Acta Cryst. (1977). B**33**, 627–630

Ethyl *N*-[*N'*-Methylbenzimidoyl]benzimidate Picrate

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(*Received* 13 *October* 1976; *accepted* 29 *October* 1976)

Abstract. $C_{17}H_{19}N_2O^+$ $C_6H_2N_3O_7^-$, M_r = 495·46, triclinic, $P\bar{1}$, a = 9·451 (3), b = 11·169 (3), c = 12·376 (2) Å, α = 103·91 (2), β = 111·14 (2), γ = 91·72 (2)°, U = 1172·9 Å^3, Z = 2, D_x = 1·403 g cm^{-3}, μ = 8·2 cm^{-1}. The cation is protonated at the methyl-substituted N atom; the acidic proton and the picrate O^- are hydrogen bonded. The structure was refined to an R of 0·044 for 2757 unique reflexions.

Introduction. The structure determination was undertaken to establish the exact nature of the liquid product *A* formed by the action of ethoxide ion on a substituted thiadiazolium salt (Crook & Sykes, 1977). Yellow plate-like crystals were obtained by the action of picric acid on *A* in ethanol solution, and were stable to air and X-rays. Intensities were measured on an automated Syntex $P2_1$ four-circle diffractometer with Cu $K\alpha$ radiation, a graphite monochromator, and a crystal 1·0 × 0·35 × 0·2 mm. Lp corrections were applied. 3532 reflexions were measured in the range $0 < 2\theta < 120°$; averaging equivalent reflexions gave 2757 unique reflexions with $F > 4\sigma(F)$. Cell dimensions were obtained by least squares from 15 strong reflexions. The cell used was both the Dirichlet and Delaunay cell; no cell of higher symmetry could be found with the program *XCELL* written by Dr R. Taylor.

The structure was solved by multisolution direct methods with 569 E values > 1·2. The best E map gave sites for all non-hydrogen atoms. Anisotropic least-squares refinement, followed by a difference synthesis, gave positions for all H atoms except the six methyl H; these appeared to be disordered. Further least-squares refinement showed that only the C(5) methyl group was disordered. This was successfully refined as a rigid group incorporating twofold disorder; the H atoms were constrained to a regular hexagon with adjacent H—H' distances of 1·018 Å, C—H distances 1·08 Å, H—C—H and H'—C—H' angles 109·5° and equal temperature factors. The site-occupation factors for the two sets of H atoms (the sum was constrained to 1) refined to 0·523 (7) for H(51), H(52) and H(53), and 0·477 (7) for H(51'), H(52') and H(53'). The C(4) methyl group was also refined as a rigid group with C—H 1·08 Å, H—C—H 109·5°. All other H atoms were allowed to refine freely. An empirical isotropic extinction parameter x was included in the refinement; it refined to 7 (2) × 10^{-7}, where F_c is multiplied by $(1 - xF^2/\sin\theta)$. The final $R' = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$ was

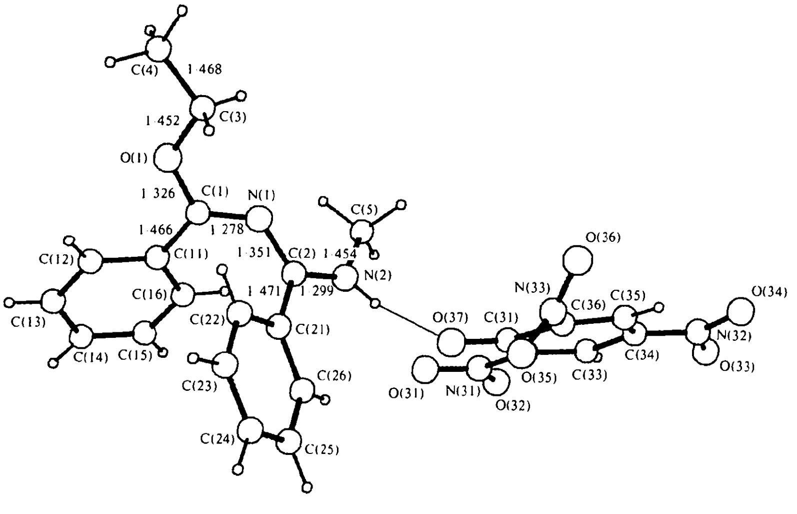

Fig. 1. A perspective view of the structure showing the atomic-numbering scheme for non-H atoms and selected bond lengths. [C(32) is obscured by O(35).]

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* External Staff, Medical Research Council.

Table 1. *Atom coordinates* (×10⁴) *and isotropic temperature factors* (Å² ×10³)

	x	*y*	*z*	
C(1)	3392 (2)	2085 (2)	7599 (2)	
C(2)	5696 (2)	1959 (2)	9151 (2)	
C(3)	1323 (2)	2336 (2)	8277 (2)	
C(4)	−302 (3)	2478 (4)	7741 (3)	
C(5)	6712 (3)	4132 (2)	10179 (2)	
N(1)	4283 (2)	2294 (2)	8702 (1)	
N(2)	6818 (2)	2805 (2)	9903 (1)	
O(1)	1914 (1)	2174 (1)	7326 (1)	
C(11)	3813 (2)	1823 (2)	6544 (2)	
C(12)	2791 (3)	1091 (2)	5433 (2)	
C(13)	3175 (3)	901 (2)	4446 (2)	
C(14)	4560 (3)	1421 (2)	4536 (2)	
C(15)	5575 (3)	2132 (2)	5624 (2)	
C(16)	5221 (2)	2336 (2)	6626 (2)	
C(21)	5926 (2)	640 (2)	8915 (2)	
C(22)	4691 (2)	−281 (2)	8535 (2)	
C(23)	4902 (3)	−1515 (2)	8351 (2)	
C(24)	6334 (3)	−1854 (2)	8534 (2)	
C(25)	7569 (3)	−952 (2)	8895 (2)	
C(26)	7374 (2)	287 (2)	9085 (2)	
C(31)	12 (2)	2937 (2)	2721 (2)	
C(32)	1156 (2)	3896 (2)	2830 (2)	
C(33)	2210 (2)	4599 (2)	3920 (2)	
C(34)	2155 (2)	4441 (2)	4965 (2)	
C(35)	1063 (2)	3584 (2)	4959 (2)	
C(36)	89 (2)	2841 (2)	3872 (2)	
N(31)	1251 (2)	4149 (2)	1760 (2)	
O(31)	337 (2)	3589 (2)	776 (2)	
O(32)	2292 (3)	4889 (2)	1880 (2)	
N(32)	3274 (3)	5184 (2)	6111 (2)	
O(33)	4324 (3)	5845 (2)	6109 (2)	
O(34)	3118 (3)	5085 (2)	7024 (2)	
N(33)	−947 (2)	1868 (2)	3909 (2)	
O(35)	−1018 (2)	822 (2)	3312 (2)	
O(36)	−1660 (3)	2164 (3)	4554 (2)	
O(37)	−955 (2)	2252 (1)	1759 (1)	
				U
H(51′)	6698	4500	9445	76 (5)
H(52′)	7686	4598	10980	76 (5)
H(53′)	5673	4284	10339	76 (5)
H(51)	5685	4323	9530	76 (5)
H(52)	7698	4638	10170	76 (5)
H(53)	6674	4421	11064	76 (5)
H(41)	−897	1679	6994	148 (7)
H(42)	−426	3309	7432	191 (7)
H(43)	−782	2551	8422	142 (6)
H(121)	1907 (26)	696 (22)	5315 (20)	73 (5)
H(131)	2478 (24)	416 (21)	3735 (20)	79 (5)
H(141)	4778 (27)	1241 (22)	3814 (21)	90 (5)
H(151)	6464 (24)	2522 (21)	5714 (20)	82 (5)
H(161)	5884 (21)	2846 (17)	7354 (17)	58 (4)
H(221)	3711 (20)	−57 (17)	8403 (16)	53 (4)
H(231)	4039 (22)	−2190 (19)	8038 (19)	68 (5)
H(241)	6456 (22)	−2769 (19)	8381 (18)	68 (5)
H(251)	8567 (27)	−1260 (24)	9061 (22)	100 (6)
H(261)	8201 (20)	870 (16)	9305 (16)	50 (4)
H(1)	7613 (23)	2620 (19)	10404 (19)	72 (5)
H(31)	1474 (31)	1532 (27)	8515 (26)	121 (6)
H(32)	1804 (30)	3011 (27)	8906 (25)	119 (6)
H(331)	2945 (23)	5239 (20)	3997 (19)	76 (5)
H(351)	1031 (24)	3411 (20)	5664 (20)	77 (5)

Table 2. *Bond lengths* (Å)

C(1)—N(1)	1·278 (3)	C(1)—O(1)	1·326 (3)
C(1)—C(11)	1·466 (4)	C(2)—N(1)	1·351 (3)
C(2)—N(2)	1·299 (3)	C(2)—C(21)	1·471 (4)
C(3)—C(4)	1·468 (4)	C(3)—O(1)	1·452 (4)
C(5)—N(2)	1·454 (4)	C(11)—C(12)	1·394 (3)
C(11)—C(16)	1·393 (4)	C(12)—C(13)	1·368 (5)
C(13)—C(14)	1·372 (5)	C(14)—C(15)	1·369 (4)
C(15)—C(16)	1·367 (5)	C(21)—C(22)	1·393 (4)
C(21)—C(26)	1·392 (4)	C(22)—C(23)	1·375 (4)
C(23)—C(24)	1·370 (5)	C(24)—C(25)	1·382 (4)
C(25)—C(26)	1·377 (4)	C(31)—C(32)	1·445 (4)
C(31)—C(36)	1·429 (4)	C(31)—O(37)	1·255 (3)
C(32)—C(33)	1·380 (3)	C(32)—N(31)	1·451 (4)
C(33)—C(34)	1·366 (4)	C(34)—C(35)	1·382 (4)
C(34)—N(32)	1·455 (3)	C(35)—C(36)	1·368 (3)
C(36)—N(33)	1·461 (4)	N(31)—O(31)	1·210 (3)
N(31)—O(32)	1·208 (4)	N(32)—O(33)	1·220 (5)
N(32)—O(34)	1·221 (5)	N(33)—O(35)	1·209 (4)
N(33)—O(36)	1·214 (5)		
C(3)—H(31)	1·009 (34)	C(3)—H(32)	0·907 (25)
N(2)—H(1)	0·853 (21)	C(12)—H(121)	0·878 (26)
C(13)—H(131)	0·913 (19)	C(14)—H(141)	0·964 (30)
C(15)—H(151)	0·891 (25)	C(16)—H(161)	0·924 (16)
C(22)—H(221)	0·933 (20)	C(23)—H(231)	0·989 (21)
C(24)—H(241)	1·012 (22)	C(25)—H(251)	0·982 (27)
C(26)—H(261)	0·916 (19)	C(33)—H(331)	0·945 (21)
C(35)—H(351)	0·949 (21)		

0·0551, with a corresponding R of 0·0438; the weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}001F^2]$ which gave mean values of $w\Delta^2$ virtually independent of sin θ or $|F_o|$. A final difference map had no peaks greater than 0·28 e Å^{-3}. Complex neutral-atom scattering factors were employed. Final atomic coordinates and isotropic thermal parameters for the H atoms are given in Table 1, with derived interatomic distances and angles in Tables 2 and 3. Diagrams of the structure are given in Figs. 1 and 2 (only one position of the disordered Me group is shown). Fig. 1 also shows the numbering scheme. The H atoms [except the acidic proton H(1)] are numbered such that H(*mn*) is the *n*th H atom on C(*m*).*

Discussion. The nature of the picrate salt has been determined as the title compound, the cation being PhC(OEt)=N–C(Ph)=N$^+$HMe. The compound *A* is thus the free base. The chemical implications of this will be discussed elsewhere (Crook & Sykes, 1977).

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* A list of structure factors and a table of the anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32248 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond angles* (°)

N(1)–C(1)–O(1)	119·4 (3)	C(33)–C(34)–N(32)	119·4 (3)	C(11)–C(16)–C(15)	120·0 (3)
O(1)–C(1)–C(11)	113·0 (2)	C(34)–C(35)–C(36)	118·0 (3)	C(2)–C(21)–C(26)	121·0 (3)
N(1)–C(2)–C(21)	120·5 (2)	C(31)–C(36)–N(33)	118·2 (2)	C(21)–C(22)–C(23)	120·6 (3)
C(4)–C(3)–O(1)	106·9 (3)	C(32)–N(31)–O(31)	120·0 (3)	C(23)–C(24)–C(25)	119·9 (3)
C(2)–N(2)–C(5)	124·2 (3)	O(31)–N(31)–O(32)	121·6 (4)	C(21)–C(26)–C(25)	119·9 (3)
C(1)–C(11)–C(12)	120·6 (3)	C(34)–N(32)–O(34)	117·4 (3)	C(32)–C(31)–O(37)	126·3 (3)
C(12)–C(11)–C(16)	119·0 (3)	C(36)–N(33)–O(35)	117·8 (3)	C(31)–C(32)–C(33)	123·3 (3)
C(12)–C(13)–C(14)	120·7 (3)	O(35)–N(33)–O(36)	124·5 (4)	C(33)–C(32)–N(31)	116·6 (3)
C(14)–C(15)–C(16)	120·6 (3)	N(1)–C(1)–C(11)	127·6 (3)	C(33)–C(34)–C(35)	121·4 (3)
C(2)–C(21)–C(22)	120·2 (3)	N(1)–C(2)–N(2)	119·0 (3)	C(35)–C(34)–N(32)	119·2 (3)
C(22)–C(21)–C(26)	118·8 (3)	N(2)–C(2)–C(21)	120·1 (3)	C(31)–C(36)–C(35)	125·5 (3)
C(22)–C(23)–C(24)	120·2 (3)	C(1)–N(1)–C(2)	127·9 (3)	C(35)–C(36)–N(33)	116·3 (3)
C(24)–C(25)–C(26)	120·5 (3)	C(1)–O(1)–C(3)	118·6 (2)	C(32)–N(31)–O(32)	118·3 (3)
C(32)–C(31)–C(36)	111·8 (2)	C(1)–C(11)–C(16)	120·4 (2)	C(34)–N(32)–O(33)	118·7 (3)
C(36)–C(31)–O(37)	121·9 (3)	C(11)–C(12)–C(13)	119·8 (3)	O(33)–N(32)–O(34)	123·9 (3)
C(31)–C(32)–N(31)	120·2 (2)	C(13)–C(14)–C(15)	119·9 (4)	C(36)–N(33)–O(36)	117·7 (3)
C(32)–C(33)–C(34)	119·7 (3)				
C(4)–C(3)–H(31)	112·0 (17)	C(25)–C(24)–H(241)	121·5 (13)	C(13)–C(14)–H(141)	117·0 (14)
C(4)–C(3)–H(32)	108·9 (20)	C(26)–C(25)–H(251)	124·1 (15)	C(14)–C(15)–H(151)	122·8 (16)
H(31)–C(3)–H(32)	112·3 (26)	C(25)–C(26)–H(261)	119·3 (13)	C(11)–C(16)–H(161)	119·1 (16)
C(5)–N(2)–H(1)	112·7 (14)	C(34)–C(33)–H(331)	116·4 (14)	C(21)–C(22)–H(221)	119·6 (12)
C(13)–C(12)–H(121)	115·4 (17)	C(36)–C(35)–H(351)	117·8 (14)	C(22)–C(23)–H(231)	122·3 (14)
C(14)–C(13)–H(131)	122·0 (19)	O(1)–C(3)–H(31)	103·0 (21)	C(23)–C(24)–H(241)	118·6 (13)
C(15)–C(14)–H(141)	123·1 (14)	O(1)–C(3)–H(32)	113·5 (24)	C(24)–C(25)–H(251)	115·2 (16)
C(16)–C(15)–H(151)	116·4 (16)	C(2)–N(2)–H(1)	121·5 (14)	C(21)–C(26)–H(261)	120·8 (13)
C(15)–C(16)–H(161)	120·9 (16)	C(11)–C(12)–H(121)	124·6 (17)	C(32)–C(33)–H(331)	123·7 (14)
C(23)–C(22)–H(221)	119·7 (12)	C(12)–C(13)–H(131)	117·3 (19)	C(34)–C(35)–H(351)	123·7 (14)
C(24)–C(23)–H(231)	117·4 (14)				

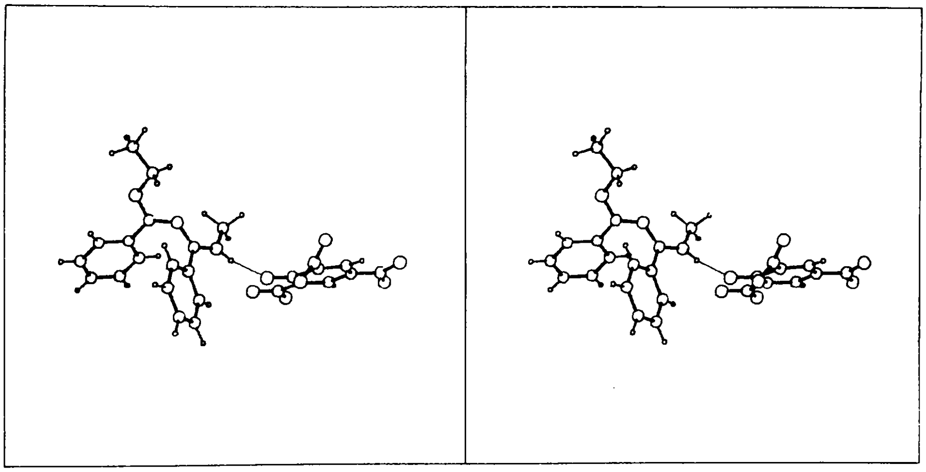

Fig. 2. A stereo pair of the structure showing the hydrogen bonding.

The protonation site is the methyl-substituted N atom; hydrogen bonding between the acidic proton and the picrate O^- connects the anion (at $1 + x, y, 1 + z$) with the cation (at x,y,z). The conformation about both C=N bonds is established. The picrate ion is approximately planar, except that one NO_2 group [N(33), O(35), O(36)] is rotated considerably out of the plane [a typical torsion angle is O(36)–N(33)–C(36)–C(31) −131·7 (2)°]. The temperature factors of this NO_2 group are high.

There is no evidence for extensive π delocalization along the system Ph–C=N–C(Ph)=N– which is not surprising since the backbone C(11)—C(1)—N(1)—C(2)—C(21) is helical. Relevant bond lengths are marked on Fig. 1.

There are no unusually short intermolecular contacts except for the hydrogen-bonded distances O(37)—N(2) (2·71 Å) and O(37)—H(1) (1·88 Å) (for necessary symmetry transformations, see above).

We are grateful to the Medical Research Council for financial support and to the Science Research Council for provision of the diffractometer. The calculations were performed on the Cambridge University IBM 370/165 computer with the *SHELX* series of programs written by Dr G. M. Sheldrick. The figures were drawn with *PLUTO* written by Dr W. D. S. Motherwell.

Reference

CROOK, S. & SYKES, P. (1977). In preparation.

SHORT COMMUNICATIONS

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Acta Cryst. (1977). B**33**, 630

The crystal and molecular structure of 2-acetamido-2,3-dideoxy-D-*threo*-hex-2-enono-1,4-lactone, $C_8H_{11}NO_5$. Erratum.

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(*Received* 11 *October* 1976; *accepted* 11 *October* 1976)

Errors in Tables 2, 3, 5 and 6 in the paper by Ružić-Toroš & Kojić-Prodić [*Acta Cryst.* (1976), B**32**, 2333–2336] are corrected.

The signs of some parameters should be the opposite of those stated in the paper, as follows: Table 2, columns x, U_{12} and U_{23}; Table 3, column x; and all the values in Tables 5 and 6.

Acta Cryst. (1977). B**33**, 630–632

Structure cristalline du tétramétaphosphate de praséodyme–ammonium, $PrNH_4P_4O_{12}$. Données cristallographiques de $NdNH_4P_4O_{12}$.

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(*Reçu le* 13 *septembre* 1976, *accepté le* 4 *octobre* 1976)

The unit cell of $PrNH_4P_4O_{12}$ is monoclinic with a = 7·916 (5), b = 12·647 (10), c = 10·672 (9) Å, β = 110·34 (8)°, Z = 4. The space group is $C2/c$. The crystal structure was solved from single-crystal diffractometer data by the Patterson method and was refined by least squares. P_4O_{12} ring anions are centrosymmetric. $NdNH_4P_4O_{12}$ is isotypic with $PrNH_4P_4O_{12}$.

Introduction

On chauffe à 200°C quelques grammes de Pr_2O_3 ou $PrCl_3$ dans 20 g de phosphate biammonique, $(NH_4)_2HPO_4$. Puis on porte le tout à 400°C pendant 24 h. On précipite ainsi des cristaux de forme allongée de formule $PrNH_4P_4O_{12}$. Si l'on part de Nd_2O_3, on obtient des cristaux de même morphologie, de formule chimique $NdNH_4P_4O_{12}$.

La maille cristalline de $PrNH_4P_4O_{12}$ a été déterminée par la méthode de Weissenberg et affinée à partir de données enregistrées au diffractomètre automatique.

Les intensités diffractées ont été mesurées à l'aide d'un diffractomètre automatique Philips, à la longueur d'onde de

Tableau 1. *Coordonnées cristallographiques des atomes*

	x	y	z	B (Å^2)
Pr	0,0	0,12086 (5)	0,25	0,62 (1)
P(1)	0,4617 (3)	0,1690 (2)	0,5024 (2)	0,65 (2)
P(2)	0,2855 (3)	0,9790 (2)	0,5611 (2)	0,62 (2)
O(L1)	0,4058 (7)	0,8756 (5)	0,5681 (6)	1,17 (10)
O(L2)	0,4312 (7)	0,0722 (4)	0,5885 (5)	0,95 (10)
O(E11)	0,2933 (8)	0,1986 (4)	0,3907 (6)	1,07 (10)
O(E12)	0,5610 (8)	0,2523 (5)	0,5983 (6)	1,14 (10)
O(E21)	0,2238 (8)	0,9727 (5)	0,6763 (6)	1,09 (10)
O(E22)	0,1518 (8)	−0,0100 (5)	0,4244 (6)	1,16 (10)
NH_4	0,0	0,8189 (8)	0,25	1,89 (20)