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Structure of 2-Methyl-1,2,4-triazol-3-yl Phenyl Ketone

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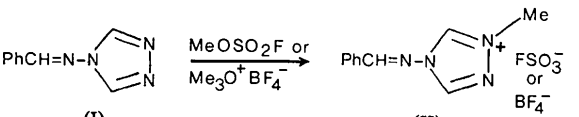
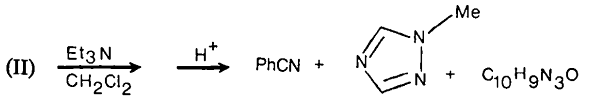
Abstract. $C_{10}H_9N_3O$, triclinic, $P\bar{1}$, $a = 7.507\,(15)$, $b = 9.060\,(5)$, $c = 14.680\,(11)$ Å, $\alpha = 99.50\,(5)$, $\beta = 106.52\,(9)$, $\gamma = 75.08\,(7)°$, $Z = 4$, $D_m = 1.3$, $D_x = 1.35$ Mg m^{-3}, $R = 0.053$ for 2326 observed reflections. Although high π-delocalization in the triazole is indicated, the triazole C=N is essentially *s-trans* to the adjacent C=O group.

Introduction. Titration of the triazolium salt (II) with Et_3N followed by a workup which includes an aqueous acid extraction yields not only the fragmentation products (III and IV) but also a compound of composition $C_{10}H_9N_3O$ (V).

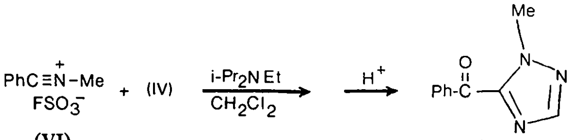


(I) (II)



(III) (IV) (V)

Since the process, (I) → (III), was being developed as the prototype for an improved and milder conversion of aldehydes to nitriles (see Becker, Hübner, Timpe & Wahren, 1968; Olofson & Pepe, 1979; Pepe, 1976; Smith & Walker, 1962), a crystal structure determination of (V) was undertaken in the hope that this knowledge would provide clues to its elimination as a side product. Once (V) was shown to be the title compound (see below), this extraordinary rearrangement product was made more efficiently by treating a presumed reaction intermediate, (VI) (Phillips, Fodor, Gal, Letourneau & Ryan, 1973), with (IV).



(VI) (V)

The salt (II) [^{1}H NMR (CD_3CN): δ 4·14 (3H, *s*), 7·4–8·2 (5H, *m*), 9·03 (1H, *s*), 9·16 (1H, *s*), 9·92 p.p.m. (1H, *s*)] was obtained by treating (I) (Olofson & Pepe, 1979) with 1·2 mol FSO_3Me and then reacted (usually without isolation) with 1·7 mol Et_3N. Workup included extraction with 1 *M* H_2SO_4 and 5% $NaHCO_3$. Benzonitrile was isolated by distillation and (V) was purified by chromatography on alumina (ether) and crystallized from hexane; m.p. 340–342·5 K; ^{1}H NMR ($CDCl_3$): δ 4·25 (3H, *s*), 7·2–7·8 (3H, *m*), 8·03 (1H, *s*), 8·2–8·6 p.p.m. (2H, *m*); ^{13}C NMR ($CDCl_3$): δ 38·7 (*q*, J = 142·8 Hz), 128·4 (*d* of *d*, 163·7, 7·4), 130·8 (*d* of *t*, 164·3, 6·5), 133·9 (*d* of *t*, 161·2, 7·6), 135·9 (*d*, 7·4), 149·1 (*m*), 149·8 (*d*, 209·0), 183·1 p.p.m. (*s*); IR (KBr); 6·02, 7·91 μm; mass spectrum *m/e* (relative intensity) 187 (61), 186 (85), 158 (33), 105 (57), 86 (36), 84 (58), 77 (56); analysis for C,H,N within 0·3%. Crystals were grown by slow evaporation of a hexane solution.

By warming a 195 K mixture of (IV) and (VI) (1·4 mol) in CH_2Cl_2 to 263 K, then cooling to 243 K, and adding iPr_2NEt (1·7 mol), (V) could be isolated in 83% yield (standard extraction workup, crystallization from acetone–water).

Data were collected on an Enraf–Nonius CAD-4 diffractometer and all programs used for this study were part of the Enraf–Nonius structure determination package (SDP) as revised in 1977 and implemented on a PDP 11/34 computer.

Cell dimensions were determined from 25 reflections at moderate 2θ angles.* The observed volume of 921 (3) Å^3 is consistent with $Z = 4$ for a calculated density of 1·35 Mg m^{-3} (observed 1·3 Mg m^{-3}). A total of 5543 unique reflections were measured using Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å) out to $2\theta = 60°$. Of these, 2326 had $I > 3\sigma(I)$ and were considered observed. These data were corrected for Lorentz and polarization factors. Starting positions for all non-hydrogen atoms in both of the unique molecules of the asymmetric unit cell (denoted *A* and *B*) were obtained from a *MULTAN E*-map synthesis where $E_{\min} = 1.75$.

Refinement was carried out by the full-matrix least-squares method. Final anisotropic refinement of

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* The working cell can be transformed to a reduced cell: $a = 9.060$, $b = 14.463$, $c = 7.507$ Å, $\alpha = 103.3$, $\beta = 104.9$, and $\gamma = 91.9°$ with the matrix: $u1 = (0\ {-1}\ 0)$, $u2 = ({-1}\ 0\ 0)$, and $u3 = (1\ 0\ 0)$.

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Table 1. *Positional coordinates and* B_{eq} (Å^2)

Here, $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$. B_{iso} for all H atoms is 4·0 Å^2. E.s.d.'s are in parentheses.

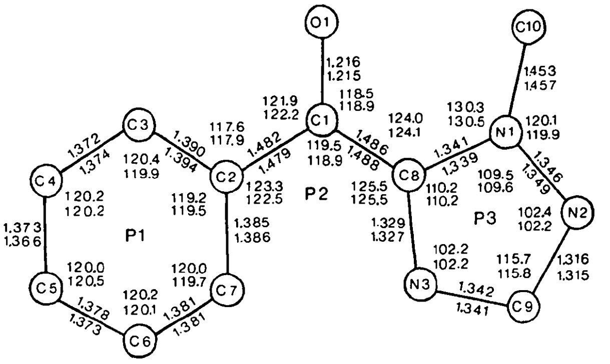
	x	*y*	*z*	B_{eq}
O(1)*A*	0·9265 (2)	0·3553 (2)	0·3454 (1)	4·7
O(1)*B*	0·2046 (3)	0·6425 (2)	0·1456 (1)	4·6
N(1)*A*	0·7420 (2)	0·6744 (2)	0·3427 (1)	3·2
N(2)*A*	0·7074 (3)	0·8188 (2)	0·3199 (1)	4·0
N(3)*A*	0·7617 (3)	0·6498 (2)	0·1948 (1)	3·6
N(1)*B*	0·2581 (2)	0·3218 (2)	0·1619 (1)	3·3
N(2)*B*	0·3493 (3)	0·1813 (2)	0·1897 (1)	4·0
N(3)*B*	0·4310 (3)	0·3640 (2)	0·3070 (1)	3·9
C(1)*A*	0·8334 (3)	0·4057 (2)	0·2702 (1)	3·1
C(2)*A*	0·7855 (3)	0·3038 (2)	0·1811 (1)	2·7
C(3)*A*	0·8863 (3)	0·1519 (2)	0·1797 (2)	3·8
C(4)*A*	0·8514 (4)	0·0524 (2)	0·0988 (2)	4·3
C(5)*A*	0·7133 (3)	0·1014 (3)	0·0191 (2)	4·1
C(6)*A*	0·6098 (3)	0·2509 (2)	0·0200 (1)	3·9
C(7)*A*	0·6462 (3)	0·3526 (2)	0·1005 (1)	3·4
C(8)*A*	0·7732 (3)	0·5748 (2)	0·2675 (1)	2·9
C(9)*A*	0·7230 (4)	0·7968 (2)	0·2314 (2)	4·1
C(10)*A*	0·7335 (3)	0·6475 (3)	0·4361 (2)	4·1
C(1)*B*	0·2442 (3)	0·5972 (2)	0·2239 (1)	3·1
C(2)*B*	0·2395 (3)	0·7037 (2)	0·3116 (1)	2·9
C(3)*B*	0·2488 (3)	0·8546 (2)	0·3092 (2)	3·5
C(4)*B*	0·2430 (4)	0·9578 (2)	0·3887 (2)	4·4
C(5)*B*	0·2245 (3)	0·9138 (3)	0·4696 (2)	4·5
C(6)*B*	0·2125 (3)	0·7661 (3)	0·4726 (2)	3·8
C(7)*B*	0·2212 (3)	0·6600 (2)	0·3940 (1)	3·2
C(8)*B*	0·3075 (3)	0·4293 (2)	0·2324 (1)	2·9
C(9)*B*	0·4504 (3)	0·2143 (2)	0·2765 (2)	4·1
C(10)*B*	0·1276 (4)	0·3366 (3)	0·0674 (2)	4·4
H(C3)*A*	0·986 (3)	0·116 (2)	0·233 (1)	
H(C4)*A*	0·920 (3)	−0·052 (2)	0·098 (1)	
H(C5)*A*	0·680 (3)	0·040 (2)	−0·038 (1)	
H(C6)*A*	0·511 (2)	0·283 (2)	−0·034 (1)	
H(C7)*A*	0·571 (3)	0·452 (2)	0·102 (1)	
H(C9)*A*	0·708 (3)	0·882 (2)	0·198 (1)	
H′(C10)*A*	0·854 (3)	0·645 (2)	0·479 (1)	
H″(C10)*A*	0·695 (3)	0·557 (2)	0·436 (1)	
H‴(C10)*A*	0·643 (3)	0·735 (2)	0·456 (1)	
H(C3)*B*	0·268 (3)	0·885 (2)	0·253 (1)	
H(C4)*B*	0·247 (3)	1·062 (2)	0·386 (1)	
H(C5)*B*	0·208 (3)	0·982 (2)	0·523 (1)	
H(C6)*B*	0·193 (2)	0·732 (2)	0·529 (1)	
H(C7)*B*	0·210 (3)	0·556 (2)	0·396 (1)	
H(C9)*B*	0·535 (3)	0·136 (2)	0·314 (1)	
H′(C10)*B*	0·189 (3)	0·358 (2)	0·025 (1)	
H″(C10)*B*	0·072 (3)	0·254 (2)	0·053 (1)	
H‴(C10)*B*	0·022 (3)	0·428 (2)	0·071 (1)	

non-hydrogen atoms with B_{iso} fixed at 4 Å^2 for H atoms gave $R = 0\cdot053$ and $R_w = 0\cdot057$ with an e.s.d. of an observation of unit weight of 1·91; $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/[\sigma(F_o)^2]$, $\sigma(F_o)^2 = [\sigma(I)^2 + (0\cdot04F^2)^2]^{1/2}/\mathrm{Lp}$. The final difference map was smooth with maxima and minima in the range $\pm0\cdot206$ e Å^{-3}. The atomic positional parameters are given in Table 1.*

Discussion. Bond distances and bond angles for the two unique molecules (*A* and *B*) in the unit cell are given in Fig. 1. The bond distances to H atoms are 0·93–0·97 Å for *A* and 0·91–0·99 Å for *B* while the corresponding angles differ from theoretical values by up to 5·5° for *A* and 10·5° for *B*. The major difference between molecules *A* and *B* is associated with differences in the dihedral angles between the ring planes and the carbonyl groups (note the small differences in dihedral angles between the two ring planes). Otherwise the bond angles and bond distances for the two molecules are almost identical.

In the structure, the essentially *s-trans* relationship between the carbonyl function and the C=N of the triazole ring is noteworthy (see Figs. 1, 2) and in accord with orbital symmetry and dipole repulsion rationalizations (Hoffmann & Olofson, 1966). However, a very high degree of delocalization in the triazole ring is indicated by the great similarity in bond distances. Much greater variations (*ca* 0·1 Å) ordinarily are found in related azoles, *e.g.* 5-methyl-1-(2-pyridyl)imidazole (Mente, Sundberg & Bryan, 1977). In the past such small variations in bond lengths have only been found in azoles wherein delocalization can be enhanced by hydrogen bonding between $>\!C{=}\ddot{N}\!\diagdown$ and $>\!N{-}H$; *e.g.* imidazole (0·05 Å, Martinez-Carrera, 1966) and 1,2,4-triazole (0·02 Å, Goldstein, Ladell & Abowitz, 1969).

The stereoscopic view of the unit cell (Fig. 2) reveals a packing pattern which may explain the variation in dihedral angle of the carbonyl plane *vs* the two sets of ring planes. Viewed down the *a* axis, it is evident that both kinds of carbonyls are nearest to the electron-rich



	P1 ∧ P2	P2 ∧ P3	P1 ∧ P3
MOLECULE A	16.8	−32.2	−44.1
MOLECULE B	22.7	−28.6	−46.2

Fig. 1. Bond distances (Å) and angles (°) for non-hydrogen atoms. The upper value refers to molecule *A*. E.s.d.'s are in the ranges 0·002–0·003 Å and 0·1–0·2°. The dihedral angles between the planes (*P*1 = the benzene ring, *P*2 = the carbonyl group including the α-carbons, and *P*3 = the triazole ring including the *N*-methyl carbon) are shown below the diagram. Deviations of atoms from these least-squares planes are no greater than 0·02 Å.

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* Lists of structure factors, thermal parameters, bond lengths, and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35772 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

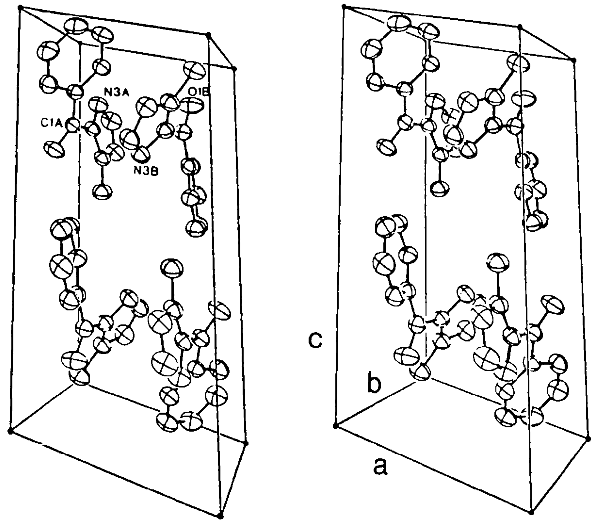

Fig. 2. Stereoscopic view of the unit cell showing the molecular packing. Thermal ellipsoids for non-hydrogen atoms represent 50% probability.

N(3) of the two adjacent molecules. Because of the size of (V), either C(1) or O(1) may be closest to N(3) and the distance variation is as predicted for the interaction of an electron-rich atom with a strong C=O dipole. When C(1) is closest to N(3), the distance is 3·34 Å [C(1)*A* to N(3)*B*]; when O(1) is closest to N(3), the distance is 4·05 Å [O(1)*B* to N(3)*A*].

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The Structure of 2-Oxo-2′-thioxobis(5,5-dimethyl-1,3,2-dioxaphosphorinanyl) Sulphide*

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Abstract. $C_{10}H_{20}O_5P_2S_2$, M_r = 346·3, $F(000)$ = 728, orthorhombic, $P2_12_12_1$, a = 13·681 (2), b = 11·144 (2), c = 10·579 (2) Å, V = 1612·9 Å^3, Z = 4, D_m = 1·42 (1), D_c = 1·430 Mg m^{-3}, Cu $K\alpha$ radiation, λ = 1·5418 Å, μ = 4·8 mm^{-1}. The structure was solved by direct methods and refined to R = 0·045 for 1142 independent reflections. The symmetry of the bicyclic molecules is approximately 2. The two structurally independent dioxaphosphorinane rings have a partially flattened chair conformation with the P=O and P=S bonds in the equatorial positions. Unusual lengths for these bonds have been observed: P—O(12) = 1·538 (7) Å is longer and P—S(2) = 1·874 (3) Å is shorter than in other similar phosphates.

Introduction. The crystal and molecular structure determination of the title compound is part of an investigation of six-membered bicyclic organic pyro- and thiopyrophosphates. Structures and conformations of substituted 1,3,2-dioxaphosphorinanes have been of interest in recent years. The rings display

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* Alternative name: 2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-ylthio)-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide.

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