

2:1 Molecular Complex of 2-(α -Hydroxyimino-2,6-dimethylbenzyl)-5-*p*-tolyl-2*H*-tetrazole with Triethylammonium 5-*p*-Tolyltetrazolide, $2C_{17}H_{17}N_5O \cdot C_6H_{16}N^+ \cdot C_8H_7N_4^-$

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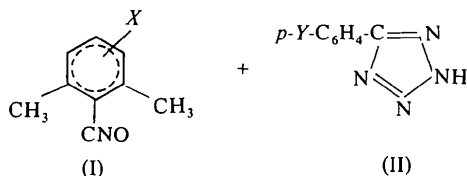
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Abstract. $M_r = 876.08$, triclinic, $P\bar{1}$, $a = 20.10$ (2), $b = 17.22$ (2), $c = 7.84$ (1) Å, $\alpha = 111.2$ (3), $\beta = 105.5$ (3), $\gamma = 93.5$ (3)° [Niggli reduced cell: $a = 16.14$ (2), $b = 19.53$ (2), $c = 7.84$ (1) Å, $\alpha = 97.3$ (3), $\beta = 95.7$ (3), $\gamma = 99.2$ (3)°; transformation matrix: $01\bar{1}/10\bar{1}/001$], $V = 2400$ (9) Å³, $Z = 2$, $D_m = 1.20$, $D_x = 1.21$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 5.96$ cm⁻¹, $F(000) = 932$, $T = 293$ K, final $R = 0.089$ for 4912 observed reflections. In the asymmetric unit the 5-*p*-tolyltetrazolide anion is hydrogen bonded to the triethylammonium cation and to the oximic hydroxyl groups of two molecules of the 2,5-disubstituted tetrazole. In all three molecules the tetrazole and benzene rings are not coplanar, which suggests there is little π -electron delocalization. The bond lengths and angles are normal.

Introduction. The mechanism of addition reactions of aryl-substituted 5-phenyltetrazoles (II) to benzonitrile oxides (I) has been investigated (Beltrame & Gelli, 1984).



- (a) $X = 4-OCH_3$; (b) $X = 4-CH_3$; (r) $Y = OCH_3$; (s) $Y = CH_3$;
 (c) $X = 4-H$; (d) $X = 4-Br$; (t) $Y = H$; (w) $Y = Cl$;
 (e) $X = 3,5-Cl_2-4-CH_3$

The reactions were carried out in chloroform in the presence of triethylamine, which, as evidenced by H NMR spectra, is always present in the reaction products obtained by crystallization from the reaction mixture: the addition compounds decompose only on silica-gel column chromatography by elution with *n*-hexane:ethyl acetate 9:1.

As chemical analysis was not conclusive concerning the nature of these products, an X-ray structural investigation was undertaken on the derivative obtained from 2,6-dimethylbenzonitrile oxide (Ic) and 5-*p*-tolyltetrazole (IIs).

Experimental. Colourless crystals m.p. 395 K, recrystallization from benzene; D_m by flotation; crystal $0.2 \times 0.5 \times 0.8$ mm mounted along *c*. Automatic Siemens AED single-crystal diffractometer, Ni-filtered $Cu K\alpha$ radiation, accurate cell dimensions by least-squares fitting of 15 reflections $27 \leq 2\theta \leq 50^\circ$; intensity measurements in $\theta-2\theta$ scan mode; 5965 unique reflections $2\theta \leq 110^\circ$ ($2\bar{1} \leq h \leq 21$, $1\bar{7} \leq k \leq 17$, $0 \leq l \leq 8$); three standard reflections ($6\bar{5}3$, $3\bar{2}3$, $3\bar{2}3$) recorded every 200 reflections showed average decline in intensity of 20% by end of data collection. Appropriate scale factors applied and intensities corrected for Lorentz-polarization factors. 4912 reflections with $I \geq 2.5\sigma(I)$ used in structure determination and refinement. Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares (Immirzi, 1967, 1973), $\sum w\Delta F^2$ refined, $w = 1/(12 + F_o + 0.025F_o^2)$. Difference Fourier synthesis in final stages of refinement indicated positions of most H atoms, residual electron density within ± 0.30 e Å⁻³. H contribution included in calculated positions and held fixed in final least-squares cycles; $R = 0.089$, $wR = 0.106$, $S = 3.0$, max. $\Delta/\sigma = 0.5$, av. $\Delta/\sigma = 0.1$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39863 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Final atomic coordinates are given in Table 1.

The structural analysis shows that this compound has the complex structure shown in Fig. 1: it is formed by two molecules of 2-(α -hydroxyimino-2,6-dimethylbenzyl)-5-*p*-tolyl-2*H*-tetrazole, hereafter molecules 1 and 2, one molecule of 5-*p*-tolyltetrazole, hereafter molecule 3, and one molecule of Et₃N.

The 5-*p*-tolyltetrazole lies in the middle of the complex with the N(31) and N(34) nitrogen atoms

engaged in short interactions with the oximic hydroxyl groups of molecules 1 and 2 and N(33) interacting with the nitrogen atom of Et₃N. The values of O(18)···N(31) 2·690 (7) Å, O(28)···N(34) 2·706 (8) Å and N(33)···N(4) 2·827 (8) Å fall in the range reported for hydrogen bonds.

The values of bond distances and angles in the molecules of the complex are given in Table 2.

Table 1. Positional parameters ($\times 10^4$) and isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
N(11)	1578 (2)	2960 (2)	1048 (5)	5·77 (7)
N(12)	2089 (2)	2672 (2)	2029 (5)	5·67 (7)
N(13)	2458 (1)	2354 (2)	859 (4)	3·85 (5)
N(14)	2222 (1)	2410 (2)	-840 (4)	4·42 (6)
C(15)	1676 (2)	2795 (2)	-657 (4)	3·51 (6)
C(16)	3024 (2)	1921 (2)	1412 (5)	3·72 (6)
N(17)	3640 (1)	2101 (2)	1307 (4)	4·20 (5)
O(18)	3730 (1)	2742 (2)	664 (4)	4·93 (5)
C(19)	1219 (2)	3019 (2)	-2158 (5)	3·77 (6)
C(110)	1419 (2)	3022 (2)	-3699 (5)	4·63 (7)
C(111)	981 (2)	3250 (2)	-5088 (5)	4·87 (7)
C(112)	358 (2)	3481 (2)	-4951 (5)	4·49 (7)
C(113)	-112 (2)	3721 (3)	-6519 (6)	5·87 (9)
C(114)	149 (2)	3461 (2)	-3417 (5)	4·89 (7)
C(115)	570 (2)	3237 (2)	-2031 (5)	4·71 (7)
C(116)	2875 (2)	1285 (2)	2133 (5)	4·13 (7)
C(117)	3052 (2)	1478 (2)	4097 (6)	5·16 (8)
C(118)	3420 (3)	2385 (3)	5575 (7)	7·27 (11)
C(119)	2917 (2)	842 (3)	4748 (7)	6·48 (10)
C(120)	2631 (2)	55 (3)	3487 (7)	6·68 (10)
C(121)	2432 (2)	-170 (3)	1499 (6)	5·75 (9)
C(122)	2562 (2)	463 (2)	839 (5)	4·91 (8)
C(123)	2348 (2)	214 (3)	-1369 (7)	6·50 (10)
N(21)	9187 (2)	1605 (2)	-2693 (5)	5·98 (7)
N(22)	8717 (2)	1960 (2)	-3524 (5)	5·59 (7)
N(23)	8359 (1)	2290 (2)	-2303 (4)	4·01 (5)
N(24)	8587 (1)	2163 (2)	-661 (4)	4·18 (5)
C(25)	9100 (2)	1738 (2)	-950 (5)	3·78 (6)
C(26)	7845 (2)	2796 (2)	-2713 (5)	3·72 (6)
N(27)	7262 (1)	2786 (2)	-2361 (4)	4·52 (6)
O(28)	7126 (1)	2207 (2)	-1611 (4)	5·15 (5)
C(29)	9547 (2)	1454 (2)	440 (5)	4·05 (6)
C(210)	10189 (2)	1209 (2)	231 (6)	5·07 (8)
C(211)	10611 (2)	960 (3)	1581 (6)	5·46 (8)
C(212)	10424 (2)	946 (2)	3161 (5)	4·95 (7)
C(213)	10923 (3)	688 (3)	4641 (7)	6·87 (10)
C(214)	9801 (2)	1202 (2)	3348 (5)	4·97 (8)
C(215)	9368 (2)	1455 (2)	2021 (5)	4·68 (7)
C(216)	8028 (2)	3381 (2)	-3556 (5)	4·14 (7)
C(217)	8458 (2)	4162 (2)	-2369 (5)	4·80 (7)
C(218)	8791 (2)	4396 (3)	-204 (7)	6·64 (10)
C(219)	8589 (2)	4730 (3)	-3171 (6)	5·88 (9)
C(220)	8333 (2)	4519 (3)	-5111 (7)	6·55 (10)
C(221)	7905 (2)	3736 (3)	-6308 (7)	6·42 (10)
C(222)	7750 (2)	3161 (2)	-5539 (6)	5·07 (8)
C(223)	7280 (3)	2284 (3)	-6907 (7)	7·30 (11)
N(31)	4984 (2)	2729 (2)	47 (4)	4·75 (6)
N(32)	5308 (2)	3501 (2)	390 (5)	5·40 (7)
N(33)	5872 (2)	3421 (2)	-164 (5)	5·31 (6)
N(34)	5916 (2)	2592 (2)	-898 (4)	4·76 (6)
C(35)	5366 (2)	2188 (2)	-731 (5)	3·65 (6)
C(39)	5197 (2)	1252 (2)	-1461 (5)	3·71 (6)
C(310)	4564 (2)	862 (2)	-1551 (6)	5·01 (8)
C(311)	4405 (2)	-13 (3)	-2245 (6)	5·65 (8)
C(312)	4865 (2)	-518 (2)	-2899 (6)	5·03 (8)
C(313)	4689 (2)	-1485 (3)	-3723 (6)	6·28 (9)
C(314)	5506 (2)	-125 (3)	-2739 (6)	5·95 (9)
C(315)	5674 (2)	758 (3)	-2016 (6)	5·34 (8)
N(4)	6180 (2)	4616 (2)	-1667 (5)	5·61 (7)
C(41)	6698 (2)	4589 (3)	-2672 (6)	6·51 (9)
C(42)	6730 (2)	5267 (3)	-3446 (7)	6·85 (9)
C(43)	5451 (2)	4697 (3)	-2561 (6)	6·36 (9)
C(44)	5110 (2)	3806 (3)	-4489 (7)	7·15 (10)
C(45)	6379 (2)	5456 (3)	370 (6)	6·68 (9)
C(46)	7027 (2)	5411 (3)	1752 (7)	7·15 (9)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

	<i>J</i> = 1	<i>J</i> = 2	<i>J</i> = 3
N(J1)-N(J2)	1·346 (7)	1·312 (7)	1·344 (6)
N(J1)-C(J5)	1·334 (6)	1·363 (6)	1·327 (7)
N(J2)-N(J3)	1·321 (7)	1·335 (6)	1·316 (7)
N(J3)-N(J4)	1·331 (6)	1·348 (6)	1·351 (6)
N(J3)-C(J6)	1·453 (7)	1·434 (6)	
N(J4)-C(J5)	1·328 (7)	1·322 (6)	1·330 (7)
C(J5)-C(J9)	1·474 (7)	1·467 (7)	1·484 (6)
C(J6)-N(J7)	1·287 (6)	1·276 (6)	
C(J6)-C(J16)	1·452 (7)	1·467 (7)	
N(J7)-O(J8)	1·390 (6)	1·374 (6)	
C(J9)-C(J10)	1·372 (7)	1·412 (6)	1·374 (7)
C(J9)-C(J15)	1·400 (7)	1·380 (7)	1·374 (7)
C(J10)-C(J11)	1·398 (7)	1·384 (8)	1·387 (7)
C(J11)-C(J12)	1·356 (6)	1·396 (8)	1·381 (7)
C(J12)-C(J13)	1·539 (8)	1·535 (8)	1·532 (7)
C(J12)-C(J14)	1·386 (7)	1·379 (6)	1·369 (7)
C(J14)-C(J15)	1·378 (7)	1·386 (7)	1·400 (8)
C(J16)-C(J17)	1·389 (7)	1·395 (8)	
C(J16)-C(J22)	1·392 (8)	1·399 (7)	
C(J17)-C(J18)	1·556 (9)	1·535 (8)	
C(J17)-C(J19)	1·406 (8)	1·388 (8)	
C(J19)-C(J20)	1·333 (9)	1·367 (8)	
C(J20)-C(J21)	1·397 (8)	1·397 (9)	
C(J21)-C(J22)	1·405 (9)	1·391 (8)	
C(J22)-C(J23)	1·552 (9)	1·561 (9)	
N(J2)-N(J1)-C(J5)	105·9 (10)	106·2 (10)	106·0 (11)
N(J1)-N(J2)-N(J3)	105·5 (7)	106·7 (7)	108·7 (10)
N(J2)-N(J3)-N(J4)	113·9 (11)	112·6 (10)	109·0 (12)
N(J2)-N(J3)-C(J6)	120·0 (7)	120·5 (7)	
N(J4)-N(J3)-C(J6)	125·9 (10)	126·6 (9)	
N(J3)-N(J4)-C(J5)	101·8 (7)	102·0 (7)	105·4 (10)
N(J1)-C(J5)-N(J4)	112·9 (8)	112·4 (8)	110·8 (10)
N(J1)-C(J5)-C(J9)	122·6 (10)	122·5 (10)	126·0 (12)
N(J4)-C(J5)-C(J9)	124·5 (8)	125·0 (7)	123·0 (11)
N(J3)-C(J6)-N(J7)	121·8 (10)	125·2 (10)	
N(J3)-C(J6)-C(J16)	117·3 (12)	116·2 (12)	
N(J7)-C(J6)-C(J16)	120·9 (12)	118·6 (12)	
C(J6)-N(J7)-O(J8)	115·9 (13)	114·8 (13)	
C(J5)-C(J9)-C(J10)	121·2 (11)	120·5 (7)	120·6 (10)
C(J5)-C(J9)-C(J15)	120·2 (7)	120·9 (11)	120·9 (11)
C(J10)-C(J9)-C(J15)	118·6 (8)	118·6 (9)	118·6 (10)
C(J9)-C(J10)-C(J11)	120·1 (11)	119·6 (9)	120·4 (13)
C(J10)-C(J11)-C(J12)	121·7 (7)	121·8 (12)	121·5 (12)
C(J11)-C(J12)-C(J14)	118·3 (9)	117·3 (8)	117·7 (10)
C(J11)-C(J12)-C(J13)	120·1 (8)	119·5 (10)	122·1 (13)
C(J14)-C(J12)-C(J13)	121·5 (11)	123·1 (7)	121·0 (10)
C(J12)-C(J14)-C(J15)	121·2 (11)	122·1 (9)	121·0 (13)
C(J9)-C(J15)-C(J14)	120·2 (9)	120·5 (11)	120·6 (13)
C(J6)-C(J16)-C(J17)	121·1 (9)	119·8 (6)	
C(J6)-C(J16)-C(J22)	119·6 (6)	119·6 (9)	
C(J17)-C(J16)-C(J22)	119·3 (8)	120·6 (9)	
C(J16)-C(J17)-C(J18)	120·4 (8)	121·0 (9)	
C(J16)-C(J17)-C(J19)	119·6 (7)	119·1 (6)	
C(J18)-C(J17)-C(J19)	119·9 (6)	119·8 (7)	
C(J17)-C(J19)-C(J20)	120·1 (7)	121·0 (13)	
C(J19)-C(J20)-C(J21)	122·6 (10)	120·0 (12)	
C(J20)-C(J21)-C(J22)	117·6 (8)	120·2 (10)	
C(J16)-C(J22)-C(J21)	120·7 (6)	119·0 (8)	
C(J16)-C(J22)-C(J23)	121·6 (9)	121·6 (8)	
C(J21)-C(J22)-C(J23)	117·7 (9)	119·4 (7)	
Triethylammonium ion			
N(4)-C(41)	1·458 (7)	C(41)-C(42)	1·503 (9)
N(4)-C(43)	1·485 (7)	C(43)-C(44)	1·659 (10)
N(4)-C(45)	1·649 (9)	C(45)-C(46)	1·482 (8)
C(41)-N(4)-C(43)	119·9 (7)	N(4)-C(41)-C(42)	119·9 (7)
C(41)-N(4)-C(45)	112·5 (10)	N(4)-C(43)-C(44)	106·1 (9)
C(43)-N(4)-C(45)	99·2 (9)	N(4)-C(45)-C(46)	109·9 (8)

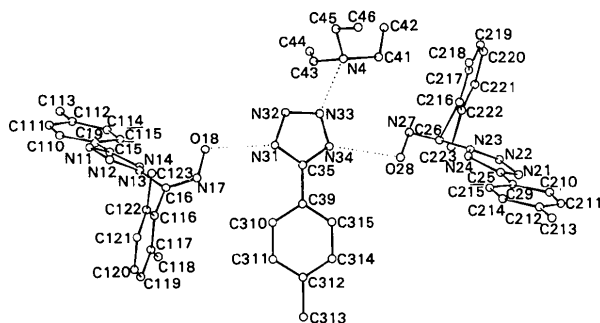


Fig. 1. A view of the molecular complex with atom labelling.

The bond lengths and angles in the tetrazole ring of molecule 3 are very close to those reported for anionic tetrazolide in hydrazinium 5-aminotetrazolide (Bryden, 1958), sodium tetrazolide monohydrate (Palenik, 1963) and dimethylammonium 5-(3-chlorobenzyl)tetrazolide (Ansell, 1975), thus suggesting the ionic form for the central molecule in the complex reported here; the negative charge on the ring is also in agreement with the presence of a surrounding network of hydrogen bonding and with *mm* symmetry of the ring: in sodium tetrazolide the *mm* symmetry is even imposed by crystallographic restrictions.

On the other hand, the *mm* symmetry is not present in the tetrazole rings of molecules 1 and 2.

The tetrazole and benzene rings are not coplanar in the three molecules, the angles between least-squares planes being $10.2(5)^\circ$ in molecule 3 and $15.1(6)$ and $14.8(7)^\circ$ in molecules 1 and 2. This result was rather unexpected, since, in the absence of steric hindrance

between *ortho* positions, molecules containing two aromatic rings linked by a single bond are usually planar because of partial delocalization of π electrons and the packing influence, and suggests that π delocalization is negligible in the examined compounds; this is in agreement with the values of the C—C inter-ring bonds, av. $1.476(5)$ Å, very close to the sum of C(sp^2) radii (1.48 Å), and with insignificant effect from the Y substituent in the phenyl ring on the tetrazole reactivity, as evidenced by the kinetics results (Beltrame & Gelli, 1984).

As is also evident from Fig. 1, the two independent molecules 1 and 2 are related by a pseudo centre of symmetry, which is at *ca* $x = 0.545$, $y = 0.247$, $z = -0.050$; therefore, by unit-cell symmetry, they are related by a pseudo translation of $\mathbf{b}/2$ and this is the main feature of the crystal packing, which is regulated by normal van der Waals contacts.

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The Structure of (\pm)-Malic Acid, (\pm)- $C_4H_6O_5$,

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Abstract. $M_r = 134.09$, monoclinic, $P2_1/c$, $a = 4.889(1)$, $b = 8.815(1)$, $c = 13.036(2)$ Å, $\beta = 102.93(1)^\circ$, $V = 547.6$ Å³, $Z = 4$, $D_x = 1.626$ Mg m⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.11$ mm⁻¹, $F(000) = 280$, $T = 294$ K, final $R = 0.049$

for 774 unique observed diffractometer data [$I \geq 2.5\sigma(I)$]. The carbon chain of the molecule is in the extended form. The molecular conformation is compared with data from other malate crystal structures, with evidence from NMR experiments and with results obtained by molecular-mechanics calculations. The molecules form infinite chains in which they are coupled

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