# Dipole Moments and Conformation of Some 1-(α-Aroyloxyarylidene-amino)-4,5-dimethyl-1,2,3,triazoles [1]

By **Nestor A. Rodios** and **Nicholas E. Alexandrou,*** Laboratory of Organic Chemistry, University of Thessaloniki, Greece

The dipole moments of four 1-(α-aroxyloxyarylideneamino)-4,5-dimethyl-1,2,3-triazoles were measured in benzene solution. The probable conformation of these compounds was determined after a theoretical calculation of the dipole moments by vector addition of the moments of all polar groups. It was found that the Z-isomer is present and the probable conformation of the ester-imino-function is similar to that of acid anhydrides and other related compounds. The conformation of the molecule in solution is in general very similar to that found in the solid state by X-ray measurements.

FROM our previous work on the n.m.r. spectra [2a] and on the mechanism of rearrangement [2b] of 1-(α-aroyloxy-arylideneamino)-1,2,3-triazoles, the problem of conformation of the ester-imino-function in solution has arisen. Therefore we have undertaken a systematic study on the conformation of these triazole derivatives by use of dipole moments.
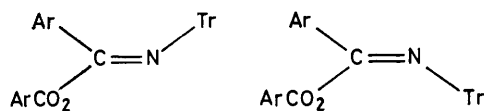
1-(α-Aroyloxyarylideneamino)-4,5-dimethyl-1,2,3-triazoles (1) are obtained by oxidation of biacetyl bisaroyl-hydrazones; several papers [3,4] have been concerned with
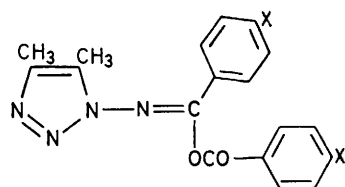
(1)

a; X = H
b; X = OCH₃
c; X = Cl,
d; X = NO₂

their structure. It is of interest to note, however, that concerning the configuration in respect to the C=N bond and the conformation of the molecule, there are several possibilities open for investigation. It is possible to have both E- and Z-isomers (Scheme 1). On the other hand

Tr = triazole ring

SCHEME 1 E- and Z-isomers of compound (1)

for each isomer (E or Z) the conformation could be established for the ester-imino function, which is similar

to that for acid anhydrides and for the triazole ring which is planar. Such extreme conformations (for the Z-isomer) are given in Scheme 2.

EXPERIMENTAL

Materials.— 1-(α-Aroyloxyarylideneamino)-4,5-dimethyl-1,2,3-triazoles (1) were prepared by oxidation [5] of biacetyl bisaroylhydrazones with lead tetra-acetate. Their spectral data (n.m.r., i.r., mass) were identical with that previously described,[2a,5] and the uncorrected m.p.s of the samples used for the dipole moment measurements were as follows: (1a) 141—142; (1b) 128—129; (1c) 168—170; (1d) 164—165°.

Benzene (May and Baker; Pronalys; b.p. 80.5°; n_D^{25} 1.4980) was used as solvent for all measurements. Other solvents used for the calibration of the instrument were cyclo-hexane (Eastman Kodak; Spectrograde; b.p. 79.5—80.5°) and carbon tetrachloride (Merck; Zur Analyse; b.p. 76—76.5°). All the solvents were stored over Linde type 4A molecular sieves for at least one week and they were distilled just before the measurements.

Dipole Moment Measurements.—Dipole moments were determined by the method of Guggenheim and Smith.[6] The dielectric constants were measured with a WTW type DM-01 dipolmeter using a DFL-2 cell (8 ml volume). The dipolmeter was calibrated using the dielectric constants † of pure cyclohexane, carbon tetrachloride, and benzene. The refractive index of each solution was measured using an Abbé high-precision refractometer (Bausch and Lomb; type 3L). A calibration equation for conversion of the di-polmeter readings into dielectric constants was calculated by the method of least squares. Dielectric constants were measured for 4—6 samples in benzene solution of concentrations ranging from 0.002 to 0.013 weight fraction. After thermal equilibrium of the dipolmeter cell five meter readings were taken for each solution, and the average was corrected with a correction diagram furnished with the instrument. Immediately after measuring the dielectric constant the refractive index of each solution was measured after

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† Values obtained from the instruction manual of the instrument.

[1] Taken in part from N. A. Rodios, Ph.D. Thesis, University of Thessaloniki, 1976.

[2] (a) N. E. Alexandrou, N. A. Rodios, and C. P. Hadjian-toniou-Louizou, *Org. Magnetic Resonance*, 1973, **5**, 579; (b) N. E. Alexandrou and C. P. Hadjiantoniou-Louizou, *J. Heterocyclic Chem.*, submitted for publication.

[3] (a) D. Y. Curtin and N. E. Alexandrou, *Tetrahedron*, 1963, **19**, 1697; (b) N. E. Alexandrou and E. D. Micromastoras, *Tetrahedron Letters*, 1968, 237; (c) H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and A. Vaciago, *J.C.S. Perkin II*, 1972, 662.

[4] For an extensive study of (1) see T. L. Gilchrist and G. E. Gymer in 'Advances in Heterocyclic Chemistry,' eds. A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1974, vol. 16, p. 52.

[5] N. E. Alexandrou and E. D. Micromastoras, *J. Org. Chem.*, 1972, **37**, 2345.

[6] (a) E. A. Guggenheim, *Trans. Faraday Soc.*, 1951, **47**, 573; (b) J. W. Smith, *ibid.*, 1950, **46**, 394.

thermal equilibrium of the refractometer. Both dipol-meter cell and refractometer were maintained at $25 \pm 0.05°$ by means of a circulating constant-temperature bath. The dipole moment was calculated from equation (1) where $k =$

$$\mu^2 = \frac{27kT \; M \; (\alpha_\epsilon - \alpha_n)}{4\pi N \; d_1 \; (\epsilon_1 + 2)^2} \qquad (1)$$

Boltzmann's constant, $N =$ Avogadro's number, $T =$ temperature, $M =$ molecular weight of the solute, $d_1 =$ density of the solvent, $\epsilon_1 =$ dielectric constant of the solvent, $\alpha_\epsilon =$ slope of the line obtained by plotting $(\epsilon_{12} - \epsilon_1)$ against w,

of compounds (1) are given in the Table. The uncertainty in the observed values is estimated to be in the range of ± 0.05 D. The dipole moments of all possible conformations of the molecule and for the E- and Z-isomers have been computed by vector addition of the bond and group moments by means of a computer program using a Univac 1106 computer.

RESULTS AND DISCUSSION

The moment of the compounds (1) can be divided into two components, one arising from the triazole ring and
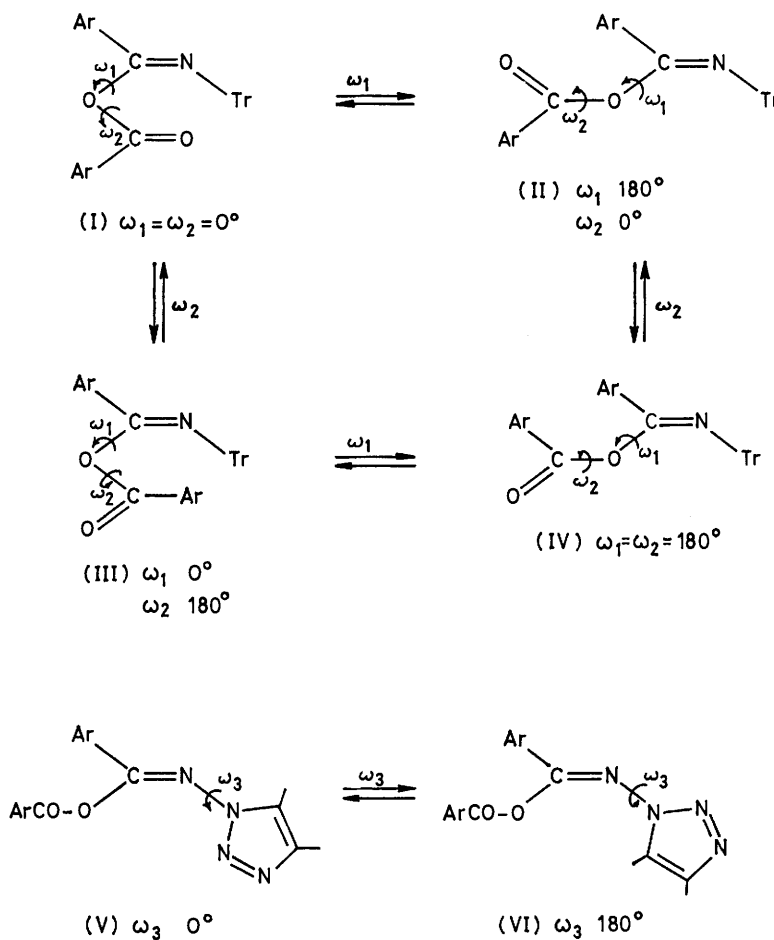
SCHEME 2   Extreme conformations of the ester-imino-function (I)—(IV) and planar orientations of the triazole ring (V) and (VI) of compounds (1)

where ϵ_{12} is the dielectric constant of a solution and w is the weight fraction of that solution, and $\alpha_n =$ slope of a line obtained by plotting $(n_{12}^2 - n_1^2)$ against w, where n_{12} is the

Dipole moments of compounds (1) at 25 °C in benzene solution

Compound	α_ϵ	α_n	μ/D (± 0.05)
(1a)	3.58	0.34	3.09
(1b)	4.55	0.37	3.82
(1c)	2.58	0.34	2.83
(1d)	5.28	0.32	4.33

refractive index of a solution and n_1 is the refractive index of the solvent. The values of α_ϵ and α_n were determined by least-squares evaluation of the data. The dipole moments

the other from the aroyloxyarylideneamino-group. In order to have information about the compound under consideration it is necessary to calculate the moments for all possible conformations and for each isomer (Scheme 1), and to compare these values with that experimentally determined. In the parent compound (1a) there are four polar groups, the triazole ring, and the benzylideneamino, benzoyl, and ether groups.

In order to calculate the dipole moments of the compounds under consideration a knowledge of the relevant angles and bond or group moments, as well as their orientation in the molecule is required. In the case of the $1H$-1,2,3-triazole ring neither the magnitude of the moment

nor the vector orientation are known. The required dipole moment data could be derived from the moment of the 1-methyl-1H-1,2,3-triazole, which was found [7] to be 4.46 D, but in this case the vector orientation is also unknown. Therefore we used theoretical data, derived from molecular orbital calculations, which give values in agreement with those experimentally determined.[7] Palmer and Findley [8] found theoretically that the magnitude of the dipole moment of 1H-1,2,3-triazole is 4.50 D, with the direction given in Scheme 3. The dipole
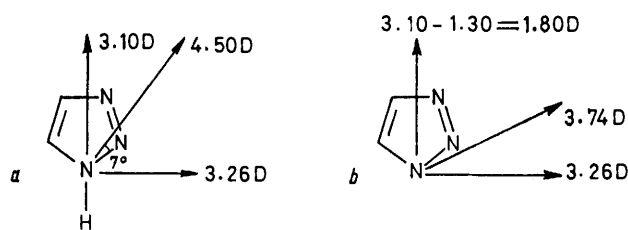
SCHEME 3 Vector orientation of the dipole moment of 1H-1,2,3-triazole

moment of the triazole ring can be found by subtracting the moment of the N-H bond, which was taken as [9] 1.30 D. From the above data the moment of the triazole ring is 3.74 D assuming, by analogy with pyrrole, that the N-H bond lies in the plane of the triazole ring. The orientation of the moment of the triazole ring is given in Scheme 3b.

The magnitude of the benzylideneamino-group moment was taken as 1.80 D, its orientation being in the direction of the C=N bond and from the carbon to the nitrogen atom. Analogous data have been used in several other calculations.[10] The magnitude of the benzoyl group moment was taken as 2.74 D, as its direction forms an angle of 9° with the direction of the C=O bond. This is in agreement with data used by other workers.[11] For the theoretical calculation of the dipole moment of the molecule the following bond or group moments were also used: [9,12] C_{ar}-H 0.0 D, N(6)-N_{tr} 0.0, CH_3-C_{tr} 0.37, C-O 0.74, C_{ar}-Cl 1.59, C_{ar}-NO_2 3.99, and CH_3O-C_{ar} 1.28 D, the last forming an angle of 76° with the direction of O-C_{ar} bond. All the angles in the molecule were taken from X-ray data given by Katritzky and his co-workers [3c] for compound (1a). Other possible sets of bond angles and bond moments were also tried in these calculations without any significant change in our configurational and conformational assignments.

Vector addition was carried out by analysing the group or bond moments in their components in the three co-ordinate axes. The total moment of the various con-

formations was computed using relation (2) where μ_{i_x}, μ_{i_y}, and μ_{i_z} are projections of the ith vector on the axes of an arbitrarily chosen system of co-ordinates. Since there

$$\mu^2 = (\sum_i \mu_{i_x})^2 + (\sum_i \mu_{i_y})^2 + (\sum_i \mu_{i_z})^2 \qquad (2)$$

are rotating polar groups in the molecule, their components for a given conformation were calculated using Gilman's [13] equations. The conformation of the ester-imino-group is expressed by means of the angles ω_1 and ω_2, whereas the planar orientation of the triazole ring with respect to the N(1)-N(6) bond by means of angle ω_3 (Scheme 4).
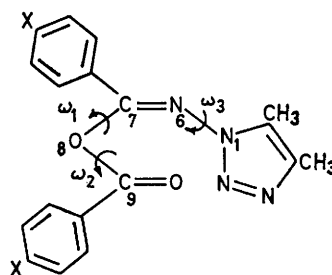
SCHEME 4 Planar structure of the Z-isomer of compound (1)

The computations for each conformer were made by changing the angle ω_1 from 0 to 180° and ω_2 from 0 to 360° in steps of 20°. For reasons of simplicity the calculations were made for the four extreme values of the angle ω_3 (0, 90, 180, 270°) and for some other intermediate values, 20, 40, 320, and 340°, which are close to the most probable conformation ($\omega_3 = 0°$). Comparing theoretical and experimental values of the dipole moments for each compound it is seen that in more than one conformer there is satisfactory agreement between these values. In order to have reliable results and to avoid any incidental coincidence of dipole moment values we used the graphical method proposed by Exner.[14] In this, a comparative study of the theoretical values relative to the possible conformations between several pairs of compounds is made. The position of the experimental values in relation to the theoretical points allows one to determine configuration and conformation along with the accuracy of the method. From this comparative study (Figures 1 and 2) it is concluded that the Z-isomer is present in solution, as observed for the solid state.[3c] In this configuration the triazole ring lies out of the plane determined by the atoms O(8)C(7)N(6)N(1) (Scheme 4) forming an angle (ω_3) between 0 and 40° with this plane. It has been found that the ester-imino-function is not planar. The plane determined by the atoms N(6)C(7)O(8) forms an angle (ω_1) of 60—80° with the previous plane. The benzoyl group tends to be found out of the plane of

[7] P. Mauret, J.-P. Fayet, M. Fabre, J. Elguero, and M. C. Padro, $J.$ $chim.$ $Phys.$, 1973, 70, 1483.

[8] M. H. Palmer, R. H. Findley, and A. J. Gaskel, $J.C.S.$ $Perkin$ II, 1974, 420.

[9] O. Exner, ' Dipole Moments in Organic Chemistry,' Georg Thieme Verlag, Stuttgart, 1975, p. 33.

[10] (a) O. Exner, V. Jehlička, and A. Dondoni, $J.C.S.$ $Perkin$ II, 1974, 567; (b) O. Exner and J. M. Kliegman, $J.$ $Org.$ $Chem.$, 1971, 36, 2041.

[11] S. Sorriso and A. Foffani, $J.C.S.$ $Perkin$ II, 1973, 2142.

[12] V. Minkin, O. A. Osipov, and Y. A. Zhdanov, ' Dipole Moments in Organic Chemistry,' Plenum, New York, 1970.

[13] T. L. Gilman, $J.$ $Amer.$ $Chem.$ $Soc.$, 1968, 88, 1881.

[14] O. Exner and V. Jehlička, $Coll.$ $Czech.$ $Chem.$ $Comm.$, 1970, 35, 1514.

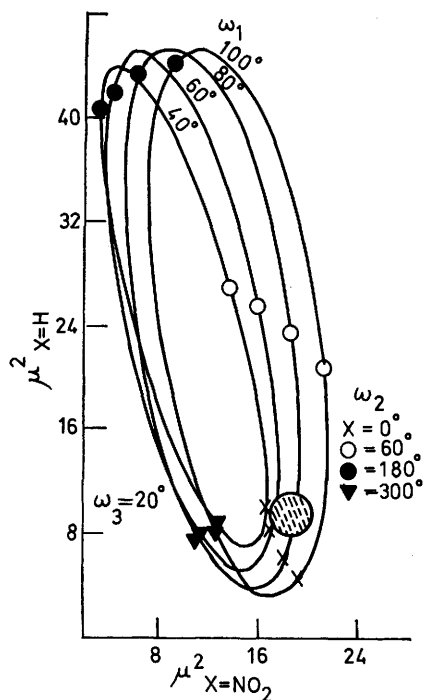the atoms C(7)O(8)C(9) forming an angle (ω_2) of 0—20° with it. This conformation of the ester-imino-function

FIGURE 1 Comparison of theoretical dipole moments squared $\mu^2_{X=H}$ *versus* $\mu^2_{X=NO_2}$ for the Z-isomers of compounds (1a and d), for ω_3 20, ω_1 40—100, and ω_2 0—360°. Hatched circles refer to the experimental dipole moments. Curves for other values of ω_1 are omitted for reasons of simplicity

is similar to that found in acid anhydrides [14] and in other analogous compounds.[15]

For compound (1b) we have found analogous results assuming that the methoxy-groups are freely rotating.

Using the graphical method of Exner for the E-isomer it was not possible to find a single conformation for all the compounds studied, with agreement between the experimental and theoretical values of the dipole mo-

[15] O. Exner, P. Dembech, G. Seconi, and P. Vivarelli, *J.C.S. Perkin II*, 1973, 1870.

ment. The same also holds for the Z-isomer and for values of angle ω_3 equal to 90, 180, 270, 320, and 340°.

From the above discussion it is concluded that the structure of these triazole derivatives in benzene solution is similar to that given in Scheme 4 with the exception that the benzoyl group lies above and the hetero-atoms of the triazole ring lie below the plane of the molecule. It is of interest to note that this structure is very close
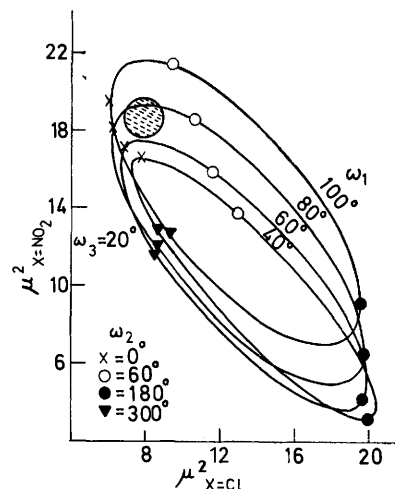

FIGURE 2 Comparison of theoretical dipole moments squared $\mu^2_{X=NO_2}$ *versus* $\mu^2_{X=Cl}$ for the Z-isomers of compounds (1c and d) for ω_3 20, ω_1 40—100, and ω_2 0—360°. Hatched circles refer to the experimental dipole moments. Curves for other values of ω_1 are omitted for reasons of simplicity

to that found in the solid state, as shown by X-ray measurements for compound (1a) by Katritzky and his co-workers[3c] and for 1-[α-(o-bromobenzoyloxy)-(o-bromo-benzylideneamino)]-4,5-diphenyl-1,2,3-triazole by Kokkou and Rentzeperis.[16]

[16] S. C. Kokkou and P. J. Rentzeperis, *Acta Cryst.*, 1975, **B31**, 2788.