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### Structure of the Mesoionic Compound *N*-[1-Methyl-3-(*p*-tolyl)-4-(1,2,3-triazolio)]acetamidate (MMTAT), $C_{12}H_{14}N_4O$

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**Abstract.**  $M_r = 230.28$ , triclinic,  $P\bar{1}$ ,  $a = 11.940$  (18),  $b = 7.642$  (9),  $c = 7.378$  (9) Å,  $\alpha = 79.76$  (1),  $\beta = 108.17$  (1),  $\gamma = 106.78$  (1)°,  $Z = 2$ ,  $V = 609.5$  Å<sup>3</sup>,  $D_x = 1.254$ ,  $D_m = 1.250$  Mg m<sup>-3</sup>, m.p. = 492–494 K,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.091$  mm<sup>-1</sup>,  $F(000) = 244$ ,  $T = 298$  K. Final  $R = 0.067$  for 641 independent non-zero reflexions. The planar mesoionic triazolio ring forms an almost coplanar conjugated system with the acetamidate group. The bond lengths found are in good agreement with CNDO2 calculations of  $\pi$ -bond order and  $\pi$ -charge densities. The possibility of the existence of an open-chain structure is excluded.

**Introduction.** Interest in mesoionic compounds has been intense during the past three decades due to the fact that some of these participate in chemical reactions providing new methods for the synthesis of a large variety of heterocyclic compounds while others show important pharmacological activity.

The crystal-structure analysis of the mesoionic title compound MMTAT was undertaken because of the need to know the exact form of the molecule in order to explain its chemical reactivity.

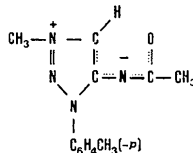
**Experimental.** Transparent, colourless, needle-like crystals prepared by one of us (Tsoleridis, 1983),  $0.08 \times 0.10 \times 0.36$  mm.  $D_m$  by flotation in a mixture of  $\text{CCl}_4$  and petroleum ether. Computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, three-dimensional data, graphite-monochromated  $\text{Mo } K\alpha$ ,  $\omega$  scan mode. Cell parameters and standard deviations by least-squares analysis of measured  $\theta$  angles of 196 strongest reflexions. Intensity statistics indicated  $P\bar{1}$ . Three standard reflexions without significant intensity variation. 2267 measured reflexions,  $\theta = 3$ –22°, max.  $hkl = 11, \pm 7, \pm 8$ ,  $R_{\text{int}} = 0.07$ , 2127 unique reflexions, 641 with  $I > 2\sigma(I)$ . No absorption correction. Direct methods with *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), phases of 140 reflexions with  $E > 1.754$ , all non-H atoms located on  $E$  map. Full-matrix least squares using  $F$  magnitudes, *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). H atoms located on difference Fourier map, included with isotropic temperature coefficients but not refined.  $w = (F_{\text{obs}}/A)^2$  if  $F_{\text{obs}} \leq A$ , otherwise  $w = (A/F_{\text{obs}})^2$  with  $A = 14.0$ ;  $R = 0.067$ ,  $R_w = 0.063$ ,  $S = 0.66$ .  $\Delta/\sigma_{\text{max}}$

$= 0.71$ ,  $\Delta/\sigma_{av} = 0.19$ .  $\Delta\rho = -0.24-0.26 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final positional parameters and equivalent isotropic temperature coefficients for the non-H atoms are given in Table 1.\* Interatomic distances and angles are given in Table 2.

A clinographic projection of the MMTAT molecule is shown in Fig. 1. The triazolio ring forms an almost coplanar conjugated system with the acetamidate group, the angle between their planes being only  $9.3(3)^\circ$ . The benzene ring is inclined at an angle of  $34.6(1)^\circ$  to the plane of the triazolio ring.

The mesoionic triazolio ring is planar to within  $\pm 0.013(11) \text{ \AA}$ . The N(2)–N(3) bond,  $1.32(1) \text{ \AA}$  in length, shows double-bond character. The same holds for the C(1)–N(4) bond, while the C(1)–C(2) bond length is significantly longer than  $1.337 \text{ \AA}$ , the usually accepted C=C distance (*International Tables for X-ray Crystallography*, 1968). All the other ring distances are intermediate between single and double-bond lengths and compare very well with the values accepted for aromatic distances. The N(3)–C(3) distance is as expected. In the acetamidate group the bond length N(4)–C(4) =  $1.35(1) \text{ \AA}$  is much shorter than the usual N–C single-bond distance and, taken in conjunction with the character of the C(1)–N(4) bond, indicates the existence of a partial double bond between N(4) and C(4). This, in turn, explains why the distance C(4)–O =  $1.26(1) \text{ \AA}$  is slightly longer than the value for normal carbonyl groups. The C(4)–C(5) bond length is normal. The description given above agrees, to a good approximation, with CNDO2 calculations of  $\pi$ -bond order and  $\pi$ -charge densities (Table 3). The combination of the observed bond distances and the result of the CNDO2 calculations leads to the following structure for MMTAT



This is in agreement with the structures proposed for other mesoionic compounds (Ohta & Kato, 1969; Ollis & Ramsden, 1976).

\* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, coordinates and isotropic temperature factors for H atoms, C–H bond distances, least-squares-plane calculations and selected intermolecular contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38733 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors for the non-H atoms in MMTAT

Here and throughout this paper the e.s.d.'s are given in parentheses and refer to the last digit.

	x	y	z	$B_{eq}^*(\text{\AA}^2)$
N(1)	0.1653 (6)	0.0355 (10)	0.6947 (11)	3.2
N(2)	0.0865 (7)	−0.0049 (10)	0.8061 (11)	4.1
N(3)	0.0192 (6)	−0.1682 (9)	0.7581 (10)	3.4
N(4)	0.2144 (6)	−0.0850 (9)	0.4631 (11)	3.7
C(1)	0.1454 (8)	−0.1019 (11)	0.5771 (14)	3.2
C(2)	0.0501 (8)	−0.2350 (12)	0.6285 (12)	3.3
C(3)	−0.0771 (8)	−0.2576 (12)	0.8518 (14)	4.6
C(4)	0.1806 (9)	−0.2159 (13)	0.3425 (13)	3.7
C(5)	0.2670 (9)	−0.1926 (14)	0.2211 (14)	5.7
C(6)	0.2519 (8)	0.2096 (13)	0.7107 (13)	3.3
C(7)	0.2190 (8)	0.3574 (12)	0.7457 (13)	3.6
C(8)	0.3053 (9)	0.5260 (12)	0.7639 (13)	4.1
C(9)	0.4212 (8)	0.5508 (13)	0.7463 (13)	3.9
C(10)	0.4510 (9)	0.3987 (13)	0.7121 (14)	4.9
C(11)	0.3681 (8)	0.2263 (11)	0.6978 (14)	4.6
C(12)	0.5119 (9)	0.7343 (14)	0.7631 (15)	5.2
O(1)	0.0877 (6)	−0.3491 (8)	0.3238 (9)	4.5

$$* B_{eq} = \frac{2}{3} \pi^2 \text{ trace } \bar{U}$$

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

N(1)–N(2)	1.37 (1)	N(1)–C(6)	1.43 (1)
N(2)–N(3)	1.32 (1)	C(6)–C(7)	1.39 (2)
N(3)–C(2)	1.35 (1)	C(7)–C(8)	1.40 (1)
C(2)–C(1)	1.39 (1)	C(8)–C(9)	1.39 (2)
C(1)–N(1)	1.40 (1)	C(9)–C(10)	1.39 (2)
N(3)–C(3)	1.46 (1)	C(10)–C(11)	1.40 (1)
C(1)–N(4)	1.32 (1)	C(11)–C(6)	1.39 (2)
N(4)–C(4)	1.35 (1)	C(9)–C(12)	1.50 (1)
C(4)–O(1)	1.26 (1)		
C(4)–C(5)	1.52 (2)		
C(1)–N(1)–N(2)	113.7 (0.7)	C(1)–N(4)–C(4)	116.5 (0.7)
N(1)–N(2)–N(3)	102.1 (0.8)	N(4)–C(4)–C(5)	113.8 (0.8)
N(2)–N(3)–C(2)	114.6 (0.8)	N(4)–C(4)–O(1)	126.5 (1.0)
N(3)–C(2)–C(1)	107.6 (0.8)	O(1)–C(4)–C(5)	119.7 (0.9)
C(2)–C(1)–N(1)	101.9 (0.9)		
C(11)–C(6)–C(7)	121.3 (0.8)	C(6)–N(1)–N(2)	116.5 (0.8)
C(6)–C(7)–C(8)	118.2 (0.9)	C(6)–N(1)–C(1)	129.8 (0.9)
C(7)–C(8)–C(9)	122.6 (1.0)	N(2)–N(3)–C(3)	117.7 (0.9)
C(8)–C(9)–C(10)	117.5 (0.8)	C(2)–N(3)–C(3)	127.6 (0.7)
C(9)–C(10)–C(11)	121.7 (1.0)	N(4)–C(1)–C(2)	136.9 (0.9)
C(10)–C(11)–C(6)	118.7 (1.0)	N(4)–C(1)–N(1)	121.1 (0.7)
		N(1)–C(6)–C(7)	118.9 (0.9)
		N(1)–C(6)–C(11)	119.7 (0.9)
		C(12)–C(9)–C(8)	121.6 (1.0)
		C(12)–C(9)–C(10)	120.9 (1.0)

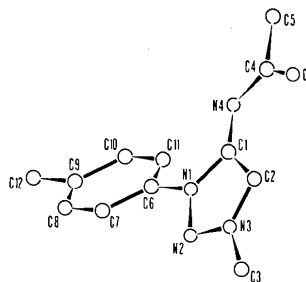


Fig. 1. Clinographic projection of the MMTAT molecule.

The bond angles around C(1), and especially the angle  $C(2)-C(1)-N(4) = 136.9(9)^\circ$  show the same deviation from their expected values, as in the case of 3-(*p*-bromophenyl)sydnone (Bärnighausen, Jellinek, Munnik & Vos, 1963) and 4,4'-dichloro-3,3'-ethylenedisynone (Thiessen & Hope, 1967). In the case of these sydnones, the deformation of angles around C(1), together with the observed bond lengths, were attributed to the significant contribution of a valence tautomeric ketene-like form to the mesomeric sydnone structures. In the case of the present structure, however, the experimental results and the calculations given above exclude the possibility of the existence of

Table 3.  $\pi$ -Bond order and  $\pi$ -charge densities according to CNDO2 calculations

$\pi$ -Bond order		$\pi$ -Charge (e)	
N(1)-N(2)	0.4293	N(1)	1.5748
N(2)-N(3)	0.6544	N(2)	1.3263
N(3)-C(2)	0.5784	N(3)	1.2791
C(2)-C(1)	0.5850	N(4)	1.4621
C(1)-N(1)	0.4615	C(1)	0.8681
N(3)-C(3)	0.1807	C(2)	1.2514
C(1)-N(4)	0.5816	C(3)	1.0140
N(4)-C(4)	0.4578	C(4)	0.7800
C(4)-O(1)	0.7628	C(5)	0.9751
C(4)-C(5)	0.2154	C(6)	1.0145
N(1)-C(6)	0.2237	C(7)	1.0068
C(6)-C(7)	0.3067	C(8)	0.9982
C(7)-C(8)	0.5144	C(9)	0.9944
C(8)-C(9)	0.3079	C(10)	0.9976
C(9)-C(10)	0.3055	C(11)	1.0011
C(10)-C(11)	0.5159	C(12)	0.9769
C(11)-C(6)	0.3044	O(1)	1.4511
C(9)-C(12)	0.1929		

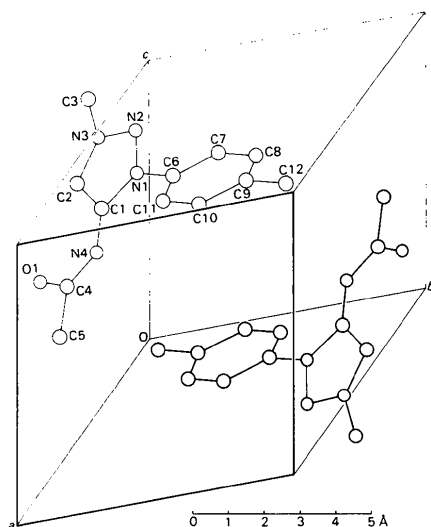


Fig. 2. Clinographic projection of MMTAT showing the molecular packing in the unit cell.

an open-chain resonance structure. On the contrary, the observed asymmetry of bond angles may be attributed to steric strain caused by the triazolio ring and the carbonyl group. In fact, the  $C(2)\cdots C(4) = 2.95(2)$  and  $C(2)\cdots O = 2.75(1)$  Å contact distances are slightly shorter than the sums, 3.06 and 2.95 Å, of the corresponding van der Waals radii (Bondi, 1964).

The coordination of N(1) is planar but the angles  $C(1)-N(1)-C(6)$  and  $N(2)-N(1)-C(6)$  differ by  $13.3^\circ$ . Since the contact distances  $N(4)\cdots C(11) = 3.00(1)$  and  $N(4)\cdots H(C11) = 2.44(1)$  Å are almost equal to the sums, 2.99 and 2.52 Å, of the corresponding van der Waals radii (Bondi, 1964), this deformation may be attributed to the steric interaction between the benzene ring and the acetamide group. In addition, this interaction is mainly responsible for the twisting of the benzene ring around the N(1)-C(6) bond.

The geometrical features of the benzene ring are in very good agreement with the usually accepted values. The mean bond length is 1.39(2) Å.

A projection of the structure showing the molecular packing of MMTAT in the unit cell is given in Fig. 2.\*

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\* A list of selected intermolecular contact distances has been deposited. See previous footnote.

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