

Figure 1. Net charge (q) distribution (in parentheses), electron density (B_{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 ± 0.025 , except for the *ipso*-carbon atom, whose net charge is *ca.* 0.115. The mean value for electrons in bonds for C-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° for (1b) and (2), respectively.

The geometry used for compounds (1) was the same as that found from crystal *X*-ray analysis¹⁰ 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°, and the aryl group is twisted counterclockwise by 34.6° about the N(3)-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 C(4)-O(6) bond length equal to 1.215 Å, as was found in 3,3'-ethylenebis-sydnone.⁴

The calculated dipole moments (Table) are higher than those experimentally found by *ca.* 30%, but this deviation is found in the range of accuracy of the method¹⁵ and analogously higher values are also given by the MINDO/3 method.⁶ Furthermore, CNDO/2 calculations¹ carried out on 3-phenylsydnone gave a dipole moment equal to 8.59 D, whereas the experimental value¹⁶ is 6.48 D. The dipole moment vector in this system was calculated to form with N(3)-C(4) bond an angle of 60°, in good agreement with that of 37° previously reported.¹⁶

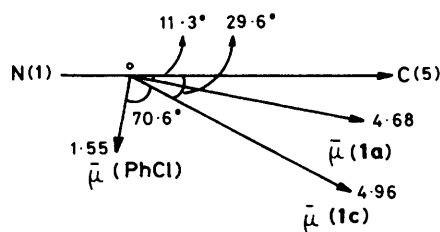
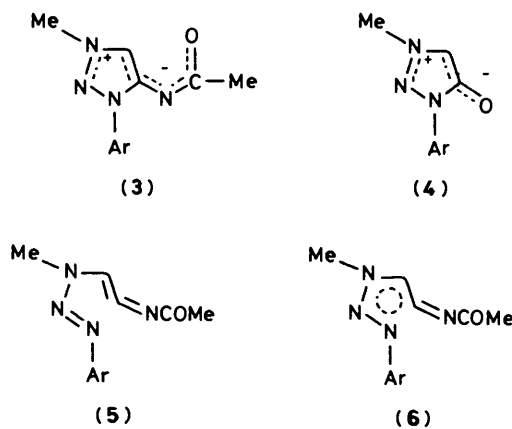


Figure 2. Theoretical calculation by vector addition of the dipole moment of (1c)



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 N(1)-C(5) bond an angle of 11.3° as found by CNDO/2, with the moment vector⁸ of the *p*-chlorophenyl dipole (1.55 D) which forms an angle of 88.9° 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° which the moment vector of 4.96 D forms with N(1)-C(5), whereas this angle was calculated by the CNDO/2 method to be 33.9°.

An examination of net charge distribution in (1b) and (2) (Figure 1) shows that, for the triazole ring, large positive values are located at N(1) and C(4), whereas the negative charge is mainly spread at the acetylimino function or at O(6) in (2), as well as at C(5) and 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 proposed⁶ for mesoionic 5-oxo- and 5-imino-oxazole derivatives.

The calculated values of electron density (B_{AB}) for compounds (1) and (2) are of special interest. Considering that B_{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_{AB} value of 1.097 and 1.039, respectively. These values are somewhat higher than those corresponding to a covalent single bond, like that of N(1)-C(10).

It is mentioned that the B_{AB} value for O(1)-C(5) bond in methylsydnone was calculated to be 0.960. These data argue that the contribution of a valence tautomer⁴ (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 $\nu(\text{CO})$ absorption at 1595 and 1655 cm^{-1} , respectively.

References

- 1 Taken in part from C. A. Tsoleridis, Ph.D. Thesis, University of Thessaloniki, 1984. Presented in part at the 'Balkan Chemistry Days' Conference, Varna, 1983.
- 2 K. T. Potts and S. Husain, *J. Org. Chem.*, (a) 1970, **35**, 3451; (b) 1972, **37**, 2049.
- 3 M. Begtrup and P. A. Kristensen, *Acta Chem. Scand.*, 1969, **23**, 2733; M. Begtrup and K. V. Poulsen, *ibid.*, 1971, **25**, 2087.
- 4 H. Hope and W. E. Thiessen, *Acta Crystallogr.*, 1969, **B25**, 1237.
- 5 T. J. King, P. N. Preston, J. S. Suffolk, and K. Turnbull, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1751.
- 6 M. J. S. Dewar and I. J. Turchi, *J. Chem. Soc., Perkin Trans. 2*, 1976, 548.
- 7 For reviews see: M. Ohta and H. Kato, in 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, pp. 117—248; W. D. Ollis and C. A. Ramsden, *Adv. Heterocycl. Chem.*, 1976, **19**, 1; C. G. Newton and C. A. Ramsden, *Tetrahedron*, 1982, **38**, 2965.
- 8 R. N. Hanley, W. D. Ollis, C. A. Ramsden, G. Rowlands, and L. E. Sutton, *J. Chem. Soc., Perkin Trans. 1*, 1978, 600.
- 9 N. A. Rodios and N. E. Alexandrou, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1779; *J. Heterocycl. Chem.*, 1979, **16**, 571.
- 10 M. Papageorgiou, S. C. Kokkou, P. J. Rentzeperis, and C. Tsoleridis, *Acta Crystallogr.*, 1983, **C39**, 1581.
- 11 E. A. Guggenheim, *Trans. Faraday Soc.*, 1951, **47**, 573; J. W. Smith, *ibid.*, 1950, **46**, 394.
- 12 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
- 13 N. A. Rodios, Ph.D. Thesis, University of Thessaloniki, 1976.
- 14 D. R. Armstrong, P. G. Perkins, and J. P. Stewart, *J. Chem. Soc., Dalton Trans.*, 1973, 838.
- 15 J. Waite, M. G. Papadopoulos, and C. A. Nicolaides, *J. Chem. Phys.*, 1982, **77**, 2536.
- 16 R. A. W. Hill and L. E. Sutton, *J. Chem. Soc.*, 1949, 746; 1953, 1482.

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