bond lengths are in the normal range of B—N double bonds (Paetzold, 1987). In contrast, the N—N single bonds are almost 0·04 Å shorter than the standard N(sp^2)—N(sp^2) single-bond length at 1·41 Å (Patai, 1975). On the other hand, the N—N double bond was found to be 0·03 Å longer than the standard value of 1·25 Å (Rademacher, 1987). The structure determination confirms C_{2v} symmetry of the BN_4 unit within standard deviations. This indicates extensive π delocalization in the BN_4 ring. All atoms in α position to the BN_4 unit are located in the ring plane. To reduce interference between the isopropyl groups, the BN_4 ring and the phenyl group, the last is twisted by an interplanar angle of 44·4° relative to the five-membered ring, as shown in Fig. 2.

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Structural Refinement of Low-Temperature Copper(II) Pyrophosphate

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Abstract. α-$Cu_2P_2O_7$, $M_r = 301{\cdot}02$, monoclinic, $C2/c$, $a = 6{\cdot}895\,(2)$, $b = 8{\cdot}113\,(3)$, $c = 9{\cdot}164\,(3)$ Å, $\beta = 109{\cdot}62\,(2)°$, $V = 482{\cdot}9$ Å^3, $Z = 4$, $D_x = 4{\cdot}14$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 9{\cdot}2$ mm^{-1}, $F(000) = 576$, room temperature, $R = 0{\cdot}036$ for 1757 unique observed reflections. CuO_5 polyhedra are connected to form sheets in (001), which are linked by P_2O_7 groups; P—O_{terminal} = 1·497 (1), 1·514 (1) and 1·540 (1), P—O_{bridging} = 1·579 (1) Å, P—O—P = 156·8 (2)°. Crystals were synthesized under hydrothermal conditions up to some tenths of a millimeter; they are colourless.

Experimental. Crystals of the title compound were obtained during synthesis of $Cu_3(PO_4)_2$ under hydrothermal conditions: 1 g elemental Cu (wire), 1 g Cu_2O (powder), 2 ml H_3PO_4 85%, and 1 ml HNO_3 65% were sealed in a 'teflon' lined stainless steel autoclave with ~7 ml capacity. H_2O was added to approximately 80% degree of filling. After heating to 500 (10) K for five days crystals of $Cu_3(PO_4)_2$ and α-$Cu_2P_2O_7$ were obtained. The latter compound was up to some tenths of a millimeter in size; the crystallographic forms $\{\bar{1}12\}$, $\{110\}$, $\{011\}$ and $\{\bar{2}21\}$ were observed. It is conspicuous that the crystals of α-$Cu_2P_2O_7$ obtained during the present studies are colourless; in contrast, Robertson & Calvo (1967) described them as 'small blue-green crystals'.

Synthetic crystal, 0·09 × 0·10 × 0·37 mm, Stoe four-circle diffractometer AED2, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 75 reflections ($40 \leq 2\theta \leq 53°$); $2\theta/\omega$ scan mode, 55 steps (increased for $\alpha_1 - \alpha_2$ dispersion, nine steps each side for background correction), step width 0·03°, step time 0·5 to 1·5 s, $2\theta \leq 90°$, three standard reflections, max. variation 5·6%, 4502 reflections measured (h: $-13 \rightarrow 13$, k: $-16 \rightarrow 0$, l: $-18 \rightarrow 18$), 1999 reflections in unique data set ($R_{\text{int}} = 0{\cdot}046$),

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1757 reflections with $F_o \geq 3\sigma(F_o)$ used for refinement. Seven reflections used to measure ψ scan data for absorption correction (transmission factors from 0·225 to 0·304), corrections for Lorentz and polarization effects. Complex neutral atomic scattering functions as incorporated in program system *STRUCSY* (Stoe & Cie, 1984), which was used for all calculations. Several cycles of structure refinement on F starting with parameters given by Robertson & Calvo (1967) with anisotropic displacement factors gave $R = 0{\cdot}036$, $wR = 0{\cdot}033$, $w = [\sigma(F_o)]^{-2}$, g.o.f. = 3·06 (52 variables); the secondary isotropic extinction was found to be negligible; max. $\Delta/\sigma < 10^{-3}$; max. and min. residual electron density $+1{\cdot}85$ and $-1{\cdot}17$ e Å^{-3}. Atomic coordinates and equivalent isotropic displacement factors are given in Table 1* (labeling of atoms according to former authors), relevant interatomic distances and bond angles in Table 2. The present work confirmed the results of Robertson & Calvo (1967) but higher accuracy for all the structural parameters was reached. Particularly, the centrosymmetric space group is supported. The total shifts for each of the atoms are 0·003 Å (Cu), 0·004 Å [P and O(1)], 0·025 Å [O(2)], 0·012 Å [O(3*c*)] and 0·019 Å [O(3*t*)]. A projection of the crystal structure is shown in Fig. 1.

Related literature. $Cu_2P_2O_7$ is one of a series of pyrophosphates which are known to have a thortveitite-type structure as high-temperature modification (β form). A related low-temperature modification (α form) occurs at room temperature. Robertson & Calvo (1967) determined the crystal structure of the title compound and discussed the transformation to its high-temperature modification β-$Cu_2P_2O_7$ (Robertson & Calvo, 1968).

The r.m.s. amplitudes were found to be smaller than given by the former authors; in particular, the atom O(1) – the bridging oxygen atom within the pyrophosphate group – has r.m.s. amplitudes of 0·21, 0·15 and 0·09 Å.

Table 1. *Atomic fractional coordinates and equivalent isotropic displacement factors* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	−0·01814 (4)	0·31288 (3)	0·50706 (2)	0·0103
P	0·19754 (7)	0·00750 (5)	0·20566 (5)	0·0075
O(1)	0	0·0466 (4)	$\frac{1}{4}$	0·0260
O(2)	0·3757 (2)	0·0002 (2)	0·3614 (2)	0·0093
O(3*c*)	0·2208 (2)	0·1559 (2)	0·1128 (2)	0·0112
O(3*t*)	0·1785 (2)	−0·1508 (2)	0·1179 (2)	0·0162

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Cu—O(3t^{ii})	1·917 (1)	O(3t^{ii})—O(3c^{i})	2·853 (2)	95·54 (6)
Cu—O(3c^{i})	1·936 (1)	O(3t^{ii})—O(2^{iv})	2·871 (2)	94·88 (6)
Cu—O(2^{iv})	1·981 (1)	O(3t^{ii})—O(2^{iii})	3·824 (2)	155·99 (8)
Cu—O(2^{iii})	1·992 (1)	O(3c^{i})—O(2^{iv})	3·882 (2)	164·73 (8)
Cu—O(3c^{v})	2·327 (1)	O(3c^{i})—O(2^{iii})	2·899 (2)	95·09 (5)
Cu—O(3t^{vi})	2·947 (1)	O(2^{iv})—O(2^{iii})	2·543 (3)	79·59 (7)
P—O(3*t*)	1·497 (1)	O(3*t*)—O(3*c*)	2·507 (2)	112·77 (8)
P—O(3*c*)	1·514 (1)	O(3*t*)—O(2)	2·508 (2)	111·30 (8)
P—O(2)	1·540 (1)	O(3*t*)—O(1)	2·558 (3)	112·53 (13)
P—O(1)	1·579 (1)	O(3*c*)—O(2)	2·509 (2)	110·47 (8)
		O(3*c*)—O(1)	2·443 (2)	104·35 (11)
P—O(1)—P^{i}	156·80 (19)	O(2)—O(1)	2·474 (1)	104·95 (5)

Symmetry code: (i) $-x, y, -z+\frac{1}{2}$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

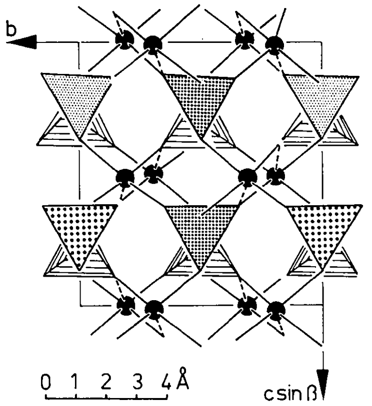

Fig. 1. The crystal structure of α-$Cu_2P_2O_7$ in a projection parallel to [100]. PO_4 tetrahedra are dotted and hatched; Cu—O bonds ≤ 2·0 Å are drawn as solid lines, Cu—O = 2·33 Å shown by broken lines.

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* Lists of structure factors and anisotropic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52273 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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