1966).
- [13] O. Exner, "Dipole Moments in Organic Chemistry", Georg Thieme Verlag, Stuttgart, 1975, p 33.
- [14] S. C. Kokkou and P. J. Rentzeperis, *Acta Cryst.*, **B31**, 2788 (1975).
- [15] O. Exner and V. Jehlicka, *Collect. Czech. Chem. Commun.*, **35**, 1514 (1970).
- [16] N. A. Rodios, unpublished results.