Cyclic Mesoionic Compounds. Part 14.[1] The Electric Dipole Moments of Mesoionic Heterocycles

By **Robert N. Hanley, W. David Ollis,** and **Christopher A. Ramsden,** Department of Chemistry, The University, Sheffield S3 7HF

Geoffrey Rowlands and **Leslie E. Sutton,** Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

The electric dipole moments of derivatives of fourteen classes of mesoionic compounds have been measured. Vector analysis gives heterocyclic ring moments whose magnitude and direction provide support for the mesoionic formulations.

DIPOLE moment studies provided excellent support for the formulation of the sydnones (1) as mesoionic [2] compounds because, by the choice of suitable derivatives, it was possible to determine not only the magnitude but also the direction of the heterocyclic ring moment.[3,4] N-Phenylsydnone (1; R^1 = Ph, R^2 = H) has a dipole moment of 6.48 D (in benzene), and results from the vectorial analysis of the dipole moments of a large

number of sydnones (1) were consistent with a sydnone ring moment of 5.5 D inclined at the indicated angle of 20° (2) to the R^1-N bond direction.

† Details of the experimental results leading to the dipole moment values listed in the Table are available as Supplementary Publication No. SUP 22117 (6 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

Similar studies have also been carried out on isosydnones [(3), (4)] [5] and on the mesoionic 1,3,4-thiadiazoles [(5), (6)],[6] and the results support their formulation as mesoionic compounds.

We now report upon the measurement of electric dipole moments of representatives of fourteen additional mesoionic systems (Table).†

EXPERIMENTAL

The dipole moments were determined by measurement of the dielectric constants of dilute solutions of the heterocycles in pure benzene or pure dioxan at 28 °C in a shielded concentric condenser using a Wayne–Kerr B331 Autobalance Precision Bridge.

The solubilities of the mesoionic 1,2,4-triazol-3-imines (7), 1,2,3,4-tetrazol-5-ylidenemalononitriles (23), and 1,2,3,4-thiatriazol-5-ylidenemalononitriles (28) in benzene at 28° were low (weight fractions 0.000 12—0.002), and the mesoionic 1,2,4-triazol-3-ones (8) and 1,2,4-triazole-3-thiones (9) were virtually insoluble in benzene, so their dipole moments were measured in dioxan solution. The remaining compounds were fairly readily soluble in benzene, but only in the cases of the mesoionic 1,2,3,4-oxatriazole-5-thiones (16) and 1,2,3,4-thiatriazol-5-ones (27) were the solubilities sufficiently high to permit the measurement of refractive indices. Consequently, the molar polarisations of the remaining compounds were calculated from bond refractivity tables.[7] A value of 30.7 cm³ was calculated for the unsubstituted mesoionic 1,2,4-triazol-3-imine system (7), using the R_D value of 102.2 cm³ for nitron (7; R^1 = R^3 = R^4 = Ph, R^2 = H) measured by Warren.[8]

[1] Part 13, C. A. Ramsden and W. D. Ollis, *J.C.S. Perkin I*, 1974, 645.

[2] W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, 1949, 307; 1950, 1542; W. Baker and W. D. Ollis, *Chem. and Ind.*, 1955, 910; *Quart. Rev.*, 1957, **11**, 15; F. H. C. Stewart, *Chem. Rev.*, 1964, **64**, 129; M. Ohta and H. Kato in ' Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, pp. 117—248; C. A. Ramsden and W. D. Ollis, *Adv. Heterocyclic Chem.*, 1976, **19**, 1.

[3] R. A. W. Hill and L. E. Sutton, *J. Chem. Soc.*, 1949, 746; 1953, 1482.
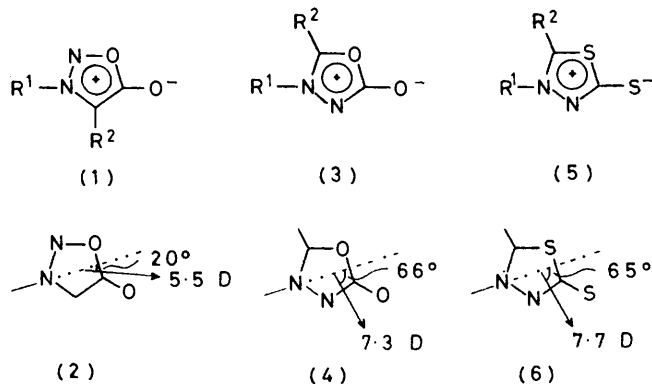
[4] J. C. Earl, E. M. W. Leake, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1948, 2269.

[5] A. R. McCarthy, W. D. Ollis, A. N. M. Barnes, L. E. Sutton, and C. Ainsworth, *J. Chem. Soc. (B)*, 1969, 1185.

[6] C. W. Atkin, A. N. M. Barnes, P. G. Edgerley, and L. E. Sutton, *J. Chem. Soc. (B)*, 1969, 1194.

[7] A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 1952, 514.

[8] F. L. Warren, *J. Chem. Soc.*, 1938, 1100.

We have estimated the molar refractions of the unsubstituted mesoionic 1,2,3,4-oxatriazole-5-thione (18) and 1,2,3,4-thiatriazol-5-one (29) systems to be 28.2 and 24.0 cm^3, respectively.

When possible, specific volumes were determined using a Sprengel–Ostwald pyknometer, but where low solubility precluded direct measurement, values of β (the slope of the v/w graph) of similarly substituted compounds were used.

Dipole moments

Compd.	μ/D †	Compd.	μ/D †
(7a)	8.17 ± 0.04	(16d)	7.62 ± 0.01
(7b)	8.20 ± 0.06	(16e)	7.85 ± 0.02
(7c)	9.86 ± 0.04	(21a)	5.28 ± 0.04
(7d)	9.79 ± 0.05	(21b)	5.42 ± 0.04
(8a)	9.11 ± 0.20 ‡	(21c)	4.41 ± 0.05
(9a)	9.89 ± 0.20 ‡	(22a)	6.52 ± 0.10
(9b)	9.25 ± 0.20 ‡	(22b)	6.47 ± 0.07
(12a)	7.56 ± 0.05	(22c)	5.61 ± 0.06
(13a)	6.68 ± 0.05	(23a)	9.54 ± 0.10
(14a)	5.42 ± 0.10	(26a)	3.71 ± 0.07
(14b)	4.17 ± 0.08	(27a)	4.39 ± 0.02
(14c)	6.29 ± 0.10	(27b)	5.01 ± 0.03
(15a)	6.14 ± 0.02	(27c)	3.68 ± 0.01
(16a)	6.83 ± 0.05	(27d)	5.57 ± 0.03
(16b)	7.08 ± 0.02	(27e)	6.11 ± 0.02
(16c)	5.08 ± 0.01	(28a)	8.84 ± 0.02

† In benzene except where indicated otherwise. ‡ In dioxan.

The experimental method [9] and the method of calculation of the dipole moments [10] have been described. The experimental results are available † and the dipole moments are given in the Table. Methods of preparing the compounds described here have been reported elsewhere.[11]

DISCUSSION

(i) *Mesoionic* 1,2,4-*Triazol*-3-*imines* (7), 1,2,4-*Triazol*-3-*ones* (8), *and* 1,2,4-*Triazole*-3-*thiones* (9).—The electric dipole moments of two mesoionic, 1,2,4-triazol-3-imines (7) have been measured previously. Jensen and Friediger [12] have reported values of 8.8 (dioxan) and 9.9 D (benzene) for the dipole moment of 1,4,5-triphenyl-1,2,4-triazolium-3-anilide (7; R^1 = R^2 = R^3 = R^4 = Ph) and Warren [8] measured a dipole moment of 7.2 D (chloroform) for 1,4-diphenyl-1,2,4-triazolium-3-anilide (nitron) (7; R^1 = R^3 = R^4 = Ph, R^2 = H). We now report the dipole moments of four mesoionic 1,2,4-triazol-3-imines (7a—d) (Table) and these results are in general agreement with the previous studies on the system (7).[8,12]

Using a vector analysis similar to that employed for the sydnones (1),[3,4] isosydnones (3),[5] and mesoionic 1,3,4-thiadiazole-2-thiones (5),[6] the magnitude and direction of the 1,2,4-triazol-3-imine ring moment [see (10)] can be estimated. Throughout this work we have made the simplifying assumption that mesoionic rings are regular pentagons.

Assuming that the dipole moment of the mesoionic 4-p-chlorophenyl-1,2,4-triazol-3-imine (7b) (8.20 D) is the

[9] K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 1951, 16.
[10] K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

resultant of the dipole moment of the mesoionic 1,2,4-triazol-3-imine (7a) (8.17 D) and the C–Cl bond moment (1.55 D; the dipole moment of chlorobenzene), a vector diagram can be constructed (Figure 1). From
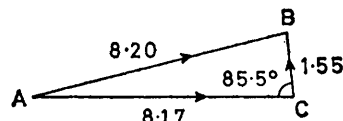

FIGURE 1

Figure 1, the angle between the Ph–N(4) bond $(\overrightarrow{BC})$ and the dipole moment of the mesoionic 1,2,4-triazol-3-imine (7a) $(\overrightarrow{AC})$ is 85.5°. Thus, there are two possibilities for the direction of the dipole moment of the mesoionic 1,2,4-triazol-3-imine (7a) and these are indicated by the positive and negative angles in Figure 2.
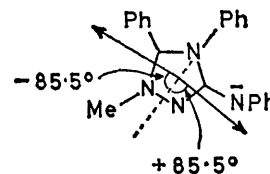

FIGURE 2

In mesoionic compounds which have previously been studied, the dipole moment has been found to have its negative pole directed towards the exocyclic heteroatom and so in this case the choice of the positive angle (Figure 2) seems most reasonable.

The validity of choosing the positive angle (Figure 2) can be checked by calculating the dipole moment of the 1,2,4-triazolium-3-p-chloroanilide (7c) by a vector addition of the dipole moments of the 1,3,4-triazolium-2-anilide (7a) and the exocyclic p-chlorophenyl dipole. It is assumed that the exocyclic C–N–C angle is 120° and that the preferred diastereoisomer is that shown in Figure 3. Molecular models show that there is considerable unfavourable interaction between aryl groups in the alternative diastereoisomer. Vector addition of the dipole moment of (7a) (8.17 D) and the exocyclic p-chlorophenyl dipole (1.55 D; the dipole moment of chlorobenzene) is shown in Figure 3 and this gives a resultant dipole moment of 9.5 D for 1-methyl-4,5-diphenyl-1,2,4-triazolium-3-p-chloroanilide (7c), which is in good agreement with the experimental value of 9.86 D (Table). It would be unreasonable to choose the

[11] (a) W. D. Ollis and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1971, 1222, 1223, 1224; Part 8, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 624; Part 9, *ibid.*, 1974, 627; Part 10, W. D. Ollis and C. A. Ramsden, *ibid.*, 1974, 633; Part 11, *ibid.*, 1974, 638; Part 12, *ibid.*, 1974, 642; Part 13, *ibid.*, 1974, 645; (b) R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1976, 306, 307; Part 16, R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, in the press; Part 17, *ibid.*, in the press; Part 18, *ibid.*, in the press; Part 19, R. N. Hanley, W. D. Ollis, C. A. Ramsden, and I. S. Smith, *ibid.*, in the press.
[12] K. A. Jensen and A. Friediger, *Kgl Danske Videnskab. Selskab.*, 1943, **20**, 1.

negative angle in Figure 2 because this would result in (7c) having a calculated dipole moment smaller than that of the parent compound (7a), a deduction inconsistent with the observed value. In accord with
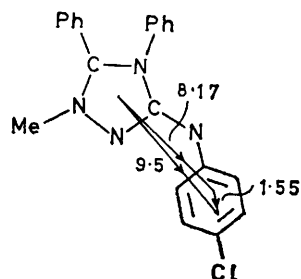

FIGURE 3

the above analysis, the dipole moment of the bis-*p*-chlorophenyl derivative (7d) (9.79 D) is of the same magnitude as that of the *p*-chlorophenyl derivative (7c) (9.86 D).

The magnitude and direction of the mesoionic 1,2,4-triazole-3-phenylimine ring moment (10) can now be estimated, assuming a value of 1.1 D for the Ph–N(4) and Me–N(1) group moments and neglecting the small Ph–C group moment. The vector diagram shown in Figure 4 gives a value of 7.5 D for the 1,2,4-triazole-3-phenylimine ring moment (10) acting at an angle of 58° to the Me–N(1) bond axis. This estimated magnitude and direction of the heterocyclic ring moment (10) compares well with those estimated for the isosydnones (4) and the mesoionic 1,2,4-thiadiazole-3-thiones (6).

For comparison we have also measured the electric dipole moments of some mesoionic 1,2,4-triazol-3-ones (8) and mesoionic 1,2,4-triazole-3-thiones (9). The compounds were found to be virtually insoluble in benzene and their dipole moments were measured in dioxan solution.

The dipole moment of 1-methyl-4,5-diphenyl-1,2,4-triazolium-3-olate (8a) was found to be 9.11 D, a value clearly consistent with the mesoionic structure.

The dipole moments of two mesoionic 1,2,4-triazole-3-thiones (9) have been measured; these [(9a) 9.89 D; (9b) 9.25 D] are consistent with the mesoionic structure. A vector analysis of the dipole moments of (9a and b),
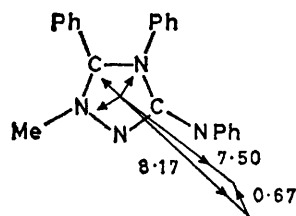

FIGURE 4

analogous to that used for the mesoionic 1,2,4-triazol-3-imines (7), gives a value of 9.2 D for the meso-ionic 1,2,4-triazole-3-thione ring moment (11) acting at an angle of 83° to the Me–N(1) bond.

Jensen and Friediger[12] have reported a value of 8.4 D for the dipole moment of the mesoionic 1,2,4-triazole-3-thione (9; $R^1 = R^3 = Ph$, $R^2 = Me$) in chloroform solution. This is in fair agreement with our measurements, particularly in view of the unsuitability of chloroform as a solvent for dielectric constant measurements.

(ii) *Mesoionic 1,3,4-Oxadiazol-2-imines* (12) *and 1,3,4-Thiadiazol-2-imines* (13).—The mesoionic 1,3,4-oxadiazol-2-imines (12) and 1,3,4-thiadiazol-2-imines (13) are two new classes of mesoionic heterocycle,[11a] and the dipole moments of one representative of each class have been measured. 4-Methyl-5-phenyl-1,3,4-oxadiazolium-2-anilide (12a) was found to have a dipole moment of 7.56 D, whereas that of 4-methyl-5-phenyl-1,3,4-thiadiazolium-2-anilide (13a) was 6.68 D. Both
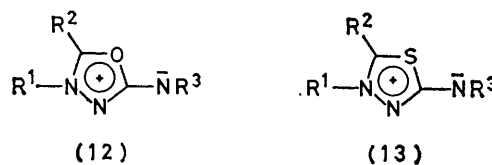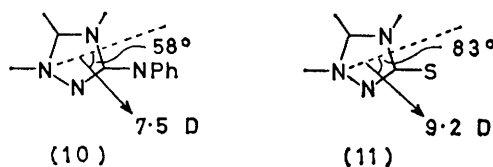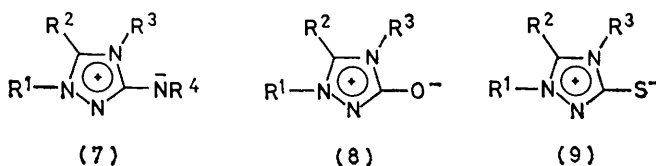
In formula (7): a; $R^1 = Me$, $R^2 = R^3 = R^4 = Ph$ b; $R^1 = Me$, $R^2 = R^4 = Ph$, $R^3 = p\text{-ClC}_6H_4$ c; $R^1 = Me$, $R^2 = R^3 = Ph$, $R^4 = p\text{-ClC}_6H_4$ d; $R^1 = Me$, $R^2 = Ph$, $R^3 = R^4 = p\text{-ClC}_6H_4$
In formulae (8), (9), (12), and (13): a; $R^1 = Me$, $R^2 = R^3 = Ph$ b; $R^1 = Me$, $R^2 = Ph$, $R^3 = p\text{-ClC}_6H_4$

these results provide support for the mesoionic formulations.

(iii) *Mesoionic 1,2,3,4-Oxatriazol-5-imines* (14), *1,2,3,4-Oxatriazol-5-ones* (15), *and 1,2,3,4-Oxatriazole-5-thiones* (16).—The electric dipole moments of three mesoionic 1,2,3,4-oxatriazol-2-imines (14a—c) are now reported (Table). A vector analysis analogous to that described for the mesoionic 1,2,4-triazol-3-imines (7) indicates that the dipole moment of the parent compound (14a) makes an angle of 31° with the Ph–N(3) bond and it is assumed that the negative pole is directed towards the exocyclic nitrogen atom. The dipole moment of 3-phenyl-1,2,3,4-oxatriazolium-5-*p*-chloroanilide (14c) can now be estimated by vector addition. However, the molecule (14c) can exist in two diastereoisomeric forms, (19) and (20), and these might be expected to be

almost equally favoured.   The estimated dipole moment of (19) is 6.24 D and of (20) is 6.44 D.   Both these values are very close to the experimental value of 6.29 D for (14c), but it is not possible to comment quantitatively on the relative proportions of the diastereoisomers (19) and (20).

The unsubstituted 1,2,3,4-oxatriazole-5-phenylimine ring moment (17) is calculated by vector addition to be 4.51 D, inclined at an angle of 38° to the Ph–N(3) bond axis.

The dipole moment of 3-phenyl-1,2,3,4-oxatriazolium-5-olate (15a) in benzene solution has been found to be 6.14 D, consistent with the proposed mesoionic structure. Sundaram and Purcell [13] have reported molecular orbital calculations which give the mesoionic 1,2,3,4-oxatriazol-5-one ring moment as 5.3 D.

Dipole moments of five mesoionic 1,2,3,4-oxatriazole-5-thiones (16a—e) (Table) have been measured in benzene solution. Using the dipole moment of the 4-tolyl derivative (16b) and assuming the C—Me bond moment to be 0.43 D (the dipole moment of toluene), vector analysis indicates that the dipole moment of the parent molecule (16a) makes an angle of 56° with the Ph–N(3) bond. The mesoionic 1,2,3,4-oxatriazole-5-thione ring moment (18) is then calculated to be 6.3 D and inclined at an angle of 64° to the Ph–N(3) bond axis.

(14)   (15)   (16)

(17)   (18)

(19)   (20)
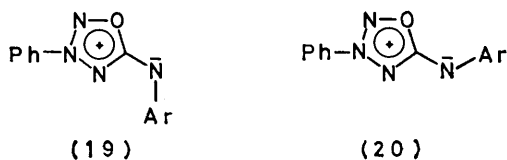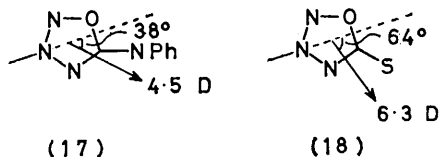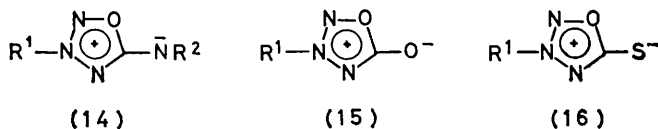
In formula (14): a; $R^1 = R^2 =$ Ph b; $R^1 = p$-ClC$_6$H$_4$, $R^2 =$ Ph c; $R^1 =$ Ph, $R^2 = p$-ClC$_6$H$_4$
In formulae (15) and (16): a; $R^1 =$ Ph b; $R^1 = p$-MeC$_6$H$_4$ c; $R^1 = p$-ClC$_6$H$_4$ d; $R^1 = p$-MeO·C$_6$H$_4$ e; $R^1 = p$-EtO·C$_6$H$_4$

(iv) *Mesoionic* 1,2,3,4-*Tetrazol-5-ones* (21), 1,2,3,4-*Tetrazole-5-thiones* (22), *and* 1,2,3,4-*Tetrazol-5-ylidenemalononitriles* (23).—The electric dipole moments of three mesoionic 1,2,3,4-tetrazol-5-ones (21a—c) have been measured (Table). Vector analysis indicates that the dipole moment of the diphenyl derivative (21a)

makes an angle of 57° to the Ph–N(3) bond axis [93° to the Ph–N(1) axis]. Vector addition of the dipole moment (5.28 D) of the diphenyl derivative (21a) to the p-chlorophenyl group moment (1.55 D) gives an estimate of

(21)   (22)   (23)

(24)   (25)
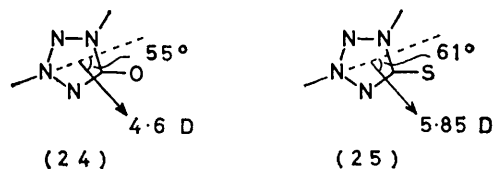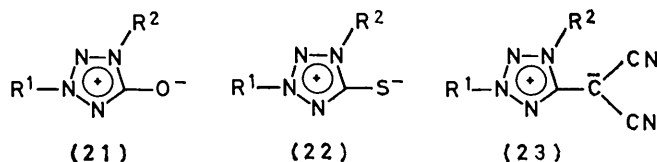
In formulae (21)—(23): a; $R^1 = R^2 =$ Ph b; $R^1 =$ Ph, $R^2 = p$-ClC$_6$H$_4$ c; $R^1 = p$-ClC$_6$H$_4$, $R^2 =$ Ph

4.62 D for the dipole moment of the 3-p-chlorophenyl derivative (21c), in good agreement with the observed dipole moment of 4.41 D (Table).

The mesoionic 1,2,3,4-tetrazol-5-one ring moment (24) is calculated to be 4.63 D and inclined at an angle of 55° to the Ph–N(3) bond axis.

The mesoionic 1,2,3,4-tetrazole-5-thiones (22) are a new class of mesoionic heterocycle.[11b] The electric dipole moments of three derivatives (22a—c) have been measured (Table). Vector analysis indicates that the dipole moment of the diphenyl derivative (22a) makes an angle of 63° with the Ph–N(3) bond axis. Using this information, the dipole moment of the 3-p-chlorophenyl derivative (22c) was calculated to be 5.98 D, in fair agreement with observed value, 5.61 D. Further analysis indicates that the 1,2,3,4-tetrazole-5-thione ring moment (25) is 5.85 D acting at an angle of 61° to the Ph–N(3) bond axis. These results are clearly consistent with the mesoionic structure (22).

The mesoionic 1,2,3,4-tetrazol-5-ylidenemalononitriles (23) are another new class of heterocycle.[11b] The dipole moment of 1,3-diphenyl-1,2,3,4-tetrazolium-5-dicyanomethanide (23a) in benzene solution has been found to be 9.54 D (Table). The large value is entirely consistent with the proposed mesoionic structure.

(v) *Mesoionic* 1,2,3,4-*Thiatriazol-5-imines* (26), 1,2,3,4-*Thiatriazol-5-ones* (27), *and* 1,2,3,4-*Thiatriazol-5-ylidenemalononitriles* (28).—The dipole moment of 3-phenyl-1,2,3,4-thiatriazolium-5-anilide (26a) was found to be 3.71 D.   Compound (26a) represents a new class of mesoionic heterocycle [11b] and, although the value of the dipole moment is rather smaller than those of other mesoionic heterocycles which we have studied, it is still consistent with the mesoionic formulation.

Another class of mesoionic heterocycle recently

13 K. Sundaram and W. P. Purcell, *Internat. J. Quantum Chem.*, 1968, 2, 145.

prepared are the 1,2,3,4-thiatriazol-5-ones (27).[11b] The dipole moments of five derivatives (27a—e) (Table) have been measured. Vector analysis indicates that the dipole moment of the phenyl derivative (27a) is directed at an angle of 53° to the Ph–N bond axis. Further analysis gives the 1,2,3,4-thiatriazol-5-one ring moment as 3.8 D, inclined at an angle of 66° to the Ar–N(3) bond axis (29). This result is clearly consistent with the mesoionic structure.

Finally, a representative of the previously unknown mesoionic 1,2,3,4-thiatriazol-5-ylidene system (28) has been prepared.[11b] 3-Phenyl-1,2,3,4-thiatriazolium-5-di-cyanomethanide (28a) was found to have a dipole moment of 8.84 D in benzene solution, a result which supports the proposed structure.

By comparing the present results with those reported previously,[5,6] some general comments can be made


(26)   (27)

(28)   (29)
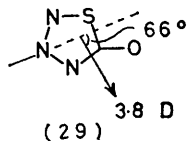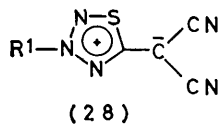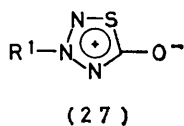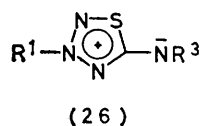
In formula (26): a; $R^1 = R^2 = Ph$
In formulae (27) and (28); a; $R^1 = Ph$ b; $R^1 = p\text{-MeC}_6H_4$
c; $R^1 = p\text{-ClC}_6H_4$ d; $R^1 = p\text{-MeO·C}_6H_4$ e; $R^1 = p\text{-EtO·C}_6H_4$

about the effect of the heteroatoms or groups, X and Y, on the magnitude of the dipole moments of the meso-ionic compounds of general structures (30) and (31).

The largest moments are associated with an exocyclic dicyanomethyl group $[Y = C(CN)_2]$. Large moments are consistently associated with an exocyclic sulphur atom (30 and 31; $Y = S$), and replacement of the

(30)   (31)
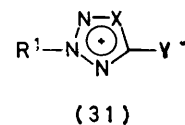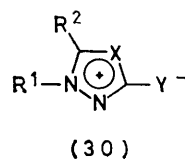
sulphur atom by oxygen (30 and 31; $Y = S \longrightarrow Y = O$) results in a reduction of the magnitude of the dipole moment (0.7—1.4 D). Similarly, replacement of the exocyclic oxygen atom by an NPh group (30 and 31; $Y = O \longrightarrow Y = NPh$) gives a further lowering of dipole moment (0.2—1.1 D).

The effect of changing the atom or group in the ring (30 and 31; X) is not general. For the molecules with general structure (30), the largest moments are observed when X is NPh. Replacement by an oxygen atom (30; $X = NPh \longrightarrow X = O$) results in reduction of the dipole moment (0.8—1.3 D) and further replacement by a sulphur atom (30; $X = O \longrightarrow X = S$) may again reduce the dipole moment (0.0—0.9 D). In the case of the molecules with general structure (31), the largest moments are observed when X is O and replacement by either S or NPh group reduces the magnitude of the moment. The observed changes are 0.3—0.8 D and 1.7 D, respectively.

Without exception, the dipole moments of the meso-ionic compounds (30; X = NR, O, or S) are substantially larger (2—4 D) than those of the corresponding compounds with the general structure (31; X = NR, O, or S).