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Picric Acid–Naphthalene 1/1 π Complex, $C_6H_3N_3O_7.C_{10}H_8$. A Disordered Structure

BY A. BANERJEE AND C. J. BROWN

*Department of Metallurgy and Materials Engineering, City of London Polytechnic, Central House, Whitechapel High Street, London E*1 *7PF*

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Abstract. $M_r = 357{\cdot}28$, monoclinic, $P2_1/a$, $a = 16{\cdot}248\,(5)$, $b = 6{\cdot}871\,(2)$, $c = 14{\cdot}306\,(5)$ Å, $\beta = 96{\cdot}62\,(5)°$, $V = 1586{\cdot}47$ Å^3, $Z = 4$, $D_m = 1{\cdot}47\,(1)$, $D_x = 1{\cdot}496$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 1{\cdot}16$ mm^{-1}, $F(000) = 736$, $T = 293$ K, $R = 0{\cdot}066$ for 918 observed reflexions ($I > 3\sigma_I$). Molecules lie in (010) parallel to each other, stacking alternately picric acid and naphthalene with hydrogen bonds linking picric acid molecules across alternative symmetry centres and also along **a**. The two arrangements are present in ratio ≈4:1, and it was not feasible to separate the two sets of atomic coordinates.

Introduction. Unit-cell dimensions have been reported (Herbstein & Kaftory, 1975) as have the crystal structure determinations of a number of homologues (Carstensen-Oeser, Göttlicher & Habermehl, 1968; Herbstein & Kaftory, 1976). Physical properties have been reported by Mindovich (1956) and by Westwood (1978). In none of these reports was there any indication of structural disorder, and this work was undertaken at the instigation of Dr Westwood in order to explain some peculiarities observed.

Experimental. Sample prepared by Dr C. V. Westwood of the Chemistry Department, City of London Polytechnic; recrystallized (*ca* 1·5 × 0·2 × 0·2 mm) from ethanol; m.p. 401 K. D_m by flotation in NaI solution. Lattice parameters from rotation and Weissenberg photographs, refined by least-squares fit to 16 selected reflexions measured on a Stoe Stadi-2 diffractometer; intensities from $h0l \rightarrow h6l$ levels on the diffractometer using ω scans, interlayer scaling and $0k0$ intensities from c Weissenberg. 1559 measured reflexions, 918 observed with $I > 3\sigma_I$; index range h 0 to 16, k 0 to 6, l −15 to +17; $2\theta_{\max} = 110°$. Seven standard reflexions, no variation. Corrections for Lp and an empirical correction for extinction to eight reflexions during refinement. No absorption correction. Structure solved by trial-and-error as direct methods failed. Patterson map indicated layer structure with $b/4$ separation. Refinement by least squares on F using initially $B_{\rm iso}$ and finally B_{ij}. H atoms included at calculated positions with $B_{\rm iso} = 8{\cdot}0$ Å^2, but not refined. Difference Fourier during refinement showed two alternative sites for the O of the picric acid OH; site occupation refinement converged to 0·80 for O(1) position and 0·20 for O(8) and these values used in further SFLS refinement until final shifts all $<0{\cdot}3\sigma$. Final $R = 0{\cdot}066$, $R_w = 0{\cdot}136$, $\sqrt{w} = 1/F_o$. Max. electron density in final difference Fourier map $\pm 0{\cdot}2$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). *NRC* programs (Ahmed, Hall, Pippy & Huber, 1970) implemented on our DEC-10 computer.

Discussion. The final atomic coordinates and equivalent isotropic temperature parameters are listed in Table 1.* Bond lengths and interbond angles are in Table 2. The arrangements of the molecules in the unit cell, together with the atom numbering and hydrogen bonds are shown in Fig. 1.

Molecules of both picric acid and naphthalene lie approximately parallel to (010) in layers with $y = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$ and π-bonding interactions across the 3·4 Å ($b/2$) spacing; the overlap diagram is shown in Fig. 2 as a normal projection along **b**. C(14) of the naphthalene ring lies almost exactly above the mid-point of the picric acid ring.

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* Lists of structure factors, anisotropic thermal parameters and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39515 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic parameters and e.s.d.'s*

$B_{eq} = \frac{4}{3}[(\beta_{11}/a^{*2}) + (\beta_{22}/b^{*2}) + (\beta_{33}/c^{*2})]$.

	x	y	z	B_{eq}(Å^2)
C(1)	0·9413 (4)	0·1182 (8)	0·1542 (4)	3·30 (14)
C(2)	0·8541 (5)	0·1027 (10)	0·1526 (4)	4·63 (15)
C(3)	0·8145 (3)	0·1105 (7)	0·2347 (3)	3·30 (10)
C(4)	0·8623 (4)	0·1189 (9)	0·3190 (4)	3·50 (14)
C(5)	0·9503 (4)	0·1096 (11)	0·3272 (5)	5·07 (16)
C(6)	0·9872 (3)	0·1123 (9)	0·2456 (5)	4·47 (13)
C(7)	0·6395 (6)	0·1211 (9)	0·5927 (6)	5·56 (17)
C(8)	0·5552 (5)	0·1325 (11)	0·6061 (5)	5·45 (16)
C(9)	0·5347 (4)	0·1231 (8)	0·7002 (4)	2·63 (12)
C(10)	0·4508 (5)	0·1413 (11)	0·7093 (5)	4·89 (17)
C(11)	0·4328 (5)	0·1152 (10)	0·7958 (6)	6·15 (17)
C(12)	0·4875 (7)	0·1229 (11)	0·8743 (6)	7·45 (20)
C(13)	0·5671 (6)	0·1294 (12)	0·8647 (6)	5·73 (20)
C(14)	0·5947 (4)	0·1259 (9)	0·7742 (5)	4·40 (15)
C(15)	0·6795 (5)	0·1116 (10)	0·7592 (6)	6·42 (17)
C(16)	0·6998 (5)	0·1180 (11)	0·6672 (5)	5·61 (17)
N(1)	0·7991 (5)	0·0996 (10)	0·0619 (5)	9·04 (19)
N(2)	0·8264 (4)	0·1093 (8)	0·4111 (4)	5·58 (13)
N(3)	1·0772 (4)	0·1259 (9)	0·2546 (6)	7·36 (17)
O(1)†	0·9799 (5)	0·1131 (10)	0·0775 (5)	7·35 (17)
O(2)	0·8301 (6)	0·1472 (14)	−0·0063 (6)	11·93 (22)
O(3)	0·7262 (5)	0·0744 (13)	0·0678 (5)	12·57 (21)
O(4)	0·7473 (4)	0·0854 (8)	0·3935 (5)	7·95 (15)
O(5)	0·8685 (5)	0·1293 (9)	0·4839 (4)	7·27 (15)
O(6)	1·1150 (4)	0·1389 (10)	0·3398 (6)	9·08 (19)
O(7)	1·1098 (4)	0·1457 (9)	0·1851 (6)	8·22 (18)
O(8)‡	1·0013 (15)	0·1302 (41)	0·4125 (17)	5·99 (51)

† 80% site occupation factor.
‡ 20% site occupation factor.

Table 2. *Bond lengths* (Å) *and interbond angles* (°)

C(1)–C(2)	1·417 (11)	C(9)–C(10)	1·389 (9)
C(1)–C(6)	1·430 (10)	C(9)–C(14)	1·354 (9)
C(1)–O(1)†	1·326 (10)	C(10)–C(11)	1·316 (11)
C(2)–C(3)	1·404 (8)	C(11)–C(12)	1·351 (12)
C(2)–N(1)	1·489 (10)	C(12)–C(13)	1·317 (15)
C(3)–C(4)	1·359 (8)	C(13)–C(14)	1·419 (10)
C(4)–C(5)	1·423 (10)	C(14)–C(15)	1·422 (10)
C(4)–N(2)	1·503 (9)	C(15)–C(16)	1·395 (11)
C(5)–C(6)	1·373 (10)	N(1)–O(2)	1·195 (11)
C(5)–O(8)‡	1·400 (26)	N(1)–O(3)	1·209 (12)
C(6)–N(3)	1·455 (9)	N(2)–O(4)	1·291 (9)
C(7)–C(8)	1·407 (13)	N(2)–O(5)	1·186 (9)
C(7)–C(16)	1·363 (11)	N(3)–O(6)	1·304 (11)
C(8)–C(9)	1·426 (9)	N(3)–O(7)	1·187 (12)

C(2)–C(1)–C(6)	115·3 (6)	C(10)–C(9)–C(14)	123·5 (6)
C(2)–C(1)–O(1)†	123·5 (6)	C(9)–C(10)–C(11)	113·7 (7)
C(6)–C(1)–O(1)†	120·6 (6)	C(10)–C(11)–C(12)	125·5 (8)
C(1)–C(2)–C(3)	122·5 (6)	C(11)–C(12)–C(13)	118·4 (8)
C(1)–C(2)–N(1)	120·9 (6)	C(12)–C(13)–C(14)	120·8 (8)
C(3)–C(2)–N(1)	116·2 (6)	C(9)–C(14)–C(13)	116·0 (6)
C(2)–C(3)–C(4)	118·3 (5)	C(9)–C(14)–C(15)	120·4 (6)
C(3)–C(4)–C(5)	122·5 (6)	C(13)–C(14)–C(15)	123·5 (7)
C(3)–C(4)–N(2)	122·4 (5)	C(14)–C(15)–C(16)	118·6 (7)
C(5)–C(4)–N(2)	114·5 (6)	C(7)–C(16)–C(15)	120·8 (7)
C(4)–C(5)–C(6)	117·6 (6)	C(2)–N(1)–O(2)	116·1 (7)
C(4)–C(5)–O(8)‡	123·7 (1·2)	C(2)–N(1)–O(3)	115·9 (7)
C(6)–C(5)–O(8)‡	117·9 (1·2)	O(2)–N(1)–O(3)	127·2 (9)
C(1)–C(6)–C(5)	123·0 (6)	C(4)–N(2)–O(4)	108·2 (5)
C(1)–C(6)–N(3)	119·5 (6)	C(4)–N(2)–O(5)	121·5 (6)
C(5)–C(6)–N(3)	117·2 (6)	O(4)–N(2)–O(5)	130·2 (6)
C(8)–C(7)–C(16)	121·2 (7)	C(6)–N(3)–O(6)	116·6 (7)
C(7)–C(8)–C(9)	117·7 (7)	C(6)–N(3)–O(7)	118·3 (7)
C(8)–C(9)–C(10)	115·0 (6)	O(6)–N(3)–O(7)	124·6 (8)
C(8)–C(9)–C(14)	120·7 (6)		

† 80% site occupation.
‡ 20% site occupation.

Hydrogen bonds link pairs of picric acid molecules related by centres of symmetry either through O(1)–O(1^{i}) 2·844 (10) Å across (0,0,0) with 80% site occupation, or through O(8)–O(8^{ii}) 3·082 (36) Å across (0,0,$\frac{1}{2}$) with 20% site occupation. These alternative sites can be occupied with only small disturbance to the coordinates of the other picric acid atoms. The OH···HO hydrogen bonds release a spare proton from half the picric acid molecules and this appears to be transferred to either O(4) or O(6) enabling H bonding to take place: O(4)···H···O(6^{iii}) 2·901 (9) Å (Fig. 1). That H bonding does occur between the nitro groups is supported by the distances N(2)–O(4) 1·291 (9) and N(3)–O(6) 1·304 (11) Å which are both appreciably longer than the other four N–O bonds [mean 1·194 (11) Å]. The stabilizing influence of the postulated H bond is also reflected in the values of B_{eq} which are ≈7·5 Å^2 for O(4) and O(5) and ≈8·5 Å^2 for O(6) and O(7) whereas for O(2) and O(3) which are

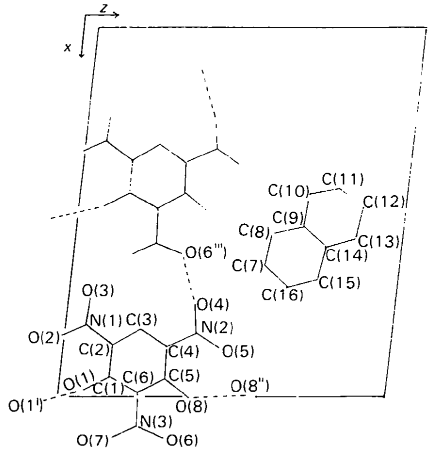

Fig. 1. Arrangement of molecules in part of the unit cell ($y = 0$ to $\frac{1}{2}$) showing atomic numbering and hydrogen bonds (dashed lines). Symmetry code: (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z$.

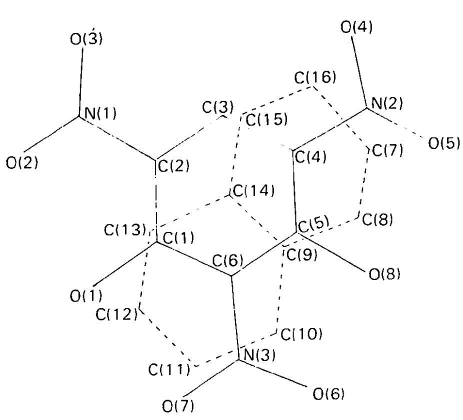

Fig. 2. Overlap of naphthalene and picric acid molecules in sections perpendicular to **b**.

not H bonded B_{eq} is $\approx$12·2 Å^2. The dihedral angles between the planes of the nitro groups and the phenyl ring are also noticeably different; N(1)O(2)O(3) makes an angle of 13·61 (5)° with the C(1)–(6) ring, N(2)-O(4)O(5) makes 7·56 (5)°, and N(3)O(6)O(7) makes 5·67 (5)°.

The bond lengths (Table 2) result from the superposition of the two disordered picric acid molecules, and it is probable that the precise positioning of the naphthalene molecules is likewise affected. Unsuccessful attempts were made to separate the two arrangements, including full-matrix least-squares refinement, but no progress was made along these lines, and the results presented are the best interpretation which can be made at present. To try to improve the resolution of the atomic parameters, two additional complete sets of intensity data were collected on the diffractometer using Mo $K\alpha$ radiation, and also a considerable amount of photographic data on the Weissenberg camera, but the quite large variations in values of F led to the belief that no two crystals used had the same proportion of disorder and the results presented here are for one particular crystal only under one particular set of experimental conditions, and these are not necessarily reproducible.

Proton transfer of the type postulated and the ability of nitro groups to abstract H atoms have already been envisaged in an investigation of the structure of picric acid (Soriano-Garcia, Srikrishnan & Parthasarathy, 1978).

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Structure of α-(Isopropylamino)salicylphosphonic Acid Hemihydrate, $C_{10}H_{16}NO_4P.0{\cdot}5H_2O$

By W. Sawka-Dobrowolska

Institute of Chemistry, University of Wrocław, 14 *Joliot-Curie* 50–383 *Wrocław, Poland*

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Abstract. $M_r = 254{\cdot}2$, monoclinic, $C2/c$, $a = 24{\cdot}686\ (4)$, $b = 6{\cdot}257\ (1)$, $c = 18{\cdot}629\ (3)$ Å, $\beta = 123{\cdot}60\ (2)$°, $V = 2396{\cdot}7$ Å^3, $Z = 8$, $D_m = 1{\cdot}41\ (1)$, $D_x = 1{\cdot}41$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}24$ mm^{-1}, $F(000) = 1080$, $T = 293$ K, $R = 0{\cdot}041$ for 1736 reflexions. The title compound exists as a zwitterion and adopts a *trans* conformation with the P—C—N—C torsion angle 179·5 (2)°. The coordination around P is distorted tetrahedral with normal P—O bond lengths. There is intermolecular, and possibly intramolecular, hydrogen bonding in the structure.

Introduction. The present structural investigation was undertaken as part of our study on the conformation and the hydrogen-bond system of this new aminophosphonic acid.

Experimental. Synthesis described by Zoń & Mastalerz (1976). Clear, colourless crystals from water at room temperature, dimensions 0·2 × 0·2 × 0·3 mm; density by flotation in bromoform/benzene; monoclinic Cc or $C2/c$ from Weissenberg photographs, $C2/c$ confirmed by refinement; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $16 \le 2\theta(\mathrm{Mo}) \le 25$° measured on diffractometer; 3183 independent reflexions; $2\theta_{\max} = 60$°; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1}, depending on intensity; two standards ($42\bar{2}$, $51\bar{2}$) every 50 reflexions with average intensities and e.s.d.'s of 193 300 (2500) and 92 800 (1900); corrected for Lorentz and polarization, not for absorption; 1736 with $I > 1{\cdot}96\sigma(I)$ used for structure determination; index range h 0 to 31, k 0 to 8, l −25 to 24; calculations performed with Syntex (1976) *XTL* system; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); direct methods, Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$;

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