Ground States of Molecules. Part XXXII.[1] A MINDO/3 Study of Mesoionic Oxazoles and Imidazoles

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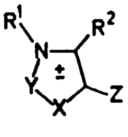
MINDO/3 Calculations are reported for a number of mesoionic species derived from oxazole and imidazole and for isomeric ' classical ' species. The mesoionic compounds are predicted to be highly polar and much less stable than their classical counterparts. The calculated geometries of the latter correspond to the expected classical structures. Those of the mesoionic compounds on the other hand mostly differ from the structures expected in terms of current treatments of resonance theory.

Of the known mesoionic heterocycles, the structure, physical properties, and reactions of sydnones (1; X = Z = O, Y = N) have drawn the closest scrutiny.[2]



(1)

Molecular orbital calculations by several methods have been applied to the sydnone ring system.[3-8] More recently calculations on sydnones by the CNDO/2,[9] *ab initio*,[10] and INDO [10] molecular orbital methods (assumed geometries) were carried out and the results of these calculations agreed qualitatively with the results obtained by a crystal structure determination of 4,4′-dichloro-3,3′-ethylenedisydnone [11] and a ^{13}C n.m.r. study of *N*-methylsydnone.[12]

Although the reactions of mesoionic oxazoles (1; X = O, Y = R–C, Z = O or NH) have been thoroughly investigated by Huisgen and his co-workers [13] and others,[14] little is known about their structure and physical properties. Derivatives of mesoionic imidazoles have been prepared; however, only very limited studies of their properties have been reported.[2a] This gap in our knowledge of these heterocyclic ring systems has prompted us to report the results of a MINDO/3 molecular orbital [15] study of their structures and energies. In all cases the geometries were calculated by minimizing the total energy with respect to *all* geometric variables.

Figure 1 shows the calculated distributions of formal charge, heats of formation (ΔH_f), dipole moments (μ/D), and geometries for the mesoionic *N*-methyl-5-oxo- and 4-oxo-oxazoles (2) and (3) and the non-mesoionic *N*-methyl-2-oxo-derivative (4), and for the mesoionic *N*-methyl-5-imino- and -4-imino-oxazoles (5) and (6) and the non-mesoionic *N*-methyl-2-imino-oxazole (7).

It will be seen that 3-methyl-3-oxazolin-2-one (4) is some 86.7 kJ mol^{-1} more stable than the 5-oxo-derivative (2) and 93.5 kJ mol^{-1} more stable than the 4-oxo-oxazole (3). Many derivatives of *N*-substituted 3-oxazolin-2-ones have been prepared and characterized [16] while the only known alkyl or aryl derivatives of the mesoionic 5-oxo-oxazoles are the 2,4-diaryl-3-methyloxazolium 5-oxides (1; X = Z = O, Y = Ar–C, R^1 = Me, R^2 = Ar).[13] No examples of mesoionic 4-oxo-oxazoles are known although attempts to synthesize these compounds have been made by the reaction of *N*-phenylbenzimidoyl chloride with glycolic acid.[17] This reaction, however, yielded a rearranged acyclic product which is thought not to arise from an intermediate 4-oxo-oxazole.

The stabilities of the imino-oxazole derivatives parallel those of their oxo-counterparts; *i.e.*, the 2-imino-oxazole (7) is 96.9 kJ mol^{-1} more stable than the 5-imino-isomer (5) and 155.4 kJ mol^{-1} more stable than the 4-imino-isomer (6). Stable derivatives of 2-imino-oxazoles have been reported [18] and derivatives of both 5- [19] and 4-imino-oxazoles [17] have also been prepared; however, these are stable only as salts.

A comparison of the heats of formation of the oxo-substituted oxazoles (2)—(4) with the imino-substituted oxazoles (5)—(7) shows that the former compounds are much more stable (190—252 kJ mol^{-1}) than the latter.

The calculated geometries and charge distributions of the non-mesoionic 2-oxo- and 2-imino-oxazoles (4) and (7) suggest that these are adequately represented by

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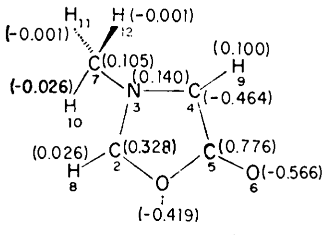
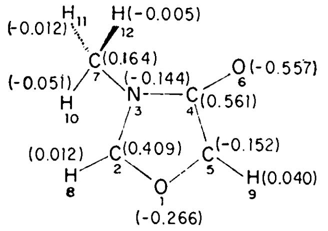
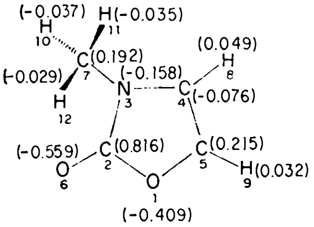


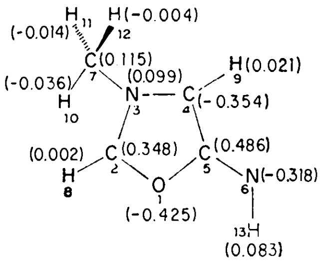
(a) (2) ΔH_f -200·5 kJ mol^{-1};μ7·38 D



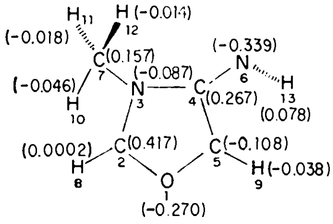
(b) (3) ΔH_f -193·7 kJ mol^{-1} ;μ5·81 D



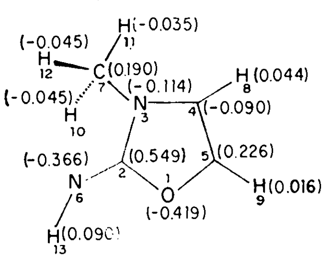
(c) (4) ΔH_f -287·2kJ mol^{-1};μ 4·60 D



(d) (5) ΔH_f -0·13 kJ mol^{-1}; μ4·88 D



(e) (6) ΔH_f 58·4 kJ mol^{-1};μ4·18 D

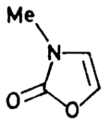


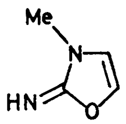
(f) (7) ΔH_f -97·0 kJ mol^{-1};μ 2·58 D

	Bond length (Å)	Bond angle (°)	Dihedral angle (°)
(a)	12 = 1.298 23 = 1.326 34 = 1.412 45 = 1.404 51 = 1.439 56 = 1.215 37 = 1.425 28 = 1.112 49 = 1.096 7 10 = 7 11 = 7 12 = 1.117	123 = 110.7 234 = 106.9 345 = 109.4 512 = 111.6 456 = 137.6 549 = 130.4 328 = 128.1 237 = 128.0 37 10 = 37 11 = 37 12 = 113.1	237 10 = −0.8 237 11 = 119.2 237 12 = 239.2
(b)	12 = 1.288 23 = 1.377 34 = 1.496 45 = 1.427 51 = 1.379 46 = 1.212 37 = 1.429 28 = 1.116 59 = 1.114 7 10 = 7 11 = 7 12 = 1.118	123 = 112.7 234 = 107.0 345 = 101.8 512 = 110.2 459 = 120.7 546 = 137.7 328 = 129.1 237 = 124.3 37 10 = 37 11 37 12 = 113.3	2345 = 5.5 7328 = 7.6 1546 = 189.0 6459 = 61.8 237 10 = −2.0 237 11 = 118.0 237 12 = 238.0
(c)	12 = 1.360 23 = 1.395 34 = 1.421 45 = 1.348 51 = 1.349 26 = 1.220 37 = 1.419 48 = 1.101 59 = 1.103 7 10 = 7 11 = 7 12 = 1.119	123 = 105.8 234 = 107.8 345 = 106.5 512 = 110.6 459 = 135.1 548 = 130.9 326 = 126.8 237 = 128.2 37 10 = 37 11 = 37 12 = 113.5	237 10 = 67.0 237 11 = 187.0 237 12 = 307.0
(d)	12 = 1.302 23 = 1.328 34 = 1.427 45 = 1.458 51 = 1.419 56 = 1.250 37 = 1.426 28 = 1.118 49 = 1.116 7 10 = 7 11 7 12 = 1.118 6 13 = 1.021	123 = 111.2 234 = 109.3 345 = 104.4 512 = 110.8 456 = 132.2 328 = 127.9 237 = 127.6 56 13 = 125.7 37 10 = 37 11 = 37 12 = 113.4	7328 = 14.9 1549 = 134.3 2345 = −4.6 237 10 = −5.5 237 11 = 114.5 237 12 = 234.5
(e)	12 = 1.280 23 = 1.346 34 = 1.464 45 = 1.475 51 = 1.382 46 = 1.273 37 = 1.427 28 = 1.118 59 = 1.312 7 10 = 7 11 = 7 12 = 1.119 6 13 = 1.029	123 = 112.8 234 = 106.7 345 = 103.4 512 = 111.5 459 = 111.2 546 = 142.6 328 = 125.8 237 = 123.6 37 10 = 37 11 = 37 12 = 113.5 46 13 = 115.1	1546 = 190.3 7328 = 12.1 6459 = 73.2 546 13 = −10.7 237 10 = −2.3 237 11 = 117.7 237 12 = 237.7
(f)	12 = 1.360 23 = 1.394 34 = 1.422 45 = 1.348 51 = 1.348 26 = 1.272 37 = 1.414 48 = 1.101 59 = 1.103 7 10 = 7 11 = 7 12 = 1.120 6 13 = 1.030	123 = 106.7 234 = 107.0 345 = 106.8 512 = 110.1 459 = 133.8 845 = 131.2 326 = 124.6 237 = 128.8 37 10 = 37 11 = 37 12 = 113.8 26 13 = 117.1	237 10 = 59.8 237 11 = 179.8 237 12 = 299.8

FIGURE 1 (a)—(f) Calculated distribution of formal charge (in parentheses), heats of formation **(ΔH_f/kJ mol^{-1})**, dipole moments **(μ/D)**, and geometries for the isomeric *N*-methyloxazoles (2)—(7)

classical valence bond structures, *i.e.* (4a) and (7a). The ring systems are calculated to be planar (all ring atoms essentially sp^2 hybridized) and to have normal bond lengths for the types of bonds present.


(4a)


(7a)

A consideration of the calculated geometries and distributions of formal charge for the mesoionic 5-oxo- and 5-imino-oxazoles (2) and (5) respectively, shows that the situation is somewhat more complex in these cases. The calculated lengths of the O(1)–C(2) bonds in (2) (1.298 Å) and (5) (1.302 Å) are much less than those of the O(1)–C(5) bond (1.439 and 1.419 Å respectively). An unusually large value for the endocyclic C–O bond length in 4,4′-dichloro-3,3′-ethylenedisydnone (1.407 Å) has been found experimentally.[11]

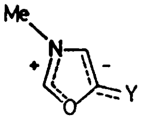
The calculated bond length of the C(5)–O(6) bond of (2) is 1.215 Å and of the C(5)–N(6) bond of (5) is 1.250 Å. The i.r. frequency for the exocyclic C–O bond of 2,4-diaryl-3-methyloxazolium 5-oxide (*ca.* 1 700 cm^{-1}) is *ca.* 100 cm^{-1} lower than that for a five-membered ring azlactone carbonyl.[13] This observation and the results presented here suggest that the exocyclic C–O bonds of mesoionic oxazoles possess a considerable amount of double bond character. Furthermore, the calculated C(5)–O(6) bond length of (2) agrees with the experimental value obtained for the exocyclic C–O of 4,4′-dichloro-3,3′-ethylenedisydnone (1.215 Å).[11]

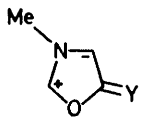
The calculated C(2)–N(3) bond lengths (1.33 Å) in (2) and (5) are nearly the same as the C–N bond length in pyridine (1.34 Å) while the calculated N(3)–C(4) bond lengths are *ca.* 0.1 Å longer. The calculated C(4)–C(5) bond lengths in (2) and (5) (1.404 and 1.438 Å) are intermediate in length between an sp^2–sp^2 carbon–carbon single and double bond.

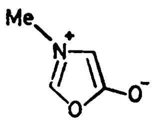
The calculated dihedral angles for (2) suggest that the ring atoms of (2) are all sp^2 hybridized while in the 5-imino-derivative (5), H(8) is twisted out of the plane formed by C(2)–N(3)–C(7) by 14.9° and H(9) is twisted out of the C(4)–C(5)–O(1) plane by 45.7°.

Examination of the calculated distributions of formal charge in (2) and (5) shows large positive charges at C(2) (0.328 and 0.348 respectively), large negative charges at C(4) (−0.464 and −0.354 respectively), and small positive charges at N(3) (0.140 and 0.099 respectively). The calculated geometries and distributions of formal charge in (2) and (5) imply that these species cannot be satisfactorily represented by single classical structures. They are, however, better represented by the structures (8) and (9) than by (10), although structures of the latter type are very often used to depict such mesoionic compounds.[20]

The calculated geometries and distributions of formal charge in the mesoionic 4-oxo- and 4-imino-oxazoles (3) and (6) show that these species are even harder to depict in terms of classical structures than the 5-oxo- and 5-imino-isomers. In these cases the calculated O(1)–C(2) bond lengths are again *ca.* 0.1 Å shorter than the O(1)–C(5) bond lengths. The calculated dihedral angles for (3) and (6) show that H(9) is twisted 61.8 and 73.2° respectively out of the plane defined by C(4)–C(5)–O(6). The C(5)–O(1) bond distances in (3) and (6) are 1.38 Å, a value which is longer than a C_{sp^2}–O bond length (*ca.* 0.03 Å) and shorter than a C_{sp^3}–O bond length (*ca.* 0.04 Å). The bond angles C(4)–C(5)–H(9) are 120.7 and 111.2° in (3) and (6). These bond angles are 10—30° smaller than the C–C–H bond angles in the other isomeric oxazoles (2), (4), (5), and (7). The calculated formal charges at O(1) and C(5) are both negative in (3) [O(1), −0.266; C(5), −0.152] and (6) [O(1), −0.270; C(5), −0.108]; the increase in p character of the orbital at C(5) probably minimizes the interaction between the negative charges at these atoms.


(8)


(9)


(10)

Y = O or NH

The calculated geometries and distributions of formal charge in (3) and (6) suggest that these are species for which no satisfactory classical structures can be written.

An examination of the calculated dipole moments of the oxazoles (2)—(7) shows the order 5-oxo (7.38 D) > 4-oxo (5.81 D) > 2-oxo (4.60 D) and 5-imino (4.88 D) > 4-imino (4.18 D) > 2-imino (2.58 D). It is quite reasonable that the mesoionic 5-oxo-, 5-imino-, 4-oxo-, and 4-imino-oxazoles should have higher dipole moments than the non-mesoionic 2-oxo- and 2-imino-isomers due to the charge separation in the former compounds. The calculated dipole moment for the 5-oxo-oxazole (2) is 7.38 D which is somewhat greater than the experimental values [21] for sydnone derivatives (5.0—6.9 D).

Very little is known about the structure and chemistry of mesoionic imidazoles. Mesoionic 4(5)-oxo- and 4(5)-imino-imidazoles have been prepared;[2a] in most cases one of the ring nitrogens is also part of a pyridine ring. A monocyclic mesoionic 4(5)-oxo-imidazole bearing an acyl group at the 4-position has been prepared and is very stable toward acids and alkali.[22]

Figure 2 shows the calculated distributions of formal charge, heats of formation, dipole moments, and geometries for the *NN*′-dimethyl-4(5)-oxo- and -4(5)-imino-imidazoles (11) and (13) and for the non-mesoionic *NN*′-dimethyl-2-oxo- and -2-imino-imidazoles (12) and (14).

The calculated heats of formation for (11)—(14) show that these species are less stable than the corresponding oxazoles by 167—233 kJ mol^{-1}. The stabilities relative

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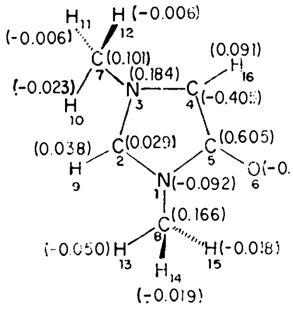
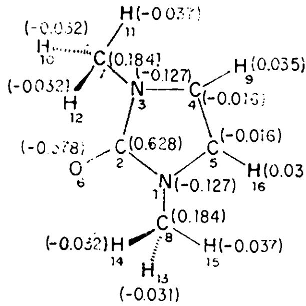
[21] R. W. Hill and L. E. Sutton, *J. Chim. phys.*, 1949, **46**, 244.

[22] A. Lawson and D. H. Miles, *J. Chem. Soc.*, 1959, 2865.

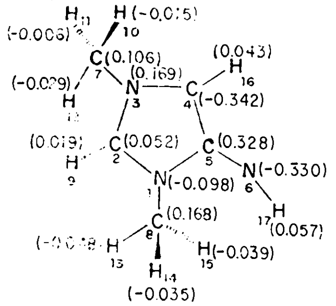
to one another parallel the oxazoles completely, *i.e.*, the 2-oxo is more stable than the 4(5)-oxo-isomer (by 101 kJ mol^{-1}) and the 2-imino is more stable than the 4(5)-imino-derivative (by 91 kJ mol^{-1}) while the oxo-derivatives are more stable than the corresponding imino-compounds (by *ca.* 250 kJ mol^{-1}).



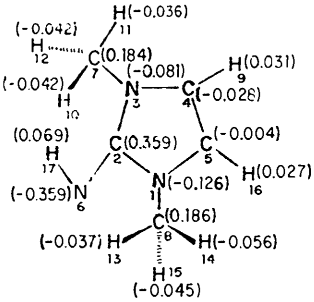
(a) (11) ΔH_f −19·3 kJ mol^{-1}; μ 6·87 D



(b) (12) ΔH_f −120·6 kJ mol^{-1}; μ 3·93 D



(c) (13) ΔH_f 227·7 kJ mol^{-1}; μ 5·23 D



(d) (14) ΔH_f 136·6 kJ mol^{-1}; μ 2·50 D

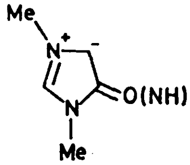
Bond length (Å)	Bond angle (°)	Dihedral angle (°)
12 = 1.365 23 = 1.333 34 = 1.394 45 = 1.410 51 = 1.448 56 = 1.221 37 = 1.427 18 = 1.429 29 = 1.113 4 16 = 1.098 7 10 = 7 11 = 7 12 = 8 13 = 8 14 = 8 15 = 1.119	123 = 108.1 234 = 109.6 345 = 109.4 512 = 110.6 456 = 136.6 518 = 128.0 329 = 124.8 237 = 126.0 54 16 = 129.7 37 10 = 37 11 = 37 12 = 18 13 = 18 14 = 18 15 = 113.5	237 10 = 0.2 237 11 = 120.2 237 12 = 240.2 518 13 = 179.5 518 14 = 299.5 518 15 = 419.5
12 = 23 = 1.394 34 = 51 = 1.408 45 = 1.354 26 = 1.220 37 = 18 = 1.422 49 = 5 16 = 1.103 7 10 = 7 11 = 7 12 = 8 13 = 8 14 = 8 15 = 1.119	123 = 104.7 234 = 512 = 110.0 345 = 107.7 45 16 = 129.9 945 = 129.8 518 = 123.6 326 = 127.6 237 = 126.4 37 10 = 37 11 = 37 12 = 18 13 = 18 14 = 18 15 = 113.6	237 10 = 59.9 237 11 = 179.9 237 12 = 299.9 518 13 = 120.7 518 14 = 240.7 518 15 = 360.7
12 = 1.369 23 = 1.328 34 = 1.403 45 = 1.450 51 = 1.450 56 = 1.264 37 = 1.427 18 = 1.425 29 = 1.116 4 16 = 1.109 6 17 = 1.026 7 10 = 7 11 = 7 12 = 1.118 8 13 = 8 14 = 8 15 = 1.120	123 = 108.7 234 = 110.9 345 = 107.0 512 = 110.5 456 = 127.6 54 16 = 121.7 518 = 128.7 329 = 124.7 237 = 125.6 56 17 = 122.9 37 10 = 37 11 = 37 12 = 113.5 18 13 = 18 14 = 18 15 = 114.1	2345 = −5.6 4518 = 176.8 7329 = 11.2 154 16 = 145.8 237 10 = 114.3 237 11 = 234.3 237 12 = 354.3 518 13 = 180.2 518 14 = 300.2 518 15 = 420.2
12 = 1.406 23 = 1.397 34 = 1.410 45 = 1.352 51 = 1.410 26 = 1.278 37 = 1.417 18 = 1.418 49 = 1.103 5 16 = 1.102 6 17 = 1.030 7 10 = 7 11 = 7 12 = 8 13 = 8 14 = 8 15 = 1.120	123 = 104.7 234 = 512 = 109.7 345 = 108.3 45 16 = 129.5 945 = 129.8 518 = 121.7 326 = 120.5 237 = 127.3 26 17 = 117.3 37 10 = 37 11 = 37 12 = 113.9 18 13 = 18 14 = 18 15 = 114.0	237 10 = 59.7 237 11 = 179.7 237 12 = 299.7 518 13 = 158.8 518 14 = 278.8 518 15 = 398.8

FIGURE 2 (a)—(d) Calculated distribution of formal charge (in parentheses), heats of formation (ΔH_f/kJ mol^{-1}), dipole moments (μ/D), and geometries for the isomeric *NN'*-dimethylimidazoles (11)—(14)

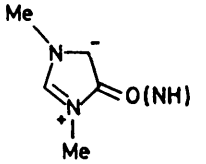
As in the case of the 2-oxo- and 2-imino-oxazoles (3) and (6), the calculated geometries and distributions of formal charge for the 2-oxo- and 2-imino-imidazoles (12) and (14) show nothing unusual about these species. These too are adequately represented by classical, non-charge-separated valence bond structures.

The calculated geometry and distribution of formal charge for the mesoionic 4(5)-oxoimidazole (11) parallel those for the 5-oxo-oxazole (2) very closely. The calculated C(5)–O(6) bond length (1.221 Å) is only slightly longer than that in (2) (1.215 Å) and again the N(1)–C(2) bond length is calculated to be *ca.* 0.1 Å shorter than the N(1)–C(5) bond length. A similar situation occurs in the 4(5)-imino-derivative (13).

An interesting point arises from the calculated geometries of these species. In both the 4(5)-oxo- and 4(5)-imino-imidazoles the N(1)–C(2) bond is longer than the N(3)–C(2) bond by 0.03—0.04 Å. This suggests that the resonance forms favouring the mesoionic 5-oxo-(imino)imidazole (15) are more important in the overall resonance hybrid than those favouring the mesoionic 4-oxo(imino)imidazole (16). This is not surprising in view of the greater stability of the 5-oxo- and 5-imino-compounds relative to the 4-oxo- and 4-imino-derivatives in the oxazole series. The charge distributions also support this view.

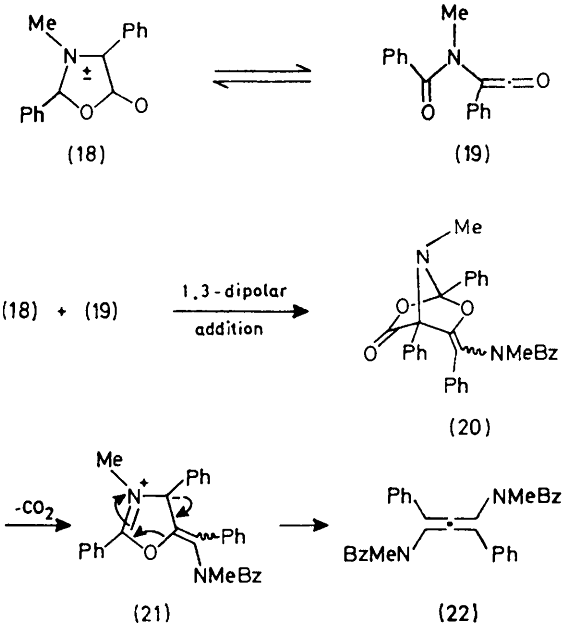


(15)



(16)

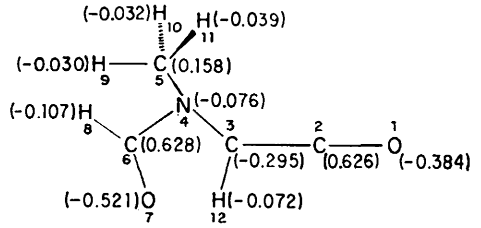
The calculated dihedral angles for the 4(5)-imino-imidazole (13) show that H(9) is twisted out of the C(2)–N(3)–C(7) plane by 11.2° and H(16) is twisted out of the N(1)–C(5)–C(4) plane by 34.2°. The conformation of (13) is consequently very similar to the 5-imino-oxazole (5).



The calculated dipole moments for (11)—(14) again show that the charge-separated mesoionic species (11) and (13) have much higher values for μ than the non-mesoionic species (12) and (14), as expected.

Finally, Huisgen and his co-workers studied the pyrolysis of 3-methyl-4,5-diphenyloxazolium 5-oxide (18) at 115—140°, leading to the allene (22).[16] The proposed mechanism for the formation of the allene (22) involves the formation of a keten valence tautomer (19) of (18). 1,3-Dipolar addition of the keten (19) to the mesoionic oxazole (18), followed by loss of CO_2 from the adduct (20) and rearrangement of the resulting zwitterionic species (21), results in the formation of the allene (22).

Figure 3 shows the calculated distribution of formal charge, heat of formation, dipole moment, and geometry for the keten (17). The calculated heat of formation of (17) is —194.2 kJ mol^{-1}, a value which is only 6.3 kJ mol^{-1} higher than that for its valence tautomer (2). However, the MINDO/3 method overestimates the stability of systems with *sp* hybridized centres by *ca.* 25—30 kJ mol^{-1} (*e.g.*, the heat of formation of keten is calculated to be some 27.2 kJ mol^{-1} lower than the experimental value). Consequently a good estimate for the heat of formation of the keten valence tautomer (18) would seem to be —164 to —169 kJ mol^{-1}, a value which is 31—36 kJ mol^{-1} higher than that calculated for (2). The keten valence tautomer (19) has not been observed spectroscopically, presumably due to its low equilibrium concentration.[3] Our calculated values for the heats of formation of (2) and (17) fully support the intermediacy of species such as (17) (albeit in low concentration) in the pyrolysis of mesoionic 5-oxo-oxazoles.



(17) ΔH_f -194·2 kJ mol^{-1}; μ 3·66 D

Bond length (Å)	Bond angle (°)	Dihedral angle (°) *
$\bar{1}\bar{2} = 1.165$	$\bar{1}\bar{2}\bar{3} = 180.6$	$\bar{3}\bar{4}\bar{6}\bar{7} = -4.0$
$\bar{2}\bar{3} = 1.327$	$\bar{2}\bar{3}\bar{4} = 126.2$	$\bar{6}\bar{4}\bar{5}\bar{9} = 3.3$
$\bar{3}\bar{4} = 1.418$	$\bar{3}\bar{4}\bar{5} = 115.7$	$\bar{6}\bar{4}\bar{5}\ \bar{1}\bar{0} = 123.3$
$\bar{4}\bar{5} = 1.430$	$\bar{3}\bar{4}\bar{6} = 120.7$	$\bar{6}\bar{4}\bar{5}\ \bar{1}\bar{1} = 243.3$
$\bar{4}\bar{6} = 1.367$	$\bar{4}\bar{6}\bar{8} = 111.6$	
$\bar{6}\bar{7} = 1.205$	$\bar{7}\bar{6}\bar{8} = 122.3$	
$\bar{6}\bar{8} = 1.140$	$\bar{2}\bar{3}\ \bar{1}\bar{2} = 115.0$	
$\bar{3}\ \bar{1}\bar{2} = 1.109$	$\bar{4}\bar{5}\ \bar{1}\bar{0} = \bar{4}\bar{5}\ \bar{1}\bar{1} =$	
$\bar{5}\ \bar{1}\bar{0} = \bar{5}\ \bar{1}\bar{1} =$	$\bar{4}\bar{5}\ \bar{1}\bar{2} = 113.7$	
$\bar{5}\ \bar{1}\bar{2} = 1.119$		

* Dihedral angle $\overline{ijkl}$ is defined as the angular displacement of the $\overline{kl}$ distance relative to that of $\overline{ij}$ measured clockwise along the direction $j \longrightarrow k$.

FIGURE 3 Calculated distribution of formal charge (in parentheses), heat of formation (ΔH_f/kJ mol^{-1}), dipole moment (μ/D), and geometry for *N*-methylformamidoketen (17)

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