# Dipole Moments and a CNDO/2 Study of Mesoionic 1,2,3-Triazoles ${ }^{1}$ 

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#### Abstract

The electric dipole moments of three 1-methyl-3-aryl-1,2,3-triazol-4-ylacetamides (1) and of the 1 -methyl-3-( $p$-tolyl)-1,2,3-triazol-4-one (2) were measured in benzene solution at $25^{\circ} \mathrm{C}$, and the orientation of the moment vector in space was determined by the CNDO/2 method. Dipole moment data in connection with charge distribution and electrons in bonds support the mesoionic formulation for (1) and (2).


The synthesis and chemical behaviour of mesoionic 1,2,3-triazol-4-ylacylimines and 1,2,3-triazol-4-ones have been extensively studied ${ }^{2,3}$ but very little is known of the dipole moment and the electronic structure of these systems. However, the molecular ${ }^{4,5}$ and electronic structure ${ }^{6}$ as well as the dipole moment determination of several other mesoionic systems have drawn the interest of many investigators. ${ }^{7}$
The electric dipole moment is a fundamental property of a mesoionic ring and recent dipole moment studies ${ }^{8}$ on several 3 -imino- and 3-oxo-1,2,4-triazoles provided strong evidence for the mesoionic character of these systems.
In a continuation of our previous work on the dipole moments of $1,2,3$-triazole derivatives ${ }^{9}$ we have undertaken the dipole moment measurements of some mesoionic $1,2,3$-triazol4 -ylacetamides (1) and the 1,2,3-triazol-4-one (2) as well as an examination of their electronic structure by CNDO/2 calculations, using the geometry of compound (1b), determined by $X$-ray crystallographic analysis. ${ }^{10}$ The results of the present study support a mesoionic formulation for compounds (1) and (2).

## Experimental

Materials.-The synthesis of mesoionic 1,2,3-triazol-4-ylacetamides (1) and 1,2,3-triazol-4-one (2) has been described previously, ${ }^{2 a}$ with the exception of compound (1c), which was prepared by the same method, ${ }^{2 a}$ m.p. $230-232{ }^{\circ} \mathrm{C}$ (decomp.) (Found: C, 52.85; H, 4.4; N, 22.4. $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{ClN}_{4} \mathrm{O}$ requires C , 52.7; H, 4.4; N, 22.35\%); $\lambda_{\text {max }}$ (MeOH) 305 and $236 \mathrm{~nm}(\log \varepsilon$ 4.05 and 4.27); $v_{\text {max. }}$ (Nujol) $3170 \mathrm{~m}(5-\mathrm{H})$ and $1595 \mathrm{~s} \mathrm{~cm}^{-1}$ (CO); $\delta_{\mathrm{H}}\left(80 \mathrm{MHz} ; \mathrm{CDCl}_{3}\right) 2.15(3 \mathrm{H}, \mathrm{s}, \mathrm{COMe}), 4.15(3 \mathrm{H}, \mathrm{s}, \mathrm{NMe})$, $7.54(2 \mathrm{H}, \mathrm{d}, J 9 \mathrm{~Hz}$, arom.), $8.09(2 \mathrm{H}, \mathrm{d}, J 9 \mathrm{~Hz}$, arom.), and 8.62 ( $1 \mathrm{H}, \mathrm{s}, 5-\mathrm{H}$ ); $m / z 252 / 250$ ( $M^{+}, 14 \%$ ).
Some 1,3-bisaryl derivatives of (1) have been synthesized analogously ${ }^{1}$ but in very low yield and insufficient amounts to carry out dipole moment measurements. On the other hand, mesoionic 1-methyl-3-phenyl-1,2,3-triazol-4-one has been synthesized but it was unsuitable for dipole moment measurements since it crystallizes ${ }^{2 a}$ with water molecules.
Benzene (Pronalys) was used as solvent in all measurements.
Dipole Moment Measurements.-Electric dipole moments were determined by the method of Guggenheim and Smith. ${ }^{11}$ The 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 Abbé high-precision refractometer (Baush and Lomb, type 3L). The temperature in all experiments was maintained at $25 \pm 0.05^{\circ} \mathrm{C}$. Details of the method used for dipole moment measurements have been described previously. ${ }^{9}$ The CNDO/2 calculations were carried out with the CNINDO program ${ }^{12}$ (QCPE 141) using a Univac 1106 computer.

(1)

(2)
a; $X=H$
b: $X=\mathrm{CH}_{3}$
c; $X=\mathrm{Cl}$

Table. Dipole moments of compounds (1) and (2)

|  |  |  | Experimental, $\mu / \mathrm{D}$ | $\mathrm{CNDO} / 2$, |
| :--- | :---: | :---: | :---: | :---: |
| Compound | $a_{\mathrm{\varepsilon}}^{*}$ | $a_{\mathrm{n}}^{*}$ | benzene, $25^{\circ} \mathrm{C}$ | $\mu / \mathrm{D}$ |
| (1a) | 11.69 | 0.58 | $4.71 \pm 0.04$ | 6.39 |
| (1b) | 11.75 | 0.61 | $4.86 \pm 0.06$ | 6.40 |
| (1c) | 10.66 | 0.57 | $4.83 \pm 0.03$ | 6.80 |
| (2) | 11.83 | 0.35 | $4.48 \pm 0.03$ | 5.98 |

* $a_{\mathrm{c}}$ and $a_{\mathrm{n}}$ are least-square slopes of the plots $\left(\varepsilon_{1.2}-\varepsilon_{1}\right)$ versus $w_{2}$ and $\left(n_{1.2}^{2}-n_{1}^{2}\right)$ versus $w_{2}$ respectively. ${ }^{9}$

The experimental dipole moments of compounds (1) and (2) and the values theoretically calculated by the CNDO/2 method are given in the Table.

## Discussion

The dipole moment values of mesoionic 1,2,3-triazoles (1) and (2) are smaller than those found for the mesoionic 3-imino- or 3-oxo-1,2,4-triazole derivatives, which have dipole moments ${ }^{8}$ in the range of $8-9 \mathrm{D}$, although several mesoionic tetrazoles ${ }^{8}$ have moment values in the range $4-6 \mathrm{D}$. Compounds (1) and (2), however, have dipole moments higher than the triazole ring system ${ }^{9}$ by 1 D . It is also mentioned that a similar dipole moment value of 4.86 D (benzene) was previously reported ${ }^{13}$ for the mesoionic 1-methyl-3-phenyl-1,2,3-triazol-4-ylbenzamide.

Figure 1 shows for two representative compounds (1b) and (2) the calculated net atomic charge distribution ${ }^{12}(q)$ and electron density ${ }^{14}\left(B_{\mathrm{AB}}\right)$, as well as the orientation of dipole moment vector $\bar{\mu}$, with the conventional direction, which is opposite to that calculated by the CNDO/ 2 method. The index $B_{A B}$ is given by equation (1) where $P_{\lambda \sigma}$ is an element of the density matrix and it was determined by an appropriate modification of the progam used.

$$
\begin{equation*}
B_{A B}=\sum_{\lambda \in A} \sum_{\sigma \in B} P_{\lambda \sigma}^{2}{ }^{2} \tag{1}
\end{equation*}
$$


(1b)

(2)

Figure 1. Net charge ( $q$ ) distribution (in parentheses), electron density ( $B_{\mathrm{AB}}$ ), and dipole moment vector ( $\bar{\mu}$ ) calculated by the CNDO/ 2 method for compounds (1b) and (2). The charge densities of all aryl atoms are less than $\pm 0.025$, except for the ipso-carbon atom, whose net charge is ca. 0.115 . The mean value for electrons in bonds for $\mathbf{C}-\mathrm{C}$ aryl bonds is equal to ca. 1.43

The vector $\bar{\mu}$ is directed below the plane of the triazole ring forming with it an angle equal to 6.9 and $1.7^{\circ}$ for (1b) and (2), respectively.

The geometry used for compounds (1) was the same as that found from crystal $X$-ray analysis ${ }^{10}$ carried out on (1b). According to this, the triazole ring, like the aryl group, is practically planar, the oxygen atom of the acetylimino group is directed below the triazole ring plane forming a dihedral angle equal to $9.3^{\circ}$, and the aryl group is twisted counterclockwise by $34.6^{\circ}$ about the $\mathrm{N}(3)-\mathrm{C}($ aryl) bond. The rotation is considered to face the molecule from aryl to triazole ring (Figure 1). The same geometry was also applied for (2) using a $\mathrm{C}(4)-\mathrm{O}(6)$ bond length equal to $1.215 \AA$, as was found in $3,3^{\prime}$-ethylenebis-sydnone. ${ }^{4}$

The calculated dipole moments (Table) are higher than those experimentally found by $c a .30 \%$, but this deviation is found in the range of accuracy of the method ${ }^{15}$ and analogously higher values are also given by the MINDO/3 method. ${ }^{6}$ Furthermore, CNDO/2 calculations ${ }^{1}$ carried out on 3phenylsydnone gave a dipole moment equal to 8.59 D , whereas the experimental value ${ }^{16}$ is 6.48 D . The dipole moment vector in this system was calculated to form with $\mathrm{N}(3)-\mathrm{C}(4)$ bond an angle of $60^{\circ}$, in good agreement with that of $37^{\circ}$ previously reported. ${ }^{16}$


Figure 2. Theoretical calculation by vector addition of the dipole moment of (1c)

(3)

(5)

(6)

The dipole moment of (1c) could be also calculated by vector addition (Figure 2) of the moment vector of (1a) (4.71 D), forming with the $\mathrm{N}(1)-\mathrm{C}(5)$ bond an angle of $11.3^{\circ}$ as found by CNDO/2, with the moment vector ${ }^{8}$ of the $p$-chlorophenyl dipole ( 1.55 D ) which forms an angle of $88.9^{\circ}$ with the previous vector. Thus, the value of 4.96 D is found, in very good agreement with the experimental value of 4.83 D . In this calculation the experimental moment vector of the parent compound (1a) was projected to the plane of the triazole ring, giving a value smaller by 0.03 D .

This calculation has also shown an angle of $29.6^{\circ}$ which the moment vector of 4.96 D forms with $\mathrm{N}(1)-\mathrm{C}(5)$, whereas this angle was calculated by the CNDO/2 method to be $33.9^{\circ}$.

An examination of net charge distribution in (1b) and (2) (Figure 1) shows that, for the triazole ring, large positive values are located at $\mathrm{N}(1)$ and $\mathrm{C}(4)$, whereas the negative charge is mainly spread at the acetylimino function or at $O(6)$ in (2), as well as at $\mathrm{C}(5)$ and $\mathrm{N}(2)$. This charge distribution suggests that the present systems could be represented by structures (3) and (4). This aspect is also supported by the orientation of dipole moment vector (Figure 1) and gives an approximate representation of the electronic configuration of the system. A similar representation was previously proposed ${ }^{6}$ for mesoionic 5 -oxo- and 5-imino-oxazole derivatives.

The calculated values of electron density ( $B_{\mathrm{AB}}$ ) for compounds (1) and (2) are of special interest. Considering that $B_{\mathrm{AB}}$ values could be taken as a measure of the 'covalency' of the bond, ${ }^{14}$ it is seen from Figure 1 that the $N(3)-C(4)$ bond in (1b) and (2) has a $B_{A B}$ value of 1.097 and 1.039 , respectively. These values are somewhat higher than those corresponding to a covalent single bond, like that of $\mathrm{N}(1)-\mathrm{C}(10)$.

It is mentioned that the $B_{A B}$ value for $\mathrm{O}(1)-\mathrm{C}(5)$ bond in methylsydnone was calculated to be 0.960 . These data argue that the contribution of a valence tautomer ${ }^{4}$ (5) or (6) to the structure of (1), similar to the nitrosoketene valence tautomer proposed for sydnone, ${ }^{4}$ should be negligible. This is also supported by i.r. data of (1b) and (2), which gave a $v(C O)$ absorption at 1595 and $1655 \mathrm{~cm}^{-1}$, respectively.

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