

1,2,3-Triazol-1-imines. **2.** Electric Dipole Moments and Semiempirical Studies of Some 2-Aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines

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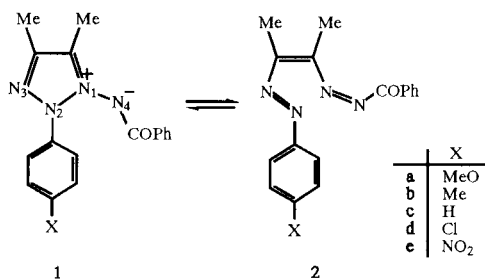
Electric dipole moments of some 2-aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines were measured in carbon tetrachloride solution and the results compared with those derived computationally using MNDO, AM1 and PM3. Good correlation of the dipole moments with σ^+ substituent constants was obtained.

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Electric dipole moment studies have provided excellent support for the formulation of *N*-acetyl-1,2,3-triazol-4-imines [1] and *N*-aryl-1,2,4-triazol-3-imines [2] as meso-ionic. Also they have led to the determination of the most probable conformations of some 1-(α -aryloxyarylidene-amino)-4,5-dimethyl-1,2,3-triazoles [3].

In this paper we describe the results of the dipole moment measurements of some zwitterionic 2-aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines **1** (Scheme 1), and the outcome of semiempirical quantum chemical calculations performed on these compounds.

Scheme 1



Results and Discussion.

The experimentally determined dipole moments of the 1,2,3-triazoleimines **1** were found in the range of 3-5 D (Table 1). Within this range were also found the dipole

Table 1. Experimental [a] and calculated dipole moments of 2-aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines **1**.

Compound	Dipole Moment, μ/D			MNDO	AM1	PM3
	α_e [b]	α_n [b]	Experimental			
1a	6.94	0.97	3.09±0.03	2.35	2.68	2.26
1b	7.41	0.99	3.12±0.04	3.35	2.77	2.69
1c	9.87	0.74	3.63±0.03	3.45	3.00	2.61
1d	8.81	0.86	4.10±0.04	4.04	3.74	2.52
1e	15.60	0.88	4.96±0.04	6.65	7.74	6.29

[a] Solvent CCl₄ at 25±0.05° C. [b] α_e and α_n are least-square slopes of the plots ($\epsilon_{1,2} - \epsilon_1$) versus w_2 and $(n_{1,2}^2 - n_1^2)$ versus w_2 respectively.

moments of some mesoionic *N*-acetyl-1,2,3-triazol-4-imines [1] and 1-(α -aryloxyarylidene-amino)-4,5-dimethyl-1,2,3-triazoles [3]. The dipole moments however, of several *N*-aryl-1,2,4-triazol-3-imines are much higher and in the range of 8-9 D [2].

The measured values of the dipole moments of the title compounds follow a very good linear correlation with the σ^+ substituent constant [4] of slope $\varphi = 1.851$ ($r^2 = 0.985$) (Figure 1). Relationships of quantitative nature such as this are rather limited, because the dipole moment measurements usually represent a composite quantity incorporating the direction and magnitude of all electronic polarisations within the molecule [5]. In the present case however, there is limited interaction between the substituent on the phenyl ring with the rest of the molecule, since the 2-phenyl ring forms with the triazole ring a dihedral angle strongly diverging from 0° (*vide infra*). The dipole moment differences therefore, between the various substituted 1,2,3-triazol-1-imines **1** most likely reflect differences in the C_X-X bond moments wherefrom the correlation arises.

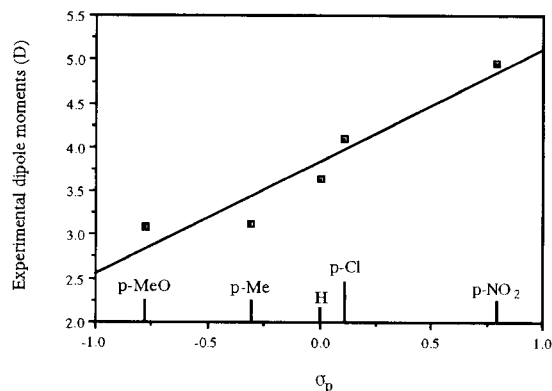


Figure 1. Plot of experimentally determined dipole moments (D) for **1** versus the σ^+ substituent constants.

From the results depicted in Table 2 it can be seen that, there is indeed a striking similarity between the values predicted for the dihedral angle between aryl and triazole

rings by all semiempirical approaches used (MNDO from 70.0° for **1a** to 81.2° for **1c**, AM1 from 51.2° for **1e** to 59.0° for **1a**, and PM3 from 36.7° for **1e** to 60.1° for **1b**). Within each computational approach used, the changes in the crucial geometric parameters are not severe (Table 2) and, therefore, the backbone of the studied compounds remains practically unaltered.

Table 2. Relevant internal parameters of the *N*-benzoyl-1,2,3-triazol-imines **1**. Bond distances in Å, angles in degrees.

		N1-N2	N2-N3	N2-Ph	N1-N4	N1-N2-N3	C6-N4-N1	Tr,Ar [a]	Tr,COPh [b]
1a	MNDO	1.385	1.302	1.446	1.315	112.5	121.9	69.9	67.3
	AM1	1.409	1.332	1.442	1.322	112.5	122.3	59.0	59.3
	PM3	1.444	1.350	1.460	1.345	110.0	120.7	36.7	106.7
1b	MNDO	1.367	1.321	1.452	1.326	112.4	120.3	79.1	84.9
	AM1	1.411	1.332	1.444	1.322	112.5	122.9	55.5	60.0
	PM3	1.430	1.358	1.459	1.344	109.4	120.8	60.1	90.3
1c	MNDO	1.382	1.320	1.452	1.327	112.2	119.8	81.2	90.5
	AM1	1.409	1.333	1.443	1.321	112.4	122.4	54.5	58.2
	PM3	1.431	1.370	1.458	1.327	108.7	123.4	39.4	135.1
1d	MNDO	1.382	1.323	1.451	1.324	112.5	120.8	77.9	81.6
	AM1	1.410	1.334	1.442	1.321	112.5	122.3	55.4	58.8
	PM3	1.428	1.371	1.456	1.328	108.9	123.3	43.5	136.1
1e	MNDO	1.372	1.323	1.449	1.323	113.5	120.4	80.6	86.4
	AM1	1.413	1.338	1.439	1.317	112.5	122.8	51.2	53.2
	PM3	1.460	1.366	1.452	1.333	108.8	122.1	36.7	136.1

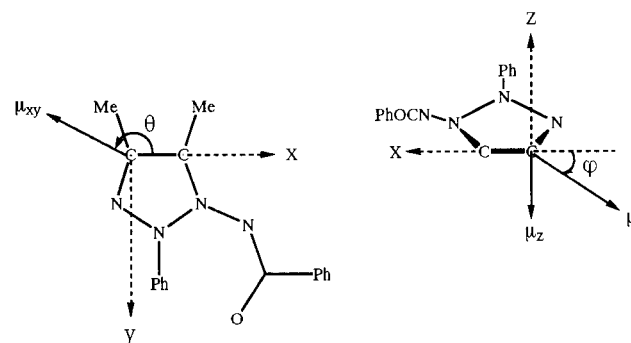
[a]. Dihedral angle between the triazole ring (Tr) and the 2-Aryl group (Ar). [b] Dihedral angle between the triazole ring (Tr) and the *N*-benzoyl group (COPh).

Plots of the computed dipole moment values *vs.* σ^+ substituent constants reveal good correlation for MNDO (slope $\varphi = 3.797$, $r^2 = 0.961$) and AM1 ($\varphi = 4.915$, $r^2 = 0.921$) and poor for PM3 ($\varphi = 3.656$, $r^2 = 0.813$). It is apparent therefore, that the MNDO values, although deviating significantly from the experimental such, when the extremes in substitution are considered, provide better overall agreement with the experimental values (Table 1).

When the computed dipole moments are compared with the experimental ones, good-to-fair correlations are realized (MNDO, $r^2 = 0.902$, AM1, $r^2 = 0.865$ and PM3, $r^2 = 0.727$). PM3 performs better with the nitro-substituted compound **1e**, perhaps because of the better treatment of the polarized N–O bonds present. It does not perform, however, equally well with the rest of the molecules and especially with the methoxy-substituted one (**1a**). Consequently it seems reasonable to use PM3 in cases where polarized bonds are present and then only in connection with AM1. Considering MNDO, it appears that it does not handle adequately the dipole moment contribution of either strong electron donors or acceptors. Yet, it is consistent in ordering the polarity of a series of analogous compounds. The same could be stated about AM1 which overestimates the contribution of strong electron acceptors.

The semiempirical methods applied here lie in the same level of approximation in the construction of their Hamiltonian [6–8] and, inasmuch the computed dipole moments depend on both geometric arrangement in space and electron delocalisation, a discussion should be made about the final geometries provided by each method. Since the only difference between the individual molecules studied is the presence of a remote, with respect to the active site of the molecule (the heterocyclic ring), substituent the methods should exhibit uniform errors. Their results could be discussed in general either on the basis of literature reports or considering their parametrisation differences. For the present group of compounds a limited, though direct, comparison can be made against the data gleaned from the X-ray crystal structure determination of **1c** [9]. When comparing them, one should keep in mind that the computations correspond to an isolated molecule (*i.e.* correspond to the gas phase situation), while the crystal structure data refer to the solid state.

The orientation of the electric dipole moment vector is of interest, especially in those cases where molecules can adopt a variety of conformations or may be subjected to certain structural modifications by the introduction of substituents. In particular, it could serve as the basis for vector addition procedures used to determine the dipole moment of different conformers or differently substituted *N*-benzoyl-1,2,3-triazol-1-imines **1**. In this respect the two angles, φ and θ defining the orientation of the individual vector components, both in the triazole plane and out of it, are reported (Figure 2).



	MNDO	AM1	PM3		MNDO	AM1	PM3
1a	171.4	150.2	179.1	1a	21.3	13.9	15.9
1b	164.0	145.0	178.7	1b	34.4	40.3	36.0
1c	165.2	145.0	170.6	1c	36.2	38.2	45.6
1d	127.8	115.8	160.9	1d	26.6	27.3	43.8
1e	105.6	94.4	98.5	1e	14.8	10.7	14.0

Figure 2. Diagrammatic representation of the electric dipole moment vector orientation in the selected coordinate system both in and out of the triazole plane.

MNDO predicts θ to vary between 105.6° and 171.4° in a monotonous dependence on σ^+ substituent constant. The

same holds true for AM1 (range 94.4° to 150.2°), while for the PM3 derived angles no such dependence is observed. The out-of-plane orientation of the dipole moment vector, defined by angle φ does not bear any relation to the nature of the substituent. Here again a comment concerning the values of φ , obtained by the methods applied is needed. MNDO and AM1, predict similar φ values (MNDO, from 14.8° for **1e** to 36.2° for **1c**, AM1 from 10.7° for **1e** to 40.3° for **1b**), while the PM3 results are quite different (from 14.0° for **1e** to 45.6° for **1c**).

Finally, since the present *N*-benzoyl-1,2,3-triazol-1-imines **1** can, in principle, exist in equilibrium in solution with their open chain isomers bis-azoethylenes **2** (Scheme 1), in much the same way *N*-aryl-1,2,3-triazole-1-imines are in equilibrium with their corresponding bis-areneazoethylenes [10], we studied with AM1 compound **2c**. This was done in an attempt to explore the potential use of computationally derived electric dipole moments in the assignment of the appropriate structure (**1** or **2**). The conformer depicted in Scheme 1 was computed to be the most stable of all open chain isomers, possessing a dipole moment of 2.85 D. This value is very close to that of **1c**. Therefore, semiempirical calculations cannot, in the present case, be used to rule out open chain structures such as **2**. Fortunately the latter structures can be easily excluded on the basis of their low (*ca.* 1610 cm⁻¹) [9] ν (CO) absorption typically found in the IR spectra of various heteroaromatic *N*-acylimines [11].

EXPERIMENTAL

Materials.

The title 2-aryl-*N*-benzoyl-4,5-dimethyl-1,2,3-triazol-1-imines **1** were prepared by lead tetraacetate oxidation of the corresponding biacetyl benzoylhydrazone arylhydrazones [9] and purified until they were analytically pure.

Carbon tetrachloride (Fluka, Puriss) was stored over Linde type 4A molecular sieves and was fractionated [12] (bp 76.2-76.8°) prior to its use. Benzene (Hay and Baker, Proanalys) and cyclohexane (Eastman Kodak, Spectrograde) were used for the calibration of the dipolemeter.

Dipole Moment Measurements.

The method of Guggenheim and Smith [13] was applied for the determination of the dipole moments. The dielectric constants were measured with a WTW type DM-01 dipolemeter using a DFL-2 cell (8 ml volume). The instrument was calibrated using the dielectric constants of pure cyclohexane, benzene and carbon tetrachloride. The refractive index of each solution was measured using an Abbé high-precision refractometer (Bausch and Lomb; type 3L). Dielectric constants were measured for 5 samples in carbon tetrachloride solution of concentrations ranging from 0.002 to 0.012 weight fraction. After thermal equilibration of the di-

polemeter and refractometer (25 ± 0.05°), five dipolemeter readings were taken for each solution, and the average was corrected using the correction diagram supplied with the instrument. Immediately after the measurement of the dielectric constant, the refractive index of each solution was measured. The dipole moment was calculated with the aid of the following equation:

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

where d_1 and ϵ_1 represent the density and dielectric constant of the solvent and the rest of the symbols have their usual meaning. Computational.

The calculations were carried out using the AM1 [6], PM3 [7], or MNDO [8] Hamiltonians as implemented in the MOPAC program [14]. The structural and energetic refinement was performed using a very tight convergence criterion (0.01 for norm gradient, 1.10⁻⁸ for SCF convergence). The symmetry constraints imposed were ideal tetrahedra for the sp³ carbon atoms and planar phenyl rings.

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