Short Communications

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The crystal structure of potassium picrate: a comparison between stationary-crystal stationary-counter, densitometer, and visual data.

By Gus J. Palenik,* *Chemistry Division, U. S. Naval Weapons Center, China Lake, California, U.S.A.*

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A comparison between three independent determinations of the crystal structure of potassium picrate is made. In one case, the stationary-crystal stationary-counter technique, with molybdenum radiation, was used to measure the intensities; in the second case, a densitometer measurement of films was employed; in the third case, the intensities were estimated visually from multiple films. The positional parameters from the three sets of data are in good agreement, with some differences in the thermal parameters. The results confirm the validity of stationary-crystal stationary-counter measurements of a measure of the integrated intensity.

Introduction

The various methods of measuring intensity data (see *e.g.* Abrahams, Hamilton & Mathieson, 1970) have stimulated a great deal of discussion. The stationary-crystal stationary-counter, or peak-height, measurement has usually been regarded as less accurate than the scan technique and more susceptible to systematic errors. The crystal structure of potassium picrate was reported by Maartmann-Moe (1969), henceforth referred to as MM, using data obtained from films with a densitometer. Since we had independently measured and refined stationary-crystal data for potassium picrate and the visually estimated determination had been reported by Bettman & Hughes (1954), henceforth referred to as BH,† an accurate comparison of the three methods was possible.

The crystal structure of potassium picrate was originally determined by BH, using 475 visually estimated reflections. The structure was refined using least-squares methods, with one over-all asymmetric temperature factor, and it converged with an $R(=\sum F_{\text{obs}}-F_{\text{calc}}|/\sum F_{\text{obs}})$ of 0·14 (Bettman, 1952). Subsequently, the author independently remeasured and refined counter data for potassium picrate. The present note briefly describes the method of data collection and the refinement of the counter data to permit a comparison of the final values with those reported by MM and BH.

Experimental

Long, thin, yellow crystals of potassium picrate, elongated along **c**, were grown from an aqueous solution. A crystal was cleaved to give a parallelepiped 0·09 × 0·11 × 0·25 mm in size, which was dipped in liquid nitrogen and used for the intensity measurements. The cell constants were measured using the diffractometer and a narrow beam of molybdenum radiation ($\lambda = 0{\cdot}71069$ Å). The values of $a = 13{\cdot}333$ (4), $b = 19{\cdot}112$ (4), and $c = 7{\cdot}118$ (5) Å are in excellent agreement with the dimensions reported by MM. The space group is *Ibca*, with eight molecules per unit cell. A total of 3211 measurements of reflections with $2\theta \leq 60{\cdot}0°$ (molybdenum radiation, $\lambda(\text{avg}) = 0{\cdot}7114$ Å) was made using a GE XRD-5 diffractometer automated by the Conrac Corporation. A large take-off angle (3·7°) was used in the intensity measurements, and the α_1–α_2 doublet was contained within the counter window under the experimental conditions. A one-mil zirconium foil was in front of the counter window and each reflection was counted for 20 sec. A background curve, as a function of 2θ, was derived from measurements of reflections required to be absent because of the space group and which were not affected by streaking or multiple reflection. After averaging equivalent reflections that were measured more than once, the 999 reflections which were greater than 1·2 times the background were considered to be observed. The 340 reflections less than 1·2 times the background were considered as unobserved, and they were not used in the refinement.

The full-matrix least-squares refinement was started using the final parameters of BH. The quantity $\sum w(\Delta F)^2$ was minimized with $\sqrt{w} = 1{\cdot}0$ if $F_{\text{obs}} \leq 30{\cdot}0$ and $\sqrt{w} = 30{\cdot}0/F_{\text{obs}}$ if $F_{\text{obs}} > 30{\cdot}0$, where the F_{obs} is on an absolute scale. The scattering-factor curves for K^+, O, N, and H were taken from *International Tables for X-ray Crystallography* (1962) and the carbon–graphite curve was taken from McWeeny (1951). After four least-squares cycles using individual isotropic thermal parameters, the *R* value, the usual residual, was 0·091 and after three cycles using anisotropic thermal parameters, *R* was 0·045.

A difference Fourier synthesis was calculated and the one hydrogen atom in the asymmetric unit was easily located. Three full-matrix least-squares cycles in which all the atoms were refined, using anisotropic thermal param-

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* Present address: Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.

† The original determination by BH preceded MM's determination by 15 years but was not acknowledged in that study.

eters for the heavy atoms and an isotropic thermal parameter for the hydrogen atom, reduced the residual R to 0·039. By comparison, MM reported a final R index of 0·05 for 559 observed reflections.

Discussion

The final parameters, together with their estimated standard deviations found in the three determinations, are given in Table 1. The largest differences between the positional parameters of MM and the present study (henceforth referred to as P) are 0·004 Å in x, 0·007 Å in y, and 0·010 Å in z, but none of these differences is significant. The positional parameters of BH are in good agreement with those of MM and P, although the y coordinate of O(1), the x and z coordinates of O(2), and the x coordinate are significantly different from the values of P. However, considering the fact that only one over-all asymmetric temperature factor was used by BH, the agreement is excellent.

The β_{11} terms for K, the β_{33} terms for O(1), and the β_{22} terms for O(3) are significantly different, with the β_{11} terms for O(3) being possibly significantly different. None of the other thermal parameters is significantly different, although in almost all cases the β_{11}, β_{22}, and β_{33} values found by MM are larger than the values found by P. These differences may be due to any one of the several possibilities considered below.

The graphite f curve from McWeeny (1951) and the K^+ f-curve from *International Tables for X-ray Crystallography* (1962) were used by P, while MM used the carbon f-curve and presumably the K f-curve from *International Tables for X-ray Crystallography* (1962). The smaller values of the thermal parameters found by P are in agreement with a study by Hanson, Mathew & Palenik (1971) on the effect of changes in the scattering factors on least-squares refinement.

A comparison of the F_{obs} values for the lower 2θ region ($2\theta < 18°$) with those of the higher 2θ region ($2\theta > 50°$), indicates that the values observed by P are larger than those found by MM. Although an absorption error may exist in the data of MM since μr varied from 0·28 to 0·48 for the crystal used for intensity measurements, the effect would presumably be in the opposite direction. Either a systematic error in the densitometer used by MM, or too high a counting rate by P with a subsequent loss of counts,

Table 1. *A comparison of the final parameters found in the three independent studies of potassium picrate*

The first line for each atom gives the values obtained from stationary-crystal stationary-counter measurements, the second line gives the values obtained from the densitometer data, and the third line from visual data. The e.s.d.'s are given in parentheses. The values for the positional parameters are × 10^4 except for K, which is × 10^5. The thermal parameters are all times 10^5. The temperature factor is of the form: $\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	11705 (5)	0000±	2500±	331 (3)	145 (1)	1615 (13)	0±	0±	−12 (4)
	11697 (9)			353 (6)	149 (6)	1611 (32)			−1 (10)
	11730 (20)								
O(1)	2500±	0569 (1)	0000±	329 (10)	131 (5)	2232 (53)	±	96 (20)	0±
		0566 (2)		372 (24)	147 (12)	2744 (140)		87 (51)	
		0556 (4)							
O(2)	0546 (1)	0720 (1)	−0832 (3)	414 (9)	196 (4)	2619 (46)	−81 (5)	−158 (16)	−2 (12)
	0547 (2)	0720 (2)	−0828 (6)	458 (20)	203 (9)	2744 (119)	−94 (12)	−176 (38)	−6 (26)
	0563 (4)	0728 (4)	−0768 (10)						
O(3)	0261 (1)	1636 (1)	−2520 (3)	437 (9)	285 (5)	2086 (40)	−5 (6)	−338 (18)	14 (12)
	0262 (2)	1633 (2)	−2527 (7)	490 (21)	317 (11)	2220 (107)	3 (13)	−343 (43)	27 (30)
	0257 (4)	1637 (4)	−2525 (11)						
O(4)	1785 (1)	3773 (1)	−0705 (3)	624 (11)	160 (4)	2895 (54)	67 (6)	−228 (20)	134 (12)
	1785 (3)	3774 (2)	−0712 (6)	629 (23)	181 (9)	3035 (126)	63 (12)	−175 (45)	146 (27)
	1791 (4)	3782 (4)	−0715 (8)						
N(1)	2500±	3471 (1)	0000±	458 (14)	140 (5)	1282 (49)	0±	122 (22)	0±
		3468 (3)		467 (33)	168 (14)	1104 (133)		36 (62)	
		3472 (5)							
N(2)	0768 (1)	1306 (1)	−1379 (3)	303 (8)	171 (4)	1540 (36)	−3 (5)	−21 (14)	−90 (10)
	0772 (3)	1310 (2)	−1382 (6)	349 (19)	177 (9)	1620 (110)	−4 (11)	−64 (40)	−63 (26)
	0743 (4)	1323 (4)	−1404 (11)						
C(1)	2500±	1221 (1)	0000±	263 (12)	138 (6)	1119 (49)	0±	132 (21)	0±
		1217 (3)		322 (30)	156 (16)	1539 (166)		135 (64)	
		1225 (6)							
C(2)	1663 (1)	1647 (1)	−0638 (3)	240 (8)	142 (4)	1224 (4)	−12 (5)	−8 (14)	−33 (10)
	1665 (3)	1647 (2)	−0623 (7)	286 (22)	159 (10)	1231 (102)	−14 (11)	64 (40)	−32 (26)
	1651 (4)	1651 (4)	−0631 (11)						
C(3)	1662 (1)	2364 (1)	−0668 (3)	314 (9)	139 (4)	1106 (35)	20 (5)	36 (16)	−4 (10)
	1658 (1)	2366 (2)	−0664 (7)	368 (22)	163 (12)	1155 (97)	24 (13)	62 (43)	−4 (25)
	1655 (4)	2368 (4)	−0668 (11)						
C(4)	2500±	2717 (1)	0000±	355 (14)	104 (5)	1072 (49)	0±	43 (22)	0±
		2716 (3)		353 (29)	132 (13)	1394 (170)		45 (60)	
		2730 (6)							
H	108 (2)	263 (1)	−115 (4)	0·45 (46)*					
	108 (4)	261 (4)	−118 (9)	0·60 (90)*					

± Value determined by the space group symmetry.
* Isotropic *B*

could also explain the observed differences in the intensity data.

The bond distances calculated from the three sets of positional parameters are presented in Table 2. The average difference in bond distances between P and MM is 0·004 Å. The largest differences are between N(2)–C(2) (0·010 Å) and C(3)–C(4) (0·007 Å), although neither of these is significantly different. There are significant differences in the values of BH compared with those of either MM or P. However, two of the three significantly different distances involve an NO_2 group, where anisotropic thermal motion is the greatest. Since BH used only one asymmetric thermal parameter, this difference is not surprising.

Table 2. *Comparison of the bond distances (in Å) found in the three studies of potassium picrate*

	P	MM	BH
C(1)–O(1)	1·245 (3)	1·243 (7)	1·282 (13)
C(1)–C(2)	1·455 (2)	1·452 (5)	1·467 (10)
C(2)–C(3)	1·370 (2)	1·372 (6)	1·373 (9)
C(3)–C(4)	1·389 (2)	1·382 (5)	1·407 (9)
C(4)–N(1)	1·440 (3)	1·436 (8)	1·423 (15)
N(1)–O(4)	1·224 (2)	1·228 (5)	1·228 (8)
C(2)–N(2)	1·459 (2)	1·457 (6)	1·472 (10)
N(2)–O(2)	1·222 (3)	1·232 (5)	1·251 (10)
N(2)–O(3)	1·230 (3)	1·229 (5)	1·194 (11)

One last point that was not discussed by MM relates to the possible existence of a C–H···O hydrogen bond involving the lone hydrogen atom and the oxygen atom O(3). The H···O(3) distance of 2·47 (2) Å is slightly less than a van der Waals contact. In addition, the C–H···O angle of 175 (2)° and the C–H distance of 0·99 (2) Å suggest that an interaction does exist. The corresponding N(2)–O(3) distance found by P is longer than the N(2)–O(2) distance, in agreement with the presence of a hydrogen bond involving O(3) but not O(2).

Conclusions

The results of three independent determinations of the crystal structure of potassium picrate using different methods for measuring the intensity data are in excellent agreement. The only significant differences in the positional parameters involve the visual data which were not completely refined. There are three significantly different thermal parameters when the values of P and MM are compared. However, the source of the differences is obscure since a number of different factors may be involved.

This present comparison indicates that the stationary-crystal stationary-counter technique can give as valid a measurement of integrated intensities as densitometer data from films. Two independent studies of histamine acid phosphate monohydrate (Veidis, Palenik, Schaffrin & Trotter, 1969) and μ-oxo-bis(nitrosyltriphenylphosphine)-diiridium(I) (Dellaca, Mathew, Palenik & Robinson, 1971) indicated that stationary-crystal stationary-counter and moving-crystal data yield identical results. A similar conclusion was reached recently by DeCamp & Stewart (1971). Therefore, one can conclude that stationary-crystal stationary-counter measurements are indeed a valid measurement of the integrated intensity and compare favorably with other methods of intensity measurements.

References

ABRAHAMS, S. C., HAMILTON, W. C. & MATHIESON, A. McL. (1970). *Acta Cryst.* A**26**, 1.

BETTMAN, M. (1952). Ph. D. Thesis. California Instit. of Technology, Pasadena, California.

BETTMAN, M. & HUGHES, E. W. (1954). *Structure Reports for* 1954 (1961) Vol. 18, pp. 715-716. N. V. A. Oosthoek's Uitgevers MIJ, Utrecht.

DECAMP, W. H. & STEWART, J. M. (1971). *Acta Cryst.* B**27**, 1227.

DELLACA, R. J., MATHEW, M., PALENIK, G. J. & ROBINSON, W. R. (1971). In preparation.

HANSON, H., MATHEW, M. & PALENIK, G. J. (1971). Unpublished results.

International Tables for X-ray Crystallography (1962). Vol. III, p. 211. Birmingham: Kynoch Press.

MAARTMANN-MOE, K. (1969). *Acta Cryst.* B**25**, 1452.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

VEIDIS, M., PALENIK, G. J., SCHAFFRIN, R. & TROTTER, J. (1969). *J. Chem. Soc.* (*A*) p. 2659.

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The crystal structure of 4-phenylazoazobenzene.

By R. D. GILARDI and I. L. KARLE, *Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C.* 20390, *U.S.A.*

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4-Phenylazoazobenzene ($C_{18}H_{14}N_4$) crystallizes in the space group $P2_1/c$, with $a=13\cdot870$ (5), $b=4\cdot617$ (2), $c=11\cdot920$ (5) Å, $\beta=113\cdot20$ (3)°, and $Z=2$. The calculated crystal density is 1·34 g.cm^{-3}. The asymmetric unit, a half-molecule, was determined using the symbolic addition procedure from 1213 reflection intensities measured on a diffractometer with Cu $K\alpha$ radiation. The structure was refined to a final R value of 0·078. The 22 atoms of a whole molecule are planar to within $\pm 0\cdot05$ Å. The molecules stack in a herringbone pattern, with the planes of adjacent parallel molecules separated by only 3·325 (5) Å.

The crystal structure of 4-phenylazoazobenzene (PAAB) was determined primarily to obtain the orientation of the molecules in the crystal. This information can be used to relate theoretically estimated molecular properties and anisotropic crystal properties (Lonsdale & Krishnan, 1936), such as the polarization of crystal absorption spectra (Anex & Fratini, 1964).

Crystals of PAAB, grown from methyl ethyl ketone, were