

Molecular Compounds and Complexes.

VII.* The Crystal Structure of Anthracene:Picric Acid

BY F. H. HERBSTEIN

Department of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel

AND M. KAFTORY

Department of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel and Laboratorium für Organische Chemie, E.T.H. Zürich, Switzerland

(Received 6 June 1975; accepted 14 June 1975)

The structure of the π -molecular compound anthracene:picric acid (monoclinic; $a=7.180$, $b=12.901$, $c=19.205$ Å, $\beta=90.52^\circ$, space group $P2_1/c$, $Z=4$) has been solved by direct methods, and refined to $R=5.0\%$ (goodness of fit = 1.67) with the intensities of 2092 non-zero reflexions measured on a diffractometer (graphite-monochromatized Mo $K\alpha$). The components are arranged alternately in quasi-hexagonally close-packed mixed stacks, extending in the [100] direction. The picric acid molecule has an intramolecular hydrogen bond between the phenol OH group and an adjacent nitro group. The individual six-membered rings of the anthracene molecule are planar but the molecule as a whole deviates significantly from planarity and is also almost but not quite centrosymmetric. The bond lengths and angles conform to mm symmetry. The small differences found between the dimensions of anthracene in its picric acid molecular compound and in crystalline anthracene are not statistically significant.

1. Introduction

Anthracene:picric acid was one of the first π -donor:acceptor molecular compounds to be prepared (Fritzsche, 1858). Determination of its crystal structure adds to our knowledge of π -molecular compounds with picric acid as electron acceptor; few such structures have been reported. Furthermore comparison of the anthracene:picric acid structure with that of anthracene:TNB† (Brown, Wallwork & Wilson, 1964) gives information about the effect of hydroxyl substitution in trinitrobenzene on the arrangement of the components in these molecular compounds, while comparison of the dimensions of anthracene in crystalline anthracene and in anthracene:picric acid may allow estimation of the effects of π -molecular compound formation on the dimensions of the molecule.

2. Experimental

Red needles of anthracene:picric acid were obtained by slow cooling of benzene solutions of the components in equimolar ratio. The crystals show oblique extinction, are elongated along [100], show {001} and {010} faces and are stable in air. Crystallographic and other information is summarized in Table 1. Cell dimensions were measured from back-reflexion Weissenberg photographs and inclined-beam oscillation photographs (Mathieson film mounting) (Herbstein, 1963) and checked on the diffractometer.

Table 1. *Crystallographic and other information for anthracene:picric acid (the stack axis is in bold type)*

$C_{14}H_{10} \cdot C_6H_3N_3O_7$, $M=407.33$
Monoclinic
$a = \mathbf{7.180}$ (3), $b = 12.901$ (6), $c = 19.205$ (9) Å
$\beta = 90.52$ (9) $^\circ$
$U = 1778.9$ Å ³
$D_m = 1.466$, $D_c = 1.521$ g cm ⁻³ for $Z=4$
$\mu = 1.27$ cm ⁻¹ for Mo $K\alpha$ radiation
Wavelengths: Cu $K\alpha_1 = 1.54050$ Å
$\alpha_2 = 1.54434$
Systematic absences: $h0l$ absent for l odd
$0k0$ absent for k odd,
Space group: $P2_1/c$

Intensities were measured from a crystal, $0.04 \times 0.02 \times 0.02$ mm, set about [100] on a four-circle diffractometer; Mo $K\alpha$ (graphite monochromator) was used. No absorption corrections were applied. The weights were assigned by the procedure:

$$\sigma(I) = k\{(I_{\text{peak}} + I_{\text{back}})^{1/2} + 0.03 I_{\text{peak}} + 10\}$$

(i) for $I > \sigma(I)$:

$$\sigma(F) = (I/LP)^{1/2} - \{(I/LP) - [\sigma(I)/LP]\}^{1/2}$$

where

$$(1/LP) = \sin 2\theta \left\{ \frac{1 + K_M}{K_M + \cos^2 2\theta} \right\}$$

and $K_M = \cos 2\theta_M$ ($= 0.9775$ for Mo $K\alpha$, graphite monochromator).

* Part VI: Herbstein & Kaftory (1975).

† TNB = 1,3,5-trinitrobenzene.

(ii) for $I \leq \sigma(I)$:

$$\sigma(F) = |F|.$$

$$w(hkl) = \frac{1}{\sigma(F)} [\exp(R \sin^2 \theta / \lambda^2)]^{1/2}$$

where $R=6$ (Dunitz & Seiler, 1973).

There was no significant variation in the standard reflexions (043, 404) during the course of the measurements. 3092 reflexions were measured; 2092 of these with $|F| > 1.5\sigma(F)$ were used in the determination and refinement of the structure.

Table 2. *Statistical and other information for structure solution by direct methods*

E-statistics	Experimental	Theoretical	
		\bar{I}	1
$\langle E \rangle$	0.764	0.798	0.886
$\langle E^2 \rangle$	1.030	1.000	1.000
$\langle E^2 - 1 \rangle$	1.071	0.968	0.736
$E > 1\%$	27.1	32.0	37.0
$E > 2\%$	5.6	5.0	1.8
$E > 3\%$	0.98	0.8	0.01

Origin-fixing reflexions

2	1	2	+6.21
4	3	$\bar{1}\bar{3}$	+5.52
7	8	$\bar{5}$	+3.95

Signs of reflexions fixed by application of Σ_1 relations

4	2	4	+3.59
---	---	---	-------

Other reflexions in starting set

6	2	$\bar{1}\bar{1}$	+5.18
0	4	16	-4.52
2	1	12	+3.17

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971); statistical and other information is summarized in Table 2. The first E map, based on 363 signs, showed all the non-hydrogen atoms. Refinement proceeded by standard methods; H atoms were found from a difference map at a late stage of the refinement, and their positions and isotropic temperature factors refined. All parameters were then refined together by block-diagonal least-squares calculations (based on F); shifts in the final cycle were less than one-tenth of the appropriate standard deviation.* The final atomic parameters are given in Table 3 and have not been corrected for thermal motion. All the geometrical features discussed below are based on these coordinates, except where explicitly stated otherwise. R and R_w were both 5.0%; the 'goodness of fit' (323 parameters) was 1.67. Structure factors were calculated for

all 2780 reflexions with net intensities greater than zero: R was 7.1%.*

3. Description of the structure

3.1. Molecular dimensions

3.1.1. *Picric acid*: The molecular dimensions and e.s.d.'s are shown in Fig. 1. The C and N atoms are coplanar (Table 4); torsion angles of the nitro groups are 3.9° [nitro groups bonded to CP(1) and CP(3)] and 50.9° [nitro group bonded to CP(5)]. The distances from the phenol O to the adjacent O atoms of the nitro

* The 212 reflexion [$F(\text{meas})=280.4$; $F(\text{calc})=369.4$] was given zero weight in all these calculations. The discrepancy is due to inadequate correction for 'lost counts' during measurements of this very strong reflexion.

Table 3. *Positional and thermal parameters*(a) Fractional atomic coordinates and e.s.d.'s ($\times 10^4$)

	x	y	z
Anthracene			
C(1)	7134 (5)	2155 (3)	1635 (2)
C(2)	6528 (5)	2877 (3)	2093 (2)
C(3)	5971 (4)	2590 (2)	2773 (1)
C(4)	5384 (4)	3314 (2)	3268 (2)
C(5)	4847 (4)	3026 (2)	3933 (2)
C(6)	4225 (4)	3755 (3)	4443 (2)
C(7)	3672 (5)	3436 (3)	5080 (2)
C(8)	3730 (5)	2379 (3)	5265 (2)
C(9)	4328 (5)	1660 (3)	4806 (2)
C(10)	4898 (4)	1949 (2)	4121 (1)
C(11)	5491 (4)	1225 (2)	3636 (2)
C(12)	6031 (4)	1514 (2)	2968 (2)
C(13)	6697 (5)	784 (3)	2469 (2)
C(14)	7228 (5)	1098 (3)	1827 (2)
HC(1)	7476 (52)	2359 (30)	1192 (19)
HC(2)	6477 (54)	3641 (31)	1978 (20)
HC(4)	5348 (51)	4045 (30)	3149 (19)
HC(6)	4251 (55)	4484 (31)	4319 (20)
HC(7)	3158 (58)	3947 (33)	5411 (21)
HC(8)	3403 (59)	2165 (33)	5735 (21)
HC(9)	4478 (59)	944 (34)	4921 (22)
HC(11)	5549 (47)	469 (26)	3744 (17)
HC(13)	6829 (54)	16 (30)	2603 (19)
HC(14)	7753 (58)	605 (32)	1524 (21)
Picric acid			
CP(1)	1004 (4)	2175 (2)	2845 (1)
CP(2)	429 (4)	3006 (2)	3240 (2)
CP(3)	-159 (4)	2826 (2)	3907 (1)
CP(4)	-194 (4)	1834 (2)	4193 (1)
CP(5)	404 (4)	1032 (2)	3784 (1)
CP(6)	1013 (4)	1152 (2)	3097 (1)
N(1)	1612 (4)	2385 (2)	2137 (1)
N(2)	-791 (4)	3703 (2)	4332 (1)
N(3)	373 (4)	10 (2)	4090 (1)
O(1)	1487 (3)	323 (2)	2730 (1)
O(2)	2033 (4)	1640 (2)	1766 (1)
O(3)	1685 (4)	3279 (2)	1941 (1)
O(4)	-866 (4)	4552 (2)	4048 (1)
O(5)	-1232 (4)	3536 (2)	4924 (1)
O(6)	-1062 (4)	-282 (2)	4373 (1)
O(7)	1796 (4)	-523 (2)	4066 (1)
HCP(2)	425 (51)	3692 (29)	3052 (19)
HCP(4)	-603 (52)	1695 (29)	4675 (19)
HOH	1817 (66)	520 (36)	2324 (24)

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31199 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3 (cont.)

(b) Anisotropic temperature factors ($\times 10^4$) for non-hydrogen atoms and isotropic temperature factors ($\times 10^3$) for hydrogen atoms
$$T_{ij} = \exp(-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij}^* h_i a_i^* a_j^*) \quad T_{iso} = \exp(-8\pi^2 U_{iso} \sin^2 \theta / \lambda^2)$$

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
Anthracene	C(1)	518 (21)	902 (25)	407 (17)	-109 (18)	22 (14)	-31 (19)	
	C(2)	474 (18)	597 (17)	467 (19)	-60 (16)	1 (14)	36 (13)	
	C(3)	326 (16)	471 (17)	397 (15)	-42 (12)	-10 (10)	7 (13)	
	C(4)	377 (16)	381 (17)	463 (17)	7 (12)	-29 (14)	7 (13)	
	C(5)	301 (16)	440 (17)	441 (15)	-6 (12)	-37 (10)	-36 (13)	
	C(6)	438 (18)	506 (17)	580 (19)	12 (14)	-0 (14)	-106 (13)	
	C(7)	490 (18)	802 (25)	526 (21)	-17 (18)	47 (17)	-229 (19)	
	C(8)	604 (21)	853 (25)	417 (17)	-71 (18)	46 (14)	-58 (19)	
	C(9)	508 (18)	641 (17)	460 (17)	-65 (16)	12 (14)	73 (19)	
	C(10)	342 (16)	491 (17)	402 (15)	-24 (12)	-41 (14)	16 (13)	
	C(11)	391 (16)	378 (17)	472 (17)	-13 (12)	-27 (14)	17 (13)	
	C(12)	321 (13)	430 (17)	435 (15)	-32 (12)	-18 (10)	-48 (13)	
	C(13)	457 (18)	503 (17)	566 (19)	-14 (14)	-32 (14)	-127 (13)	
	C(14)	513 (21)	755 (25)	560 (21)	-23 (18)	27 (17)	-258 (19)	
Picric acid	CP(1)	341 (13)	433 (17)	333 (13)	-26 (12)	20 (10)	34 (13)	
	CP(2)	349 (16)	401 (17)	444 (15)	-36 (12)	-37 (10)	4 (13)	
	CP(3)	343 (16)	398 (17)	424 (15)	0 (12)	-5 (10)	-77 (13)	
	CP(4)	362 (16)	487 (17)	364 (15)	-29 (12)	11 (10)	-14 (13)	
	CP(5)	374 (16)	364 (17)	379 (15)	-43 (12)	14 (10)	30 (13)	
	CP(6)	343 (16)	400 (17)	355 (13)	-4 (12)	-6 (10)	-54 (13)	
	N(1)	458 (16)	511 (17)	396 (13)	-37 (12)	31 (10)	57 (13)	
	N(2)	442 (16)	504 (17)	565 (15)	-17 (12)	53 (10)	-131 (13)	
	N(3)	630 (16)	443 (17)	344 (13)	-21 (12)	25 (10)	-2 (13)	
	O(1)	610 (13)	428 (8)	396 (11)	22 (9)	82 (10)	-36 (6)	
	O(2)	813 (18)	609 (17)	397 (11)	-38 (12)	191 (10)	-39 (13)	
	O(3)	805 (18)	546 (17)	525 (13)	-33 (12)	98 (10)	174 (13)	
	O(4)	822 (18)	419 (17)	862 (19)	53 (12)	136 (14)	-99 (13)	
	O(5)	748 (18)	727 (17)	520 (13)	25 (14)	154 (10)	-185 (13)	
	O(6)	716 (16)	636 (17)	588 (15)	-200 (12)	80 (10)	148 (13)	
	O(7)	864 (18)	547 (17)	669 (17)	216 (14)	145 (14)	129 (13)	
		U_{iso}		U_{iso}		U_{iso}		U_{iso}
	HC(1)	68 (11)	HC(6)	75 (13)	HC(9)	89 (14)	HC(14)	79 (13)
	HC(2)	73 (11)	HC(7)	84 (13)	HC(11)	54 (9)	HCP(2)	63 (11)
	HC(4)	66 (10)	HC(8)	86 (13)	HC(13)	71 (11)	HCP(4)	62 (11)
							HOH	99 (15)

groups in positions 2 and 6 are 2.55 and 2.81 Å respectively. The existence of a hydrogen bond between O(1) and O(2) is confirmed by the appearance of a peak in the difference synthesis in the ring plane (Fig. 2). The six atoms of the internally hydrogen-bonded ring are coplanar (Table 4), with their plane at an angle of 2.0° to the benzene-ring plane. The intramolecular hydrogen bonding causes the pattern of torsion angles of the nitro groups to differ somewhat from those found in related molecules (*e.g.* Herbstein & Kaftory, 1975).

3.1.2. *Anthracene*: The molecular dimensions and e.s.d.'s are shown in Fig. 3. The molecule has a slightly zigzag shape, approximating to symmetry $C_i-\bar{1}$ but deviating significantly from this symmetry in the displacement of atoms from the mean molecular plane (Table 5). The three six-membered rings can each be fitted to separate planes without significant deviations.

3.2. Arrangement of the component molecules

The anthracene and picric acid molecules are in quasi-hexagonally close-packed mixed stacks, whose

axes are in the [100] direction (Fig. 4). Each picric acid molecule, including the region of the intramolecular ring formed by hydrogen bonding of adjacent hydroxyl and nitro groups (see above), is sandwiched between translationally equivalent anthracene molecules (Fig. 5); a description in terms of anthracene sandwiched between picric acid molecules is equivalent. The nitro group at CP(5) (torsion angle 50.9°) protrudes beyond the stack; it is related by a centre of symmetry at $(\frac{1}{2}0\frac{1}{2})$ to the analogous nitro group in another stack. The dipole-dipole interaction of these antiparallel nitro groups presumably contributes significantly to the cohesion of the stacks.

The angle between the plane of the benzene ring of picric acid (plane 1, Table 4) and the mean plane of anthracene (plane 6, Table 5) is 0.8°. The distance between molecular planes does not have any strict meaning, when these planes are not parallel; however we have obtained a measure of the distances to the anthracene above and below the reference picric acid molecule by calculating the distances of the midpoints of C(3)-C(12) (anthracene above picric acid) and

C(5)–C(10) (anthracene below picric acid) from plane 1. The values obtained are 3.34 and -3.31 Å respectively. The distances between atoms in adjacent molecules in a stack (Table 6) are also sensibly equal in opposite directions. Thus there is no indication of 'pairing' of molecules within a stack. These distances, and those between molecules in different stacks, are rather similar to the values given by Iwasaki & Saito (1970) for 1,3,5-triaminobenzene:TNB.

The thermal vibration factors of the atoms in the two molecules are given in Table 3(b). A rigid-body analysis of the thermal vibrations was performed for each of the molecules. Since neither molecule occupies a crystallographic centre, the full treatment of Schomaker & Trueblood (1968), including the screw tensor, is required. The method, which included allowance for librations of the nitro groups about the C–N bonds, is due to Dunitz & White (1973); the program was written

Table 4. Picric acid molecule – best planes and deviations from planarity

The starred atoms have been given zero weight in the calculations. The planes in this paper are defined with respect to the crystal axes and were determined by the method of Schomaker, Waser, Marsh & Bergman (1959); interplanar angles were determined by the method of Waser, Marsh & Cordes (1973). A negative value of the deviation from the plane means that the atom is displaced from the plane towards the origin.

	Deviations (10^{-3} Å) from planes				
	1	2	3	4	5
CP(1)	–1	0.9			–11
CP(2)	1				
CP(3)	1		–2		
CP(4)	–4				
CP(5)	5			4	
CP(6)	–3				2
HCP(2)	–8*				
HCP(4)	5*				
O(1)	–54*				–4
HOH	–58*				10
N(1)	–7*	–0.5			18
O(2)	–83*	0.5			–16
O(3)	64*	0.8			
N(2)	–9*		8		
O(4)	–99*		–2		
O(5)	43*		–2		
N(3)	7*			–13	
O(6)	–818*			5	
O(7)	860*			6	

by E. Huber-Buser. The results are summarized in Table 7. When both molecules are assumed to behave as rigid bodies, the r.m.s. discrepancies between ob-

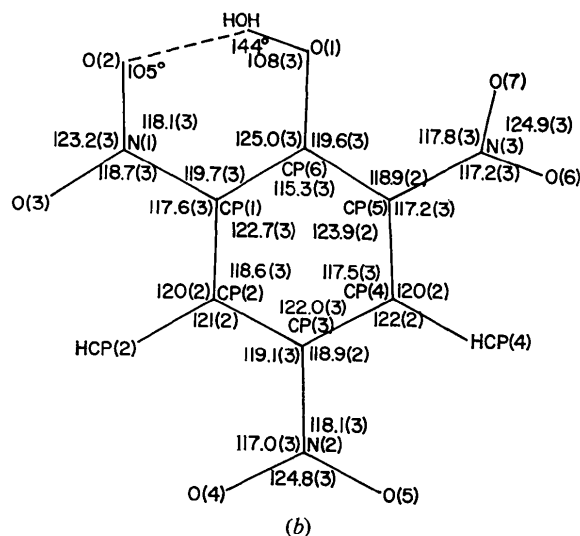
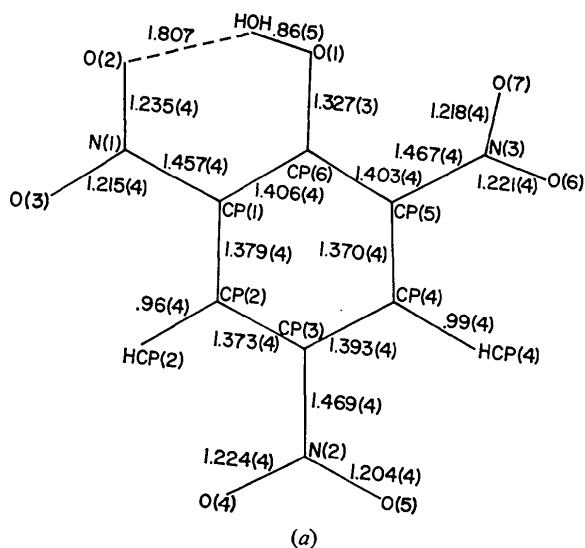


Fig. 1. Picric acid: (a) bond lengths (Å), (b) bond angles (°).

Table 4 (cont.)

Equations of planes expressed in the form $AX+BY+CZ+D=0$ where X, Y, Z are coordinates in Å with respect to the crystal axes, and D is the origin-to-plane distance in Å.

Plane	Description	A	B	C	D
1	Carbon atoms of benzene ring	0.9323	0.1273	0.3300	–2.833
2	CP(1) and nitro group at CP(1)	0.9438	0.0614	0.3162	–2.580
3	CP(3) and nitro group at CP(3)	0.9387	0.1790	0.2860	–2.694
4	CP(5) and nitro group at CP(5)	0.3082	0.3863	0.8665	–6.898
5	Internally hydrogen-bonded six-membered ring	0.9441	0.1062	0.3063	–2.648

Interplanar angles

1 A 2	–3.9°
1 A 3	–3.9
1 A 4	–50.9
1 A 5	2.0

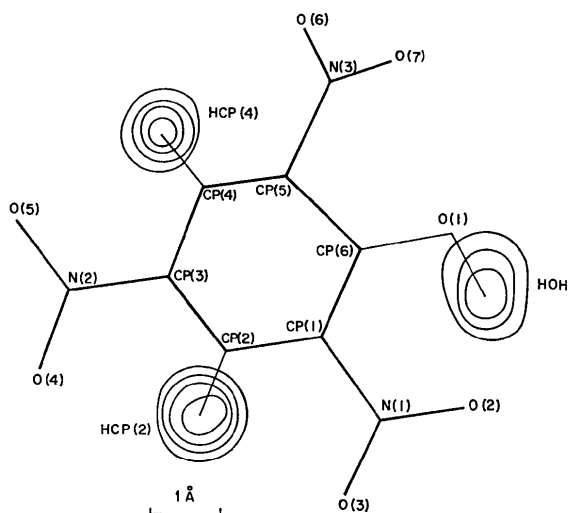


Fig. 2. Picric acid: difference synthesis in the plane of the benzene ring (contours at $0.1 e \text{ \AA}^{-3}$, starting at $0 e \text{ \AA}^{-3}$; F_{calc} based on non-hydrogen atoms of structure).

Table 5. Anthracene molecule - deviations (10^{-3} \AA) of atoms from various planes and equations of these planes

	Plane 6	Plane 7	Plane 8	Plane 9
C(1)	-3	-4	30*	-47*
C(2)	-18	-2	1*	-60*
C(3)	-15	7	-4	-45*
C(4)	6	46*	2	-21*
C(5)	13	59*	1	-2
C(6)	20	85*	-6*	8
C(7)	-5	64*	-39*	-6
C(8)	-10	45*	-37*	-1
C(9)	0	27*	-13*	6
C(10)	2	33*	-3	-4
C(11)	-8	5*	1	-17*
C(12)	-15	-7	2	-36*
C(13)	13	2	45*	-10*
C(14)	20	4	60*	-15*
HC(1)	-17*	-22*	21*	-69*
HC(2)	-9*	18*	5*	-58*
HC(4)	18*	68*	9*	-16*
HC(6)	70*	145*	39*	51*
HC(7)	-69*	14*	-113*	-68*
HC(8)	28*	89*	-4*	45*
HC(9)	64*	91*	55*	76*
HC(11)	-16*	-14*	-1*	-18*
HC(13)	65*	43*	102*	48*
HC(14)	112*	83*	161*	75*

* The starred atoms were given zero weight in the best-plane calculation. For definition of planes see Table 4.

served and calculated values of U_{ij}^r are 0.0016 \AA^2 for anthracene and 0.0035 \AA^2 for picric acid, whereas the estimated standard deviations of the $U_{ij}^r(\text{obs})$ values

Table 6. The shorter intermolecular distances ($< 3.5 \text{ \AA}$) between the reference picric acid molecule and the surrounding molecules (distances from a heavy atom to hydrogen are not included)

The reference molecule is at (xyz) and is designated 01; the symmetry-related molecules are

$$02 \text{ at } x, \frac{1}{2} - y, \frac{1}{2} + z \quad 03 \text{ at } \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$$

$$04 \text{ at } \bar{x}\bar{y}\bar{z}.$$

The unit-cell designator follows the system of Johnson (1965); the origin unit cell is 555 and translational shifts along a, b, c are shown as integral changes in the first, second or third of these digits.

Atom in picric acid reference molecule	Atom in neighbour molecule in unit-cell designator	Distance (\AA)
Anthracene below picric acid, both in same stack		
N(1)	C(1)	01455 3.361
CP(2)	C(3)	01455 3.359
N(2)	C(4)	01455 3.444
O(4)	C(4)	01455 3.460
CP(3)	C(4)	01455 3.475
N(2)	C(5)	01455 3.334
O(5)	C(5)	01455 3.447
CP(5)	C(6)	01455 3.394
CP(4)	C(11)	01455 3.361
O(6)	C(11)	01455 3.441
CP(6)	C(13)	01455 3.349
Anthracene above picric acid, both in same stack		
N(1)	C(3)	01555 3.360
CP(2)	C(5)	01555 3.429
CP(4)	C(9)	01555 3.452
CP(5)	C(10)	01555 3.491
CP(6)	C(11)	01555 3.370
Molecules in different stacks		
O(7)	C(1)	03645 3.376
O(7)	C(2)	03645 3.272
O(1)	C(2)	03645 3.478
O(2)	C(7)	02554 3.456
O(2)	C(8)	02554 3.384
O(6)	C(8)	04556 3.391
O(6)	C(9)	04556 3.348
N(3)	O(6)	04556 3.011
N(3)	O(3)	03545 3.304
O(2)	O(4)	03545 3.222
O(4)	O(2)	03555 3.322
O(4)	O(5)	04566 3.493
O(6)	O(6)	04556 2.929
O(6)	O(3)	03545 3.162
O(6)	O(7)	04556 3.220

Table 5 (cont.)

Plane	Description	A	B	C	D (\AA)
6	All carbon atoms of anthracene molecule	0.9364	0.1165	0.3224	-6.136
7	C(1), C(2), C(3), C(12), C(13), C(14)	0.9289	0.1284	0.3287	-6.171
8	C(3), C(4), C(5), C(10), C(11), C(12)	0.9397	0.1098	0.3152	-6.079
9	C(5), C(6), C(7), C(8), C(9), C(10)	0.9345	0.1114	0.3296	-6.179

Angles between planes ($^\circ$)

	7	8	9
7	-	1.4	1.0
8		-	0.9
9			-

are 0.0018 and 0.0013 Å² respectively. Thus, anthracene behaves as a rigid body but picric acid does not. When allowance is made for libration of the nitro groups about the C–N bonds, the r.m.s. discrepancy between observed and calculated values of U_{ij}^2 falls to 0.0028 Å². Thus inclusion of libration improves the model used for the thermal motion of picric acid, but significant shortcomings remain. The libration amplitudes of the three nitro groups are 9 (4), 8 (4) and 8 (4)°, somewhat smaller than those found (14, 11 and 9°) by Dunitz & White (1973) for the three nitro groups of TNB in *s*-triaminobenzene:TNB (Iwasaki & Saito, 1970). The corrections to the bond lengths in picric acid range from 0.003 to 0.005 Å and are not given in detail here; those for anthracene are slightly larger (0.004–0.006 Å) and corrected mean bond lengths have been included in Table 8 for comparison with those of anthracene in crystalline anthracene, where corrections have been applied.

4. Discussion

4.1. The picric acid molecule

The dimensions found here are more accurate than those given for picric acid in the partially-disordered π -molecular compound 1-bromo-2-naphthylamine:picric acid (Carstensen-Oeser, Göttlicher & Habermehl, 1968); agreement is generally good. No other values have been reported. The dimensions of the nitro groups agree well with those found in other molecules (the difference of 0.02 Å between N(2)–O(4) and N(2)–O(2) is presumably due to systematic error; many similar examples have been reported in the literature).

The angles at the ring atoms to which the nitro groups are bonded are $\sim 123^\circ$, and the O–N–O angles are $\sim 124^\circ$; these values have been explained in terms

of steric effects (Trueblood, Goldish & Donohue, 1961; Coppens, 1962).

Intramolecular hydrogen bonding in molecules of the *o*-nitrophenol type has been widely studied by

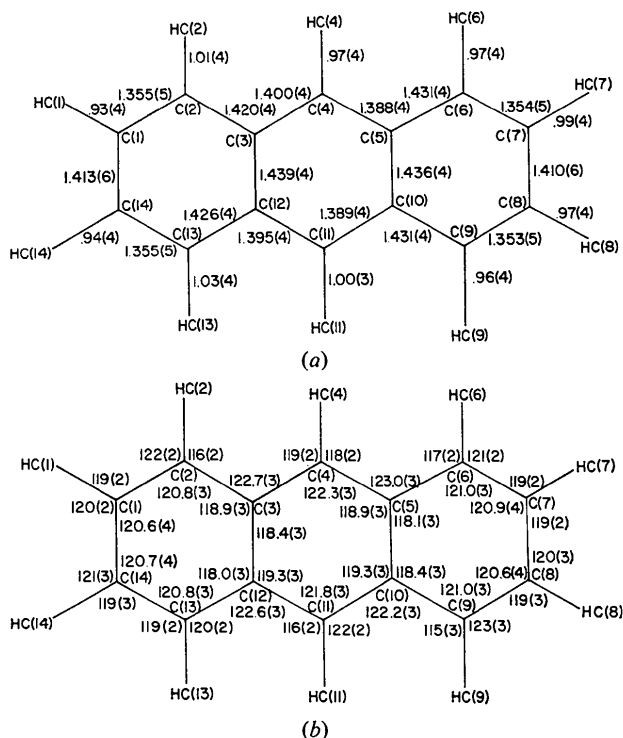


Fig. 3. Anthracene (a) bond lengths (Å) [averaged values for crystalline anthracene (Lehmann & Pawley, 1972) are given in Table 8]; (b) bond angles (°) – the averaged values for crystalline anthracene (Lehmann & Pawley, 1972) are: C(14)–C(1)–C(2) 120.4 (2), C(1)–C(2)–C(3) 120.9 (1), C(2)–C(3)–C(12) 119.1 (1), C(12)–C(3)–C(4) 119.1 (1), C(3)–C(4)–C(5) 121.1 (2)°.

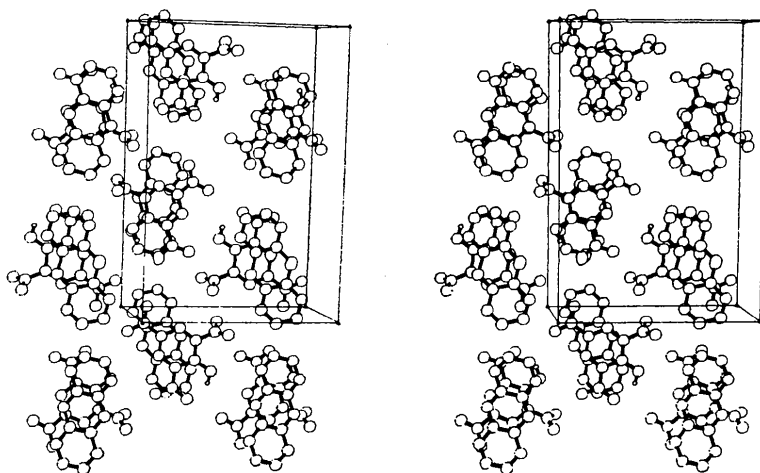


Fig. 4. ORTEP stereo view (Johnson, 1965) of the unit cell (some molecules along the edges have been removed for clarity). The origin is at the far left-hand corner at the bottom, *c* is vertical, *b* towards the right and the direction of view is approximately down towards the origin. The reference anthracene and picric acid molecules are in the central stack, surrounded by six other stacks.

infrared spectroscopy (Baitinger, Schleyer, Murty & Robinson, 1964) but direct diffraction evidence for such bonding has been presented only for dilutric acid

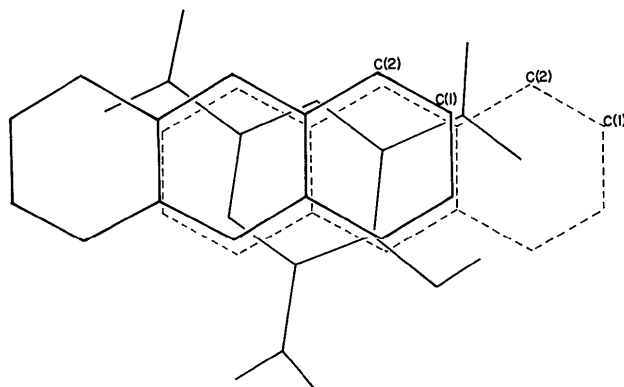


Fig. 5. Overlap diagram of the picric acid reference molecule (coordinates in Table 3) and the anthracene molecules above (the reference anthracene molecule) and below it. The molecules are projected onto the plane of the benzene ring of the picric acid molecule.

(5-nitro-2,6-dioxo-4-hydroxypyrimidine) (Bolton, 1963). However, it seems probable that there is a similar intramolecular hydrogen bond in picric acid in 1-bromo-2-naphthylamine:picric acid (Carstensen-Oeser *et al.*, 1968) between the phenol OH and the nitro group with a torsion angle of -3.4° ($O \cdots O = 2.48 \text{ \AA}$); the second adjacent nitro group has a torsion angle of -11.2° ($O \cdots O = 2.50 \text{ \AA}$). H atom positions were not determined because of disorder in the crystals; disorder of the intramolecular hydrogen bonds is not ruled out by the experimental values of $O \cdots O$ or of the nitro group torsion angles. Cell dimensions but not structures have been reported for the following compounds relevant in the present context: 2,4-dinitrophenol, 2,6-dinitrophenol, the red and yellow polymorphs of 4-bromo-1-naphthylamine:2,6-dinitrophenol, picric acid [for references see *Crystal Data* (1972)].

The dimensions of the picric acid molecule may be averaged in terms of a hypothetical mirror plane through C(1)–C(4) [Fig. 6(a)]. The deviations of the actual bond lengths [Fig. 6(c)] from the hypothetical

Table 7. Results of the rigid-body thermal motion analysis for anthracene and picric acid

(a) Anthracene (rigid body; in the inertial frame)

$$\begin{aligned}
 \mathbf{T} \quad (10^{-4} \text{ \AA}^2) &= \begin{pmatrix} 419 (6) & 8 (6) & 7 (6) \\ & 384 (8) & -5 (8) \\ & & 262 (15) \end{pmatrix} & \begin{matrix} (\text{\AA}) \\ 0.205 \\ 0.196 \\ 0.162 \end{matrix} & \begin{matrix} l \\ 0.9753 \\ 0.2175 \\ 0.0384 \end{matrix} & \begin{matrix} m \\ -0.2155 \\ 0.9752 \\ -0.0510 \end{matrix} & \begin{matrix} n \\ -0.0485 \\ 0.0415 \\ 0.9980 \end{matrix} \\
 \mathbf{L} \quad (10^{-4} \text{ rad}^2) &= \begin{pmatrix} 50 (8) & -3 (1) & 2 (2) \\ & 18 (1) & 4 (1) \\ & & 37 (1) \end{pmatrix} & \begin{matrix} (\text{deg}) \\ 4.1 \\ 3.5 \\ 2.3 \end{matrix} & \begin{matrix} l \\ 0.9881 \\ -0.0852 \\ 0.1284 \end{matrix} & \begin{matrix} m \\ 0.1071 \\ -0.2196 \\ -0.9697 \end{matrix} & \begin{matrix} n \\ 0.1108 \\ 0.9719 \\ -0.2078 \end{matrix} \\
 \mathbf{S} \quad (10^{-4} \text{ rad \AA}) &= \begin{pmatrix} -5 (4) & 3 (5) & -5 (3) \\ -2 (2) & 4 (2) & 3 (1) \\ 2 (2) & 0 (1) & 1 (2) \end{pmatrix} \\
 \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} &= \begin{pmatrix} 2.5096 & -2.9380 & -17.5143 \\ -0.2192 & 12.4717 & -4.8723 \\ 6.7236 & 1.5033 & 6.1922 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}
 \end{aligned}$$

Origin of X, Y, Z system at $(x, y, z) = (-0.45597, 0.22687, 0.34513)$

(b) Picric acid (in the inertial frame; non-rigid nitro groups)

$$\begin{aligned}
 \mathbf{T} \quad (10^{-4} \text{ \AA}^2) &= \begin{pmatrix} 386 (10) & -29 (9) & 13 (12) \\ & 364 (11) & -17 (12) \\ & & 287 (19) \end{pmatrix} & \begin{matrix} (\text{\AA}) \\ 0.202 \\ 0.186 \\ 0.168 \end{matrix} & \begin{matrix} l \\ 0.8042 \\ -0.5716 \\ 0.1629 \end{matrix} & \begin{matrix} m \\ 0.5897 \\ 0.8016 \\ -0.0983 \end{matrix} & \begin{matrix} n \\ -0.0744 \\ 0.1751 \\ 0.9817 \end{matrix} \\
 \mathbf{L} \quad (10^{-4} \text{ rad}^2) &= \begin{pmatrix} -21 (4) & 9 (2) & -3 (2) \\ & 40 (4) & 0 (2) \\ & & 23 (2) \end{pmatrix} & \begin{matrix} (\text{deg}) \\ 3.8 \\ 2.8 \\ 2.4 \end{matrix} & \begin{matrix} l \\ -0.3625 \\ -0.9311 \\ 0.0414 \end{matrix} & \begin{matrix} m \\ 0.3210 \\ -0.1664 \\ -0.9323 \end{matrix} & \begin{matrix} n \\ 0.8750 \\ -0.3247 \\ 0.3592 \end{matrix} \\
 \mathbf{S} \quad (10^{-4} \text{ rad \AA}) &= \begin{pmatrix} -2 (4) & -6 (5) & 0 (4) \\ -7 (5) & -7 (4) & -20 (3) \\ 0 (2) & -15 (2) & 9 (3) \end{pmatrix} \\
 \text{Non-rigid parameters} & \begin{matrix} \text{N(1) nitro group } 8.8 (3.9)^\circ \\ \text{N(2) nitro group } 7.6 (3.9) \\ \text{N(3) nitro group } 7.7 (3.8) \end{matrix} \\
 \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} &= \begin{pmatrix} 2.0946 & -10.9933 & -8.3934 \\ 1.7235 & 6.5141 & -15.9642 \\ 6.6479 & 1.7749 & 6.5957 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}
 \end{aligned}$$

Origin of X, Y, Z system at $(x, y, z) = (0.04786, 0.19018, 0.34609)$

values conform qualitatively rather well to the effects expected from the resonance structure favoured by the intramolecular bond [Baitinger *et al.*, 1964, Fig. 6(b)].

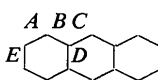
The dipole moment and bond orders in picric acid have been calculated (Owen, 1969) by the Hückel molecular orbital method, assuming that the molecule is planar. The dipole moments agree well (predicted 1.70, found 1.51 D) and the derived and experimental bond lengths also agree well, except for the length of the C–NO₂ bond which is calculated at 1.40 but measured at 1.464 Å (mean), indicating that the resonance integral β has been given too high a value. Incorrect values of the HMO parameters for the nitro groups would not affect the overall dipole moment of the molecule because the nitro group contributions cancel. An *ab initio* SCF-LCAO-MO calculation of the electronic structure of 2,4,7-trinitro-9-fluorenone (Batra, Bagus, Clementi & Seki, 1974) shows that the N atoms are slightly positive (deficiency of ~ 0.23 e) while the O atoms of the nitro groups are all slightly negative (excess charge of ~ 0.12 e) (in these calculations C–N = 1.40 Å was assumed).

4.2. Anthracene

Dimensions have been determined for anthracene in four different environments: (1) in crystalline anthracene by X-rays [Mason (1964), who refers to earlier work] and neutrons, [Lehmann & Pawley (1972), who studied perdeuteroanthracene], (2) in anthracene:TNB (Brown *et al.*, 1964), (3) in anthracene:pyromellitic dianhydride (Boeyens & Herbstein, 1965) and (4) in anthracene:picric acid. The anthracene molecules are at centres of symmetry in the first three crystals; only the neutron diffraction results for crystalline anthracene are accurate enough to warrant detailed discussion. Lehmann & Pawley (1972) show that there are small but significant distortions from its D_{2h} - mmm free-state symmetry; however, for comparison (Table 8), we shall use their model I (see their Table 3) which is 'the best symmetry-averaged molecule determinable from diffraction data'; these bond lengths have been corrected for librational effects. In anthracene:picric acid the anthracene molecules are at general positions and thus no symmetry is required. The pattern of bond lengths [Fig. 3(a)] and bond angles [Fig. 3(b)] conforms to mm

Table 8. Averaged bond lengths (according to symmetry mm) for anthracene in crystalline anthracene* (Lehmann & Pawley, 1972) and in anthracene:picric acid

Diagram shows nomenclature of bonds. E.s.d.'s of means are given in brackets after lengths.



Bond	Anthracene:picric acid		Anthracene* corrected for thermal motion	$\Delta =$ ($l_{MC} - l_A$) (Å)	$\frac{ \Delta }{(\sigma_M^2 + \sigma_A^2)^{1/2}}$
	(before correction for thermal motion) (Å)	(after correction for thermal motion) (Å)			
A	1.354	1.359 (3)	1.368 (2)	-0.009	2.50
B	1.428	1.432 (2)	1.433 (2)	-0.001	0.35
C	1.393	1.397 (2)	1.402 (2)	-0.005	1.77
D	1.437	1.444 (4)	1.439 (3)	0.005	1.00
E	1.412	1.418 (4)	1.432 (3)	-0.014	2.80
Mean	1.400	1.405	1.409		

(D and E given half weight of A, B, C).

* $C_{14}D_{10}$.

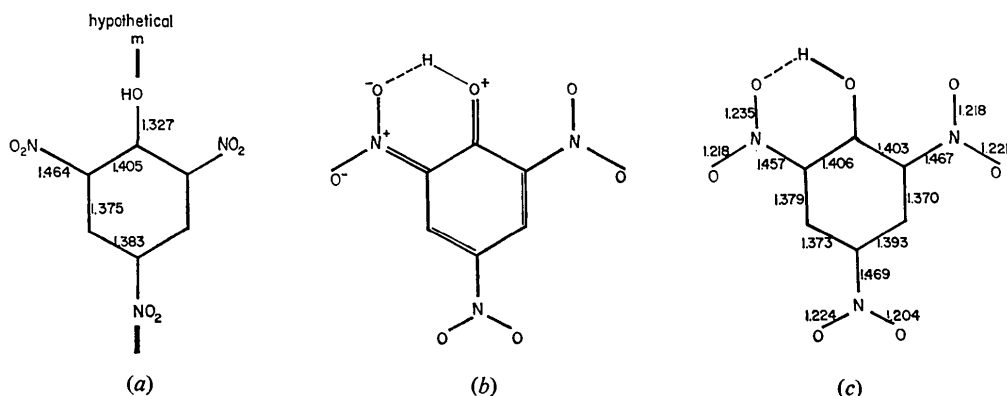


Fig. 6. (a) Averaged dimensions of picric acid, assuming a hypothetical mirror plane through CP(6)–CP(3); (b) the resonance structure favoured by intramolecular hydrogen-bonding (Baitinger *et al.*, 1964); (c) the experimental molecular dimensions.

symmetry, but there are significant deviations from planarity (§ 3.1.2) and the molecular symmetry therefore approaches $C_i\bar{1}$ (but significant deviations remain) and not $D_{2h}\text{-}mmm$.

The mean bond length in anthracene in crystalline anthracene (Lehmann & Pawley, 1972) is 1.409 Å, somewhat larger than that in benzene (1.397 Å) [see Brown & Strydom (1974) for summary of results], as would be expected for 14 π electrons distributed over 16 bonds. If there is any appreciable electron donation from anthracene to picric acid in the molecular compound, then one would expect the mean bond length to be even longer than in anthracene itself. The mean bond length in anthracene:picric acid is 1.405 Å (after correction for molecular libration) so this is not so. However, this comparison must be viewed with some caution because of the difficulties involved in making reliable thermal motion corrections to the bond lengths.

The bond lengths in anthracene in crystalline anthracene and in the picric acid molecular compound may both be averaged in terms of mm symmetry (Table 8). Comparison of the individual bond lengths shows good agreement, the differences not being statistically significant. Larsen, Little & Coppens (1975) report analogous results for the pyrene:tetracyanoethylene π -molecular compound.

The deviations from planarity can be explained in terms of the arrangement of the molecules in the stacks (Fig. 5). Consider the displacements of the C atoms of the reference anthracene molecule from the plane of the central ring (plane 8, Table 5). C(1), C(2), C(13), C(14) have a picric acid molecule below them and are displaced upwards (away from the origin) by a few hundredths of an ångström; conversely C(6), C(7), C(8), C(9) have a picric acid molecule above them and

are displaced downwards in the stack, towards the origin. Thus the non-planarity of the anthracene is ascribed to intermolecular *repulsions* within the mixed stacks and is not due to charge-transfer interactions, which are attractive. The strain energy involved in these deviations from planarity is not likely to exceed a few hundred cal mol⁻¹ (Ali & Coulson, 1959). Somewhat smaller deviations from planarity have been reported for anthracene in crystalline anthracene (Cruikshank, 1956) and ascribed to packing forces. As would be expected, there is no resemblance between the patterns of displacements in anthracene in these two different environments. Ovalene is another aromatic molecule which shows significant deviations from planarity in the crystalline state; it has a corrugated shape (Hazell & Pawley, 1973).

4.3. Arrangement of the component molecules

The component arrangement in anthracene:picric acid is very similar to that in 1,3,5-triaminobenzene:TNB [Iwasaki & Saito (1970); compare Fig. 4 of this paper with Fig. 5 of Iwasaki & Saito]. 1-Bromo-2-naphthylamine:picric acid (Carstensen-Oeser *et al.*, 1968) also has a similar crystal structure. The several molecular compounds of anthracene with TNB, picryl chloride and picryl bromide all have different crystal structures (Herbstein & Kaftory, 1975). In particular there are appreciable differences between the arrangements of the components in anthracene:TNB and anthracene:picric acid, the only two of these structures known in detail. Despite these overall differences, the overlap diagram of anthracene:picric acid (Fig. 5) resembles those of other TNB and substituted TNB molecular compounds [*e.g.* Fig. 26 of Herbstein (1971)]. The resemblance between the overlap diagrams of anthracene:TNB (Fig. 26g) and anthracene:picric acid is close insofar as mutual orientation is concerned, but the eclipsing of the nitro-substituted C atoms of TNB found in anthracene:TNB is avoided in anthracene:picric acid by a mutual lateral shift of the two components.

The translational components of the rigid-body motion are rather similar in direction and r.m.s. amplitude for both molecules (Fig. 7) and this suggests that the stacks vibrate as units in the crystal. In particular the r.m.s. amplitude of translational motion normal to the molecular planes is 0.16–0.17 Å for both molecules [similar values have been found for the corresponding motion of the molecules normal to their planes in pyrene:benzoquinone (Bernstein, Regev, Herbstein, Main, Risvi, Sasvari & Turcsanyi, 1975)], and the r.m.s. translational amplitudes are approximately isotropic in the planes of both molecules. The r.m.s. libration amplitudes are about the same for both molecules. Anthracene has its greatest libration amplitude about the long (A1) molecular axis, which is the axis of least inertia of the molecule; this behaviour is found in many molecular crystals (Trueblood, 1969). A similar situation is found for picric acid, particularly

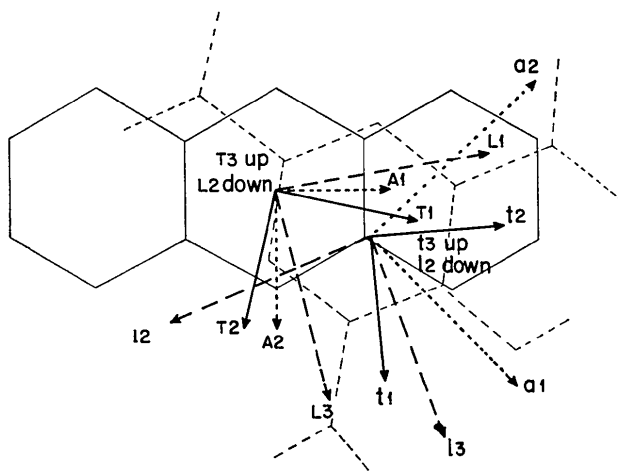


Fig. 7. The principal axes of the molecular translational and librational tensors (in the inertial system) are projected onto the mean planes of the reference anthracene (upper case lettering) and picric acid (lower case lettering) molecules. The relative translation amplitudes (Table 7) are roughly indicated for both molecules but the principal axes of the librational tensors are not depicted quantitatively.

when the effect of the intramolecular hydrogen bonding is taken into account.

The thermodynamic parameters for crystalline anthracene:picric acid have been discussed by Herbstein (1971; see pp. 231–235); it was pointed out that this compound has a negative entropy of formation ($\Delta S_f^\circ = -5.8$ e.u.) and thus becomes less stable, relative to crystals of its components, as the temperature is raised. If one makes the approximation that ΔH_f° and ΔS_f° for anthracene:picric acid do not vary with temperature then $\Delta G_f^\circ = 0$ at $T = (\Delta H_f^\circ / \Delta S_f^\circ) = (-2210 / -5.8) = 381$ K. Kofler (1944) found a phase change at 358 K, in reasonable agreement with the value calculated from the thermodynamic parameters. We have measured the enthalpies of transformation (at 358 K) and fusion (at 411 K) with a Perkin–Elmer differential scanning calorimeter and obtain $\Delta H_{tr} = 1500$ cal mole⁻¹ and $\Delta H_{fus} = 4700$ cal mole⁻¹. $\Delta S_{tr} = 4.4$ e.u. and thus the entropy of formation of the high-temperature phase will be approximately zero. We have not been able to retain the high-temperature phase on quenching to room temperature.

Anthracene:picric acid has $\Delta H_f^\circ = -2.2$ kcal mole⁻¹ while anthracene:TNB has $\Delta H_f^\circ = -0.3$ kcal mole⁻¹ (and $\Delta S_f^\circ = 1.7$ e.u.). In accordance with these enthalpies and entropies, the intermolecular bonding appears to be stronger in anthracene:picric acid than in anthracene:TNB and the amount of thermal motion less.

5. Summary

The structure of anthracene:picric acid resembles those of other crystalline π -molecular compounds. The differences between anthracene:picric acid and anthracene:TNB are compatible with the different thermodynamic parameters of these two molecular compounds. The dimensions of anthracene in anthracene:picric acid are similar to those of anthracene in crystalline anthracene; the differences are not significant at the present levels of accuracy. The anthracene molecule has been found to be significantly non-planar, due to intrastack intermolecular interactions. The picric acid molecule has an intramolecular hydrogen bond between the hydroxyl group and one of the adjacent nitro groups.

We are grateful to Professor J. D. Dunitz (E. T. H., Zürich) for his encouragement of this work and for the facilities placed at our disposal for its execution.

References

- ALI, M. A. & COULSON, C. A. (1959). *J. Chem. Soc.* pp. 1558–1563.
- BAITINGER, W. F., SCHLEYER, P. VON R., MURTY, T. S. S. R. & ROBINSON, L. (1964). *Tetrahedron*, **20**, 1635–1647.
- BATRA, I. P., BAGUS, P. S., CLEMENTI, E. S. & SEKI, H. (1974). *Theor. Chim. Acta*, **32**, 279–293.
- BERNSTEIN, J., REGEV, H., HERBSTEIN, F. H., MAIN, P., RISVI, S. H., SASVARI, K. & TURCSANYI, B. (1975). *Proc. Roy. Soc. A*. In the press.
- BOEYENS, J. C. A. & HERBSTEIN, F. H. (1965). *J. Phys. Chem.* **69**, 2160–2176.
- BOLTON, W. (1963). *Acta Cryst.* **16**, 950–956.
- BROWN, D. S., WALLWORK, S. C. & WILSON, A. (1964). *Acta Cryst.* **17**, 168–176.
- BROWN, G. M. & STRYDOM, O. A. W. (1974). *Acta Cryst.* **B30**, 801–804.
- CARSTENSEN-OESER, E., GÖTTLICHER, S. & HABERMEHL, G. (1968). *Chem. Ber.* **101**, 1648–1655.
- COPPENS, P. (1962). *J. Chem. Phys.* **36**, 2523–2525.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 915–923.
- Crystal Data (Determinative Tables)* (1972). 3rd ed., edited by J. D. H. DONNAY & H. M. ONDIK, Vol. I. *Organic Compounds*. Washington and Philadelphia: NBS and JCPDS.
- DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* **B29**, 589–595.
- DUNITZ, J. D. & WHITE, J. D. N. (1973). *Acta Cryst.* **A29**, 93–94.
- FRITZSCHE, J. (1858). *J. prakt. Chem.* **73**, 282–292.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAZELL, R. G. & PAWLEY, G. S. (1973). *Z. Kristallogr.* **137**, 159–172.
- HERBSTEIN, F. H. (1963). *Acta Cryst.* **16**, 255–263.
- HERBSTEIN, F. H. (1971). *Perspectives in Structural Chemistry*, Vol. 4, pp. 166–395, edited by J. D. DUNITZ & J. A. IBERS. London: John Wiley.
- HERBSTEIN, F. H. & KAFTORY, M. (1975). *Acta Cryst.* **B31**, 68–75.
- IWASAKI, F. & SAITO, Y. (1970). *Acta Cryst.* **B26**, 251–260.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KOFLER, A. (1944). *Z. Elektrochem.* **50**, 200–207.
- LARSEN, F. K., LITTLE, R. G. & COPPENS, P. (1975). *Acta Cryst.* **B31**, 430–440.
- LEHMANN, M. S. & PAWLEY, G. S. (1972). *Acta Chem. Scand.* **26**, 1996–2004.
- MASON, R. (1964). *Acta Cryst.* **17**, 547–555.
- OWEN, A. J. (1969). *Tetrahedron*, **25**, 3693–3699.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.
- TRUEBLOOD, K. N. (1969). *Molecular Dynamics and Structure of Solids*, pp. 355–379, edited by R. S. CARTER & J. J. RUSH. N.B.S. Spec. Publ. No. 301.
- TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009–1017.
- WASER, J., MARSH, R. E. & CORDES, A. W. (1973). *Acta Cryst.* **B29**, 2703–2708.