Molecular Compounds and Complexes. VI. The Crystal Structure of 3/2 Pyrene: Picryl Bromide

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$\frac{3}{2}$ Pyrene:picryl bromide, $(C_{16}H_{10})_{3/2}:C_6H_2(NO_2)_3Br$, is monoclinic with $a = 8\cdot189$ (2), $b = 21\cdot070$ (6), $c = 14\cdot607$ (4) Å, $\beta = 91\cdot7$ (1)°, space group $P2_1/c$, $Z = 4$. Intensities of 2893 reflexions were measured on a Stoe Weissenberg diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares calculations to a final R of $0\cdot103$. All the atoms have fairly large Debye–Waller factors, suggesting the occurrence of large in-plane librations and/or disorder. The crystal structure can be described in terms of mixed stacks along [001] and interstitial pyrene molecules whose centres lie at $(0,0,\frac{1}{2})$ and $(0,\frac{1}{2},0)$. The donor: acceptor arrangement within the stacks is similar to that in anthracene:1,3,5-trinitrobenzene [Brown, Wallwork & Wilson (1964). *Acta Cryst.* **17**, 168–176].

1. Introduction

Most π-molecular compounds have an equimolar donor:acceptor ratio; there are a number of examples with 1:2 and 2:1 ratios while a few examples of ratios such as 3:2, 1:3 and even 3:4 have been reported (Herbstein, 1971, especially pp. 235–237). At the time this work was started, some structures of 1:2 (or 2:1) molecular compounds had been reported but none of compounds with other stoichiometries. We therefore decided to determine the structure of $\frac{3}{2}$ pyrene:picryl bromide, which was encountered during a broad survey of the molecular compounds formed between various aromatic hydrocarbons and substituted *s*-trinitrobenzenes (Herbstein & Kaftory, 1975). Our results resemble those found for a number of π-molecular compounds with a 3:2 stoichiometric ratio, and for a number of coordination compounds (see §4.1). One of the components fills a double structural role in all these crystals.

2. Experimental

Two different compounds crystallize on cooling a hot equimolar solution of pyrene and picryl bromide in cyclohexane: unstable needles with equimolar stoichiometry and stable red prisms of composition $\frac{3}{2}$ pyrene: picryl bromide. This latter composition is in accord with chemical analysis (wt.% measured, wt.% calculated for $\frac{3}{2}C_{16}H_{10}:C_6H_2Br(NO_2)_3$ $C=61\cdot01$, $60\cdot48$; $H=3\cdot04$, $2\cdot86$; $N=7\cdot09$, $7\cdot06$; $O=15\cdot62$, $15\cdot13$; $Br=13\cdot24$, $13\cdot44$) and the results of the structure analysis described below. The melting-point diagram for the system pyrene–picryl bromide (Fig. 1) shows both the

1:1 and $\frac{3}{2}$:1 binary compounds, but no other compounds.

The crystal data are summarized in Table 1; the cell dimensions were measured from back-reflexion Weissenberg and Mathieson inclined-beam oscillation photographs (Herbstein, 1963). Intensities of 2893 $hk0–hk8$ independent reflexions were measured on a Stoe Weissenberg diffractometer with graphite-monochromated Cu $K\alpha$ radiation and the ω–2θ scan method. The scan speed was $2°$ 2θ per min; backgrounds were counted
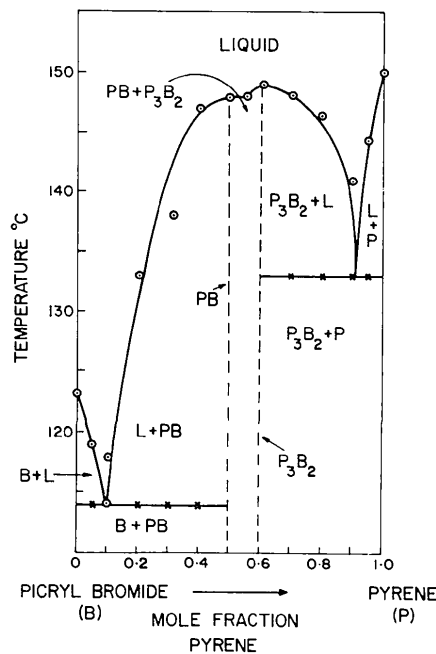

Fig. 1. Melting-point diagram for the system pyrene:picryl bromide. Thaw points are indicated by crosses. The form of the diagram in the region of the melting points of the two binary compounds is known only approximately.

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$\frac{1}{2}$ Pyrene:picryl bromide	$\frac{1}{2}$ $C_{16}H_{10}:C_6H_2Br(NO_2)_3$
Monoclinic	F.W. 594·9
Space group, $P2_1/c$	m.p. 149°C
$a=$ 8·189 (2) Å	$Z=4$
$b=21\cdot070$ (6)	$D_m=1\cdot59$ g cm^{-3}
$c=14\cdot607$ (4)	$D_x=1\cdot57$
$\beta=91\cdot7$ (1)°	$\mu=17\cdot81$ cm^{-1} (for Cu $K\alpha$)
$V=2519$ Å^3	λ(Cu $K\alpha_1$) = 1·54050 Å
	λ(Cu $K\alpha_2$) = 1·54434

for 20 s at the extrema. All reflexions in two quadrants of reciprocal space out to $2\theta' = 130°$ were surveyed.

The crystal used had dimensions $0\cdot54 \times 0\cdot20 \times 0\cdot14$ mm. Geometrical and absorption corrections (Busing & Levy, 1957) were applied.

3. Structure determination and refinement

As there are six pyrene molecules in the unit cell, it is probable that two of these are at centres of symmetry and the remaining four at general positions; the four picryl bromide molecules must be at general positions. The position of the bromine atom was found from the Harker sections $(2x,\frac{1}{2},\frac{1}{2}+2z)$ and $(0,\frac{1}{2}+y,\frac{1}{2})$. The posi-

Table 2. *Non-hydrogen atoms: fractional coordinates (standard deviations) and anisotropic temperature factors (standard deviations)*

$$T=\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}^r h_i h_j a_i^* a_j^*\right).$$

|	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Picryl bromide									
Br	0·0635 (1)	0·05573 (4)	0·2239 (1)	0·098 (1)	0·052 (1)	0·048 (2)	−0·0257 (4)	0·0163 (6)	0·0006 (8)
C(1)	0·1775 (8)	0·1256 (3)	0·1803 (8)	0·054 (4)	0·040 (3)	0·035 (10)	−0·008 (3)	−0·001 (4)	0·012 (4)
C(2)	0·1180 (7)	0·1883 (3)	0·1841 (7)	0·037 (3)	0·040 (3)	0·008 (8)	−0·005 (2)	0·006 (3)	0·007 (4)
C(3)	0·2099 (7)	0·2406 (3)	0·1644 (6)	0·036 (3)	0·030 (3)	0·013 (8)	−0·003 (2)	−0·001 (3)	0·011 (3)
C(4)	0·3711 (7)	0·2301 (3)	0·1358 (7)	0·032 (3)	0·031 (3)	0·036 (9)	−0·003 (2)	0·008 (3)	0·006 (3)
C(5)	0·4372 (7)	0·1696 (3)	0·1325 (7)	0·041 (3)	0·045 (3)	0·030 (10)	0·001 (10)	−0·006 (4)	0·009 (4)
C(6)	0·3381 (8)	0·1200 (3)	0·1541 (7)	0·055 (3)	0·030 (3)	0·014 (9)	0·003 (2)	0·002 (4)	−0·006 (4)
N(1)	−0·0539 (7)	0·2042 (3)	0·2120 (7)	0·039 (3)	0·063 (4)	0·044 (9)	−0·013 (3)	−0·007 (4)	0·014 (4)
N(2)	0·4724 (6)	0·2854 (3)	0·1174 (6)	0·031 (2)	0·050 (3)	0·017 (7)	−0·010 (2)	−0·001 (3)	−0·002 (3)
N(3)	0·4142 (11)	0·0569 (3)	0·1451 (9)	0·086 (5)	0·044 (4)	0·092 (12)	0·022 (3)	−0·011 (5)	−0·037 (6)
O(1)	−0·1595 (7)	0·1652 (3)	0·1982 (7)	0·053 (3)	0·077 (4)	0·109 (10)	−0·013 (3)	−0·008 (3)	−0·018 (4)
O(2)	−0·0734 (6)	0·2556 (3)	0·2462 (6)	0·056 (3)	0·067 (4)	0·056 (7)	0·002 (2)	0·003 (4)	0·027 (3)
O(3)	0·4197 (6)	0·3378 (3)	0·1346 (6)	0·065 (3)	0·043 (3)	0·076 (8)	−0·009 (4)	−0·009 (2)	0·015 (4)
O(4)	0·6094 (6)	0·2754 (3)	0·0908 (6)	0·047 (3)	0·076 (4)	0·057 (8)	−0·011 (2)	−0·001 (4)	0·028 (3)
O(5)	0·5248 (17)	0·0465 (4)	0·1980 (12)	0·191 (11)	0·083 (6)	0·227 (19)	0·060 (6)	−0·074 (8)	−0·117 (12)
O(6)	0·3517 (11)	0·0173 (3)	0·0978 (8)	0·132 (6)	0·058 (4)	0·107 (12)	0·024 (4)	−0·028 (5)	−0·050 (6)
Pyrene (C.T.)									
CP(1)	−0·1157 (9)	0·3288 (5)	0·4789 (10)	0·040 (3)	0·085 (6)	0·092 (13)	0·005 (4)	0·004 (7)	0·000 (5)
CP(2)	−0·0840 (11)	0·3935 (5)	0·4727 (9)	0·073 (5)	0·081 (6)	0·064 (12)	0·026 (4)	−0·018 (4)	−0·017 (6)
CP(3)	0·0595 (13)	0·4161 (4)	0·4467 (10)	0·099 (7)	0·054 (5)	0·043 (12)	0·006 (4)	−0·003 (6)	−0·007 (7)
CP(4)	0·1894 (10)	0·3732 (3)	0·4251 (7)	0·072 (4)	0·043 (3)	0·008 (9)	−0·002 (3)	0·000 (4)	−0·012 (5)
CP(5)	0·3419 (13)	0·3951 (5)	0·3964 (9)	0·089 (7)	0·065 (6)	0·051 (12)	−0·019 (5)	0·032 (6)	−0·011 (7)
CP(6)	0·4626 (11)	0·3533 (5)	0·3729 (9)	0·071 (5)	0·085 (6)	0·012 (11)	−0·031 (4)	0·028 (6)	−0·001 (5)
CP(7)	0·4380 (9)	0·2853 (4)	0·3798 (8)	0·046 (3)	0·074 (5)	0·008 (10)	−0·005 (3)	0·012 (5)	0·007 (4)
CP(8)	0·5555 (9)	0·2377 (7)	0·3543 (10)	0·043 (4)	0·136 (11)	0·046 (12)	0·005 (5)	−0·013 (9)	0·005 (5)
CP(9)	0·5296 (11)	0·1763 (6)	0·3652 (9)	0·060 (5)	0·098 (7)	0·032 (12)	0·021 (5)	−0·021 (7)	0·000 (5)
CP(10)	0·3803 (10)	0·1547 (4)	0·3943 (8)	0·083 (5)	0·057 (4)	0·023 (10)	0·024 (4)	−0·008 (5)	−0·010 (5)
CP(11)	0·2559 (8)	0·1963 (3)	0·4161 (7)	0·061 (4)	0·038 (3)	0·004 (9)	−0·001 (3)	0·006 (4)	−0·002 (4)
CP(12)	0·1006 (10)	0·1778 (4)	0·4484 (8)	0·067 (4)	0·049 (4)	0·034 (11)	−0·020 (3)	0·030 (5)	−0·013 (5)
CP(13)	−0·0190 (9)	0·2175 (4)	0·4671 (9)	0·040 (4)	0·079 (5)	0·042 (11)	−0·012 (3)	0·030 (6)	0·005 (4)
CP(14)	0·0039 (8)	0·2847 (8)	0·4580 (7)	0·037 (3)	0·063 (4)	0·014 (10)	−0·001 (3)	0·006 (5)	−0·002 (4)
CP(15)	0·1583 (7)	0·3072 (3)	0·4293 (6)	0·035 (3)	0·042 (3)	−0·004 (8)	−0·003 (2)	0·004 (3)	−0·003 (3)
CP(16)	0·2820 (7)	0·2626 (3)	0·4096 (7)	0·039 (3)	0·040 (3)	−0·001 (9)	−0·002 (2)	0·002 (4)	−0·013 (3)
Pyrene (interstitial)									
CPI(1)	0·0001 (20)	0·4074 (4)	0·1951 (11)	0·165 (12)	0·039 (4)	0·052 (14)	0·016 (6)	−0·004 (6)	−0·022 (10)
CPI(2)	0·1403 (14)	0·4391 (5)	0·1728 (11)	0·100 (7)	0·063 (6)	0·071 (14)	0·041 (5)	−0·019 (7)	−0·030 (7)
CPI(3)	0·1402 (9)	0·4747 (4)	0·0987 (8)	0·061 (4)	0·045 (4)	0·025 (10)	0·017 (3)	−0·024 (3)	−0·014 (4)
CPI(4)	0·2853 (10)	0·5092 (5)	0·0705 (11)	0·043 (4)	0·089 (7)	0·056 (14)	0·006 (4)	−0·018 (7)	−0·025 (5)
CPI(5)	−0·1509 (15)	0·4117 (4)	0·1430 (9)	0·139 (8)	0·047 (4)	0·030 (11)	−0·022 (4)	−0·028 (5)	0·030 (7)
CPI(6)	−0·1441 (10)	0·4489 (4)	0·0647 (9)	0·066 (4)	0·048 (4)	0·041 (11)	−0·009 (3)	−0·021 (5)	0·015 (5)
CPI(7)	−0·2859 (11)	0·4567 (6)	0·0042 (12)	0·055 (5)	0·096 (7)	0·068 (17)	−0·002 (4)	−0·024 (8)	−0·008 (6)
CPI(8)	−0·0024 (8)	0·4811 (3)	0·0393 (7)	0·047 (3)	0·037 (3)	0·014 (10)	0·013 (2)	−0·014 (3)	0·005 (4)
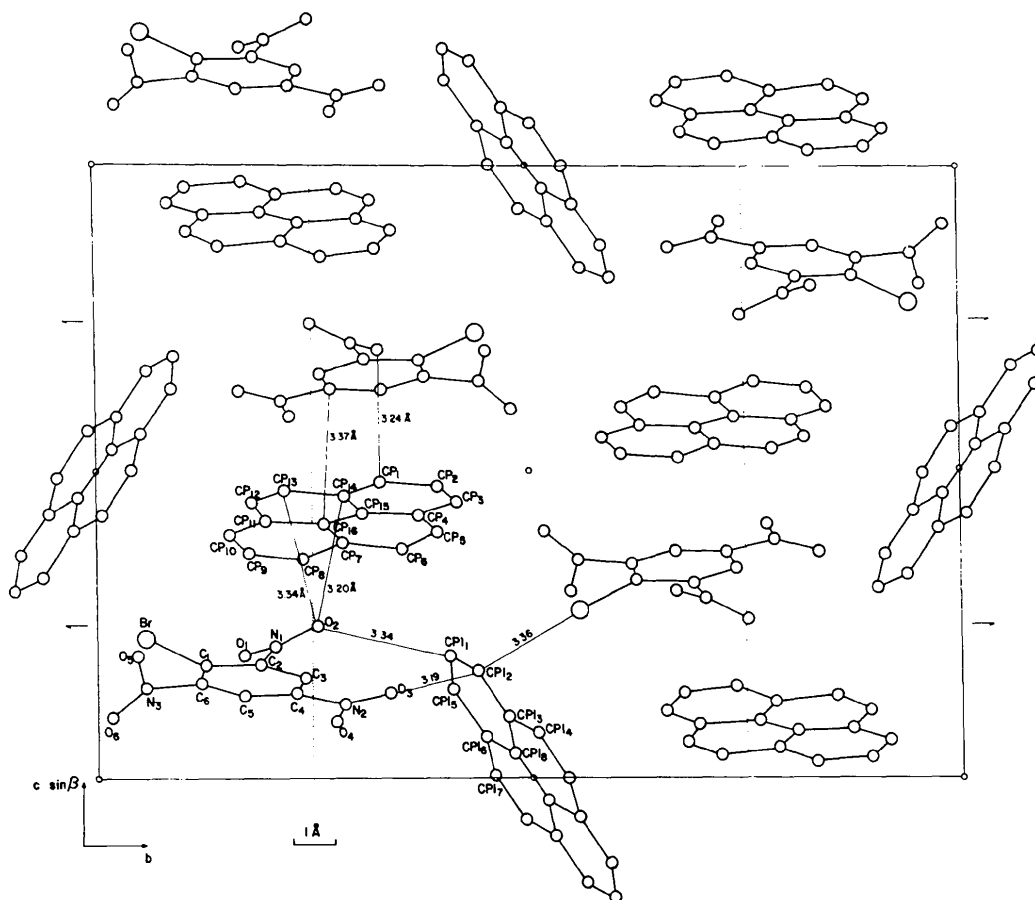
Fig. 2. Projection of $\frac{1}{2}$ pyrene:picryl bromide on (100) plane. Hydrogen atoms have been omitted. The coordinates of the numbered atoms are given in Table 2.

tions of all the non-hydrogen atoms in picryl bromide and in one pyrene molecule were found from the bromine-phased electron-density synthesis. Repetition of this procedure, with phases determined from all the atoms found at this stage, gave the positions of the non-hydrogen atoms of another pyrene molecule, centred at $(0,0,\frac{1}{2})$. After refinement of scale factors, coordinates and anisotropic temperature parameters in three separate blocks, the positions of all hydrogen atoms were found from a difference synthesis. The parameters included in the final least-squares refinement were coordinates and anisotropic temperature factors for all non-hydrogen atoms, coordinates and isotropic temperature factors for hydrogen atoms. The scattering factors were taken from Hanson, Herman, Lea & Skillman (1964) and dispersion corrections for bromine from *International Tables for X-ray Crystallography* (1962). The same weighting scheme was used as for fluoranthene:picryl bromide (Herbstein & Kaftory, 1975). Refinement was stopped with $R = 0.103$, weighted $R = 0.023$, goodness of fit $= 1.61$. Observed and calculated structure factors, based on the

final atomic parameters (Tables 2 and 3), are given in Table 4.

Table 3. *Hydrogen atoms: fractional coordinates and isotropic temperature factors*

Standard deviations of fractional coordinates are: $\sigma(x) \sim 0.01$; $\sigma(y) \sim 0.005$; $\sigma(z) \sim 0.01$; $\sigma(U) \sim 0.02$ Å^2.

$$T = \exp\left(-8\pi^2 U \sin^2\theta/\lambda^2\right).$$

	x	y	z	U (Å^2)
H(3)	0.15	0.27	0.16	0.02
H(5)	0.53	0.17	0.09	0.09
HP(1)	−0.22	0.31	0.49	0.11
HP(2)	−0.19	0.43	0.50	0.12
HP(3)	0.08	0.46	0.43	0.02
HP(5)	0.36	0.44	0.38	0.07
HP(6)	0.57	0.37	0.36	0.17
HP(8)	0.65	0.26	0.36	0.12
HP(9)	0.58	0.14	0.35	0.15
HP(10)	0.34	0.11	0.41	0.01
HP(12)	0.10	0.13	0.44	0.03
HP(13)	−0.11	0.19	0.50	0.12
HPI(1)	0.03	0.38	0.25	0.09
HPI(2)	0.24	0.45	0.22	0.10
HPI(4)	0.37	0.49	0.12	0.08
HPI(5)	−0.18	0.38	0.14	0.12

4. Description and discussion of the structure

4.1. *Crystal structure*

The crystal contains equimolar mixed stacks with alternating pyrene and picryl bromide molecules, and interstitial pyrene molecules steeply inclined to the stack axes (Fig. 2). The usual approximately hexagonal arrangement of the mixed stacks is not found; instead one can describe the crystal as consisting of sheets of mixed stacks, and partial sheets of interstitial pyrene molecules, both parallel to (010) (Fig. 3). Other descriptions are possible.

Within any one stack one can pick out a pair of almost parallel pyrene and picryl bromide molecules (*e.g.* the numbered molecules of Fig. 2). This pair of reference molecules has an interplanar angle of 3°3' but does not show much overlap [Fig. 4(*a*)]. There is considerably more overlap [Fig. 4(*b*)] between the reference pyrene molecule and the succeeding picryl bromide molecule, obtained from its reference molecule by operation of the *c* glide plane; the angle between these pyrene and picryl bromide molecules is 7°52'. Thus the larger tilt is found between the more overlapped pair of molecules. The shorter intermolecular distances between these two pairs are rather similar (Fig. 2), the shortest values (3·20, 3·24 Å) hinting perhaps at some localized interactions. The arrangement found is a generalization of the intrastack arrangement in anthracene:TNB* (Brown, Wallwork & Wilson, 1964),

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* 1,3,5-Trinitrobenzene.

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where there are symmetry restrictions on the possible relative orientations of donor and acceptor molecules. However, both structures have a similar sort of mutual offset of donor and acceptor molecules within a stack. In contrast to this, the pyrene:TNB structure (Prout & Tickle, 1973) shows a centre-on-centre positioning within the stacks which is consistent with a maximization of the charge-transfer stabilization energy (Mayoh & Prout, 1972). Judging from the resemblance in cell dimensions, it seems probable that pyrene:picryl bromide has a structure similar to that of pyrene:TNB. Thus it seems that the differences in the energy of different component arrangements within stacks must be rather small and it follows that packing effects can be as important as charge-transfer effects in determining the details of the component arrangement in the crystal.

The major contribution to the interaction between the interstitial pyrene molecule and its closest neighbours presumably comes from dispersion forces, but localized interactions (O···C, Br···C) between picryl bromide and pyrene may also play a role.

Several crystal structures have been reported which resemble $\frac{3}{2}$ pyrene:picryl bromide in the sense that the major component fills two different structural roles. Thus sesqui-naphthalene-2,7-diol:10-methylisoalloxazinium bromide monohydrate (Langhoff & Fritchie, 1970) has mixed equimolar donor:acceptor stacks with the extra naphthalene-2,7-diol molecule at centres of symmetry (and hence necessarily disordered) and inclined steeply to the stack axis. A rather similar situation occurs in (lumiflavinium bromide)$_2$:(hydroquinone)$_3$ (Tillberg & Norrestam, 1972). In (naphthalene-2,3-diol)$_2$: lumiflavin mixed donor–acceptor stacks are found, with the additional naphthalene-2,3-diol molecules highly tilted with respect to the stacked molecules and participating in the extensive hydrogen-bonding system of the crystal (Wells, Trus, Johnston, Marsh & Fritchie, 1974).* A somewhat similar structure has been proposed for (pyrene)$_2$: pyromellitic dianhydride (Ilmet & Kopp, 1966) on the basis of spectroscopic evidence; the structure has not yet been reported. In sesqui-complexes of zinc phthalocyanine with n-alkylamines, one alkylamine molecule is coordinated to each zinc atom, with the other molecules at unspecified locations in the cell (Kobayashi, Ashida, Uyeda, Suito & Kakudo, 1971). Bis(piperidine)-α,β,γ,δ-tetraphenyl-porphinatocobalt(III) nitrate (or bicarbonate) crystallizes with two molecules of piperidine of solvation per porphinatocobalt cation (Scheidt, Cunningham & Hoard, 1973). The piperidines of solvation are at definite positions in the structure and hydrogen-bonded to the anions; however there is appreciable disorder (static or dynamic) in their positions.
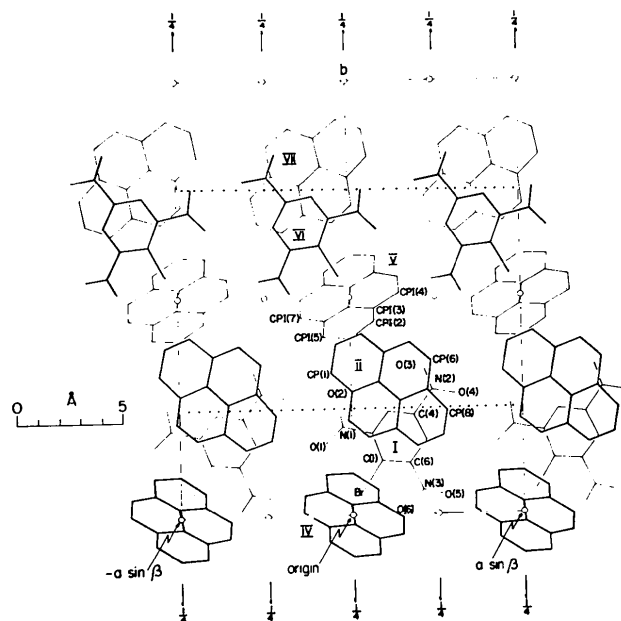

Fig. 3. Projection of $\frac{3}{2}$ pyrene:picryl bromide on (001) plane. Only a part of the unit-cell contents in the [001] direction is shown to reduce the complexity of the diagram. The numbering of atoms and molecules is the same as in Fig. 2 and Table 2. Hydrogen atoms have been omitted.

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* *Note added in proof*: – Similar results have been reported for (naphthalene-2,3-diol)$_2$: 10-propylisoalloxazine (Kuo, Dunn & Fritchie, 1974).

4.2. *Structures of the component molecules*
Pyrene

As the Debye–Waller factors of the atoms of the two crystallographically independent pyrene molecules suggest the occurrence of appreciable in-plane libration and/or disorder, the geometrical parameters of pyrene obtained here are not considered accurate enough to warrant their reproduction in detail. There are no significant discrepancies with published values (Hazell, Larsen & Lehmann, 1972).

Picryl bromide

Bond lengths and angles, and the deviations of atoms from the plane of the benzene ring are shown in Fig. 5. The internal bond angles at the three carbon atoms carrying nitro groups are increased by 2–3°, while those at the other carbons are correspondingly decreased. A similar effect is found in other substituted 2,4,6-trinitrobenzenes (Holden & Dickinson, 1969; Christoph & Fleischer, 1973; Herbstein & Kaftory, 1975).

Comparison of torsion angles, defined according to Klyne & Prelog (1960), of the nitro groups in a number of substituted *s*-trinitrobenzenes is made in Table 5. The torsion φ_4 (*i.e.* of the nitro group at position 4) is due essentially to packing effects, while the torsions φ_2 and φ_6 are due to steric hindrance between the group at the 1-position and the nitro groups at the 2- and 6-positions, and to packing effects. The role of the latter is demonstrated by the different values of φ_2 and φ_6 in the two picryl bromide molecules in fluoranthene: picryl bromide and $\frac{3}{2}$ pyrene:picryl bromide and the similar values found in the isomorphous potassium and ammonium picrates.

The rotations of the nitro groups at the 2- and 6-positions can be in the same or opposite senses; the former may be called 'conrotatory' and the latter 'disrotatory' following the terminology used by Woodward & Hoffmann (1970) in a different context. In the ideal situation of otherwise planar molecules, equal

(a)

(b)
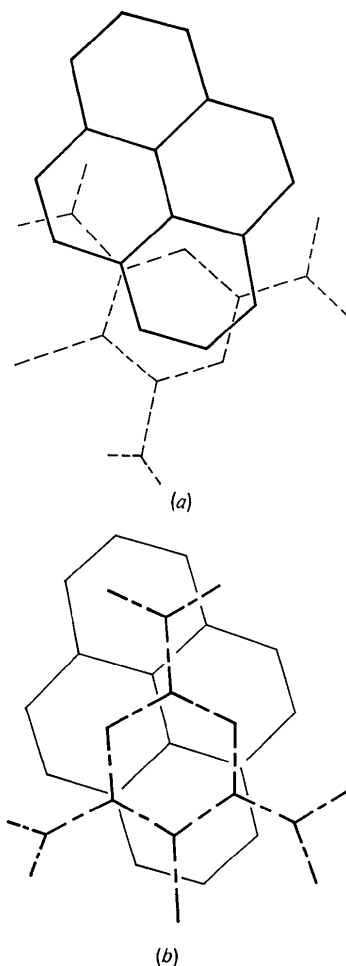
Fig. 4. (*a*) Overlap diagram for a pair of molecules in a stack inclined at 3° 3′ to each other [*e.g.* the numbered (reference) pyrene and picryl bromide molecules shown in Fig. 2]. (*b*) Overlap diagram for reference pyrene molecule and succeeding picryl bromide molecule, obtained from its reference molecule by operation of the *c* glide plane. The angle between these two molecules is 7° 52′.

Fig. 5. Bond lengths (Å) and bond angles (°) in picryl bromide and deviations of the atoms (10^{-2} Å) from the mean plane of the benzene ring.

Table 4. *Absolute values of measured and calculated structure factors*

Table 4 (cont.)

conrotatory rotations will give a molecule of symmetry 2 (C_2) while equal disrotatory rotations will give molecular symmetry m (C_s). In the limits $\varphi_2 = \varphi_6 = 0°$ or 90°, the molecular symmetry will be $mm2$ (C_{2v}). Of the molecules (ions) listed in Table 5, seven have conrotatory rotations of the 2- and 6-nitro groups while six have disrotatory rotations. Three examples of 2 symmetry are found but none of m symmetry. Picryl iodide has exact 2 symmetry but approaches $mm2$ symmetry quite closely. Cell dimensions have been reported for two polymorphs of picryl bromide (Hertel & Romer, 1933) but neither crystal structure has been determined.

Three different methods of relieving the overcrowding are employed in the various picryl halide molecules. Picryl iodide has a crystallographic twofold axis and the oxygen–iodine distances are increased only by rotation of the nitro groups out of the benzene ring plane by equal and opposite amounts. In the two picryl bromide molecules studied, the bromine atoms are displaced (by 0·16 Å and 0·23 Å) out of the benzene ring plane so as to increase distances from the closer oxygen atoms, 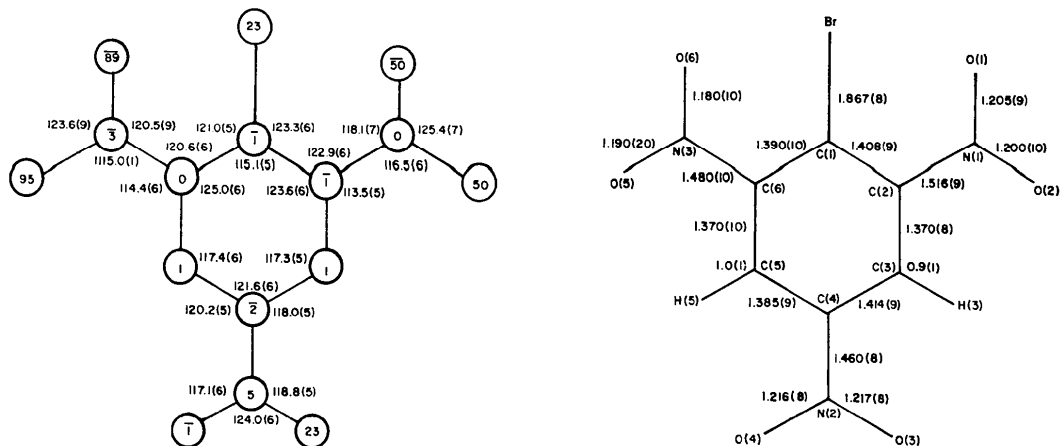and the nitro groups are also rotated out of the benzene ring plane. In picryl chloride the chlorine atom has a component of in-plane displacement in addition to an out-of-plane displacement of 0·08 Å and there is also rotation of the nitro groups. Presumably intermolecular interactions play a role in determining to what extent the various intramolecular mechanisms of strain-relief are adopted in different situations.

All calculations were carried out on the IBM 370/165 computer of the Technion with standard programs. We are grateful to many colleagues for copies of their programs.

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Table 5. *Comparison of torsion angles found for nitro groups in some picryl halides and picrates* [*for other values see Holden & Dickinson* (1969) *and Christoph & Fleischer* (1973)]

The signs of the torsion angles of the moieties in the table do not have any absolute significance as both enantiomers are present in the crystals [apart from picryl iodide, see note (2)]. The signs given refer to the molecules whose coordinates have been tabulated in the references listed.

Moiety/crystal	Torsion angles[1] of nitro groups (°)			Sense of φ_2, φ_6 rotations	Symmetry of moiety	Reference
	φ_4	φ_2	φ_6			
Picric acid in 1-bromo-2-aminonaphthalene: picric acid	−11·2	−16·5	−3·4	con	−	a
Ammonium picrate	−2·2	25·7	25·7	con	2	b
Potassium picrate	−5·0	26·6	26·6	con	2	b
2,4,6-Trinitrophenetole	3·8	61·3	−31·8	dis	−	c
2,4,6-Trinitroaniline	4·0	22·5	−8·5	dis	−	d
N-Methyl-2,4,6-trinitroacetanilide	4	54	36	con	−	e
N-Methyl-N,2,4,6-tetranitroaniline	−23	25	44	con	−	f
N-Trifluoroethyl-N,2,4,6-tetranitroaniline	12	−19	39	dis	−	g
Picryl azide in bis-(8-hydroxyquinolinato)copper(II): picryl azide	7	−58	−14	con	−	h
Picryl chloride	−13	−33	81	dis	−	i
Picryl bromide in fluoranthene: picryl bromide	11·6	16·1	−37·3	dis	−	j
Picryl bromide in ⅔(pyrene): picryl bromide	7·5	−26·6	60·6	dis	−	k
Picryl iodide[2]	0	−80	−80	con	2	l

References: (a) Carstensen-Oeser, Göttlicher & Habermehl (1968). (b) Maartman-Moe (1969). (c) Gramaccioli, Destro & Simonetta (1968). (d) Holden, Dickinson & Bock (1972). (e) Christoph & Fleischer (1972). (f) Cady (1967). (g) Holden & Dickinson (1969). (h) Bailey & Prout (1965). (i) Willis, Stewart, Ammon, Preston, Gluyas & Harris (1971). (j) Herbstein & Kaftory (1975). (k) Present paper. (l) Huse & Powell (1940).

Notes: (1) Listed according to the benzene-ring carbon to which the nitro group is bonded. (2) The signs of these torsion angles refer to the coordinates listed in (l) above [but note correction in *Structure Reports*, **8**, 303–304 (1940–1941)]. As picryl iodide is optically active (space group $P4_12_12$ or $P4_32_12$), the absolute signs of the torsion angles can be determined. This was not done by Huse & Powell (1940), their work antedating that of Bijvoet, Peerdeman & van Bommel (1951).

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