

Function minimized $\sum w(|F_o| - |F_c|)^2$, $w = \sigma^{-2}(F_o)$ (derived from counting statistics). Geometrical considerations by *CSU* program (Vicković, 1985); atomic scattering factors and anomalous-dispersion coefficients as defined by *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). All calculations performed on a Univac 1110/42 computer at the University Computing Centre, Zagreb.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* main bond lengths and angles and hydrogen-bond geometry in Table 2. An *ORTEP* view (Johnson, 1971) of the molecule is shown in Fig. 1 with the numbering scheme and the hydrogen-bonding pattern.

The ring-twisted conformation of the *cis*-fused bicyclic system [N(3)—C(4)—C(5)—N(7) 91.4 (1)°] and important conformational features of (1), defined by the torsion angles (Table 3, deposited), are reminiscent of those found in 4,5-dihydro-4,5-dimethoxy-3,7-dimethyluric acid (Poje & Vicković, 1987b); moreover, there is a coincidental short N(3)⋯C(10) intramolecular contact of 2.796 (3) Å. The N(7) and N(9) atoms also showed a distinct pyramidalization; the distances from the planes through their three adjacent atoms are 0.107 (1) and -0.157 (1) Å, respectively.

A nearly orthogonal N(3)—C(4)—N(9)—C(8) array of -93.5 (1)° along with the suitably oriented non-bonded electron pair on O(4) weaken the N(3)—C(4) bond of the ester aminal function (Fig. 2). The ring contractions can again be rationalized on the basis of the arguments derived from the principles of stereo-electronic control in the hydrolysis of uric acid glycol ethers, and results are consistent only if these are taken into consideration. The difference in behaviour of

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43421 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1987). C43, 549–552

The 1:1 Complex of Pyrene with 2,4,6-Trinitrotoluene

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(Received 25 July 1986; accepted 7 October 1986)

Abstract. C₁₆H₁₀·C₇H₅N₃O₆, $M_r = 429.4$, triclinic, $P\bar{1}$, $a = 8.046$ (1), $b = 15.067$ (1), $c = 16.433$ (3) Å, $\alpha = 82.03$ (1), $\beta = 89.10$ (1), $\gamma = 87.52$ (1)°, $U =$

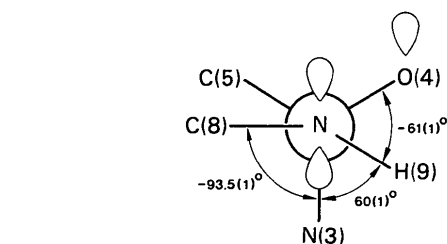


Fig. 2. The Newman projection along the N(9)—C(4) axis showing the alignment of non-bonded electron pairs and the N(3)—C(4) bond; N and O electron escorts are pictured as sp^2 - and sp^3 -hybridized, respectively.

ring-opening products can, however, be readily explained by the effect of substitution at N(1) imposing restrictions on the stable orientation of the ureide side chain (Poje, Paulus & Ročić, 1980).

We thank the Croatian Republic Research Fund for financial support and M. Bruvo, MSc, for data collection.

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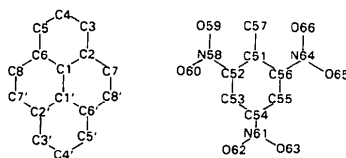
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0108-2701/87/030549-04\$01.50

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structure of the title compound shows conventional donor-acceptor stacks with all molecules ordered, whereas, the corresponding 2,4,6-trinitroanisole complex has disordered pyrene. The donor-acceptor overlap patterns in the two unique stacks are different, with interplanar spacings ranging from 3.461 (8) to 3.499 (9) Å. The presence of disorder and the twist angle of the nitro groups are correlated with the interplanar spacings in a series of pyrene-substituted 1,3,5-trinitrobenzene complexes.

Introduction. In spite of widespread interest in polynitro-aromatic compounds, the crystal structure of 2,4,6-trinitrotoluene (TNT) was not determined until 1982 (Carper, Davis & Extine, 1982). Although molecular complexes of TNT with electron donors have been prepared (Kitaigorodskii, 1984) no structures have been reported. The structure of the 1:1 complex of pyrene with TNT has now been determined as part of a study of complexes of substituted trinitrobenzenes both in the solid state and in solution (Barnes, Chudek, Foster, Jarrett, Mackie, Paton & Twisleton, 1984).



Experimental. Crystals were grown as pale orange tablets by diffusion of 60–80° petroleum into a Sephadex LH-20 gel in methanol-toluene-petroleum containing both components (Desiraju, Curtin & Paul, 1977; Barnes & Gallacher, 1984). After preliminary oscillation and Weissenberg photographs had indicated a triclinic system, unit-cell parameters were refined from 23 strong reflexions in the 2θ range 25–28° which were accurately centred on the Syntex P_2 diffractometer at Helsinki Technical University used for data collection. One standard reflection varied by less than 2.0%. Data were collected by the ω , 2θ scan technique for 5209 reflexions with $2\theta \leq 65.0^\circ$ for ranges $h = 0, 12$; $k = -22, 22$; $l = -24, 24$ using a 1° scan range. Of the 5196 unique reflexions ($R_{int} = 0.058$) 3006 with $F > 5\sigma(F)$ were used in the refinement.

All calculations were performed on the Dundee University DEC 10 computer using the *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) program packages. Atomic scattering parameters were from *International Tables for X-ray Crystallography* (1974).

The structure was solved by the direct-methods routine *TANG* of *SHELX76*. Initial difficulties with the model were resolved when it became apparent that the pyrene molecules lie at crystallographic centres of

symmetry so that the asymmetric unit consists of two TNT molecules but four separate halves of pyrene molecules. The structure developed in the usual way with least-squares refinement and difference synthesis to R 0.17 with all non-hydrogen atoms included with isotropic thermal parameters. Refinement continued with anisotropic thermal parameters for non-hydrogen atoms; 26 H atoms were located on difference maps, with the remaining four H atoms [on C(34), C(73), C(75) and C(77)] placed at calculated positions. The H atoms of each molecule were assigned a single refinable isotropic thermal parameter. At convergence some parameters were oscillating slightly. There was no evidence of disorder. Final refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, 664 refined parameters, $wR = 0.064$, $w = 2.7627/[\sigma^2(F) + 0.000467F^2]$, mean shift/e.s.d. = 0.062, max. shift/e.s.d. = 0.534, max., min. difference peaks = 0.3, $-0.18 e \text{ \AA}^{-3}$. No corrections for absorption or secondary extinction.

Discussion. Atomic coordinates are given in Table 1,* with bond lengths in Table 2. The structure contains two independent but very similar stacks of alternate pyrene and TNT molecules, parallel to **b**. The pyrene molecules are at the centres of symmetry 0,0,0 and 0,0,5,0 (stack I, Fig. 1a) and 0,5,0,0,5 and 0,5,0,5,0,5 (stack II, Fig. 1b) with the unique TNT molecules close to 0,0,25,0 and 0,5,0,25,0,5 respectively.

The dimensions of the pyrene molecules are consistent with those reported from a neutron diffraction study of pyrene (Hazell, Larsen & Lehmann, 1972), within the relatively large standard deviations found in the present structure (Table 2).

The bond lengths and angles in the two TNT molecules are closely similar and agree well with those in TNT itself (Table 2). The benzene ring shows the usual distortion found in nitrobenzenes: C atoms which carry nitro groups have ring angles greater than 120° (Carper *et al.*, 1982; Dickinson, Stewart & Holden, 1966). The methyl group C(57), C(77) is displaced from its ideal position towards N(64), N(84) when viewed normal to the ring, with C(57) 0.081 (1) and C(77) 0.114 (1) Å above the ring plane and N(64) 0.036 (1) and N(84) 0.056 (1) Å below the plane. A similar distortion is present in one of the two unique molecules in TNT itself (molecule 2, Table 2). The nitro groups in the present compound are twisted from the ring plane by, an average, 26 (2), 1.6 (1) and 40 (2)° (Table 3). A *MINDO/3* calculation has predicted these angles as 45, 0 and 45° for the free molecule (Carper *et al.*, 1982). In the two unique molecules in TNT itself the

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angles are 51, 60; 24, 30; and 43, 45°, so that the average deviation and particularly the deviation at the 4-NO₂ group is closer to the theoretical in the complex than in pure crystalline TNT, in which very extensive intra- and intermolecular hydrogen bonding has been postulated. Although the intramolecular hydrogen bonding would not be influenced by complexation with pyrene, the pyrene matrix would preclude inter-TNT interactions while introducing different steric constraints (see below).

Table 1. Coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	x	y	z	U_{eq}
C(1)	-114 (5)	5191 (2)	9580 (2)	41 (1)
C(2)	-1694 (5)	5555 (3)	9314 (3)	51 (1)
C(3)	-1852 (7)	5921 (3)	8485 (3)	64 (2)
C(4)	-556 (7)	5922 (3)	7955 (3)	67 (2)
C(5)	986 (7)	5571 (3)	8200 (3)	60 (2)
C(6)	1227 (5)	5201 (3)	9019 (3)	52 (1)
C(7)	-3002 (6)	5535 (3)	9911 (4)	65 (2)
C(8)	2812 (6)	4814 (3)	9313 (3)	59 (1)
C(11)	5458 (5)	33 (3)	5348 (3)	49 (1)
C(12)	4745 (7)	9790 (3)	6143 (3)	63 (2)
C(13)	5680 (11)	-162 (4)	6833 (4)	94 (3)
C(14)	7242 (11)	141 (4)	6772 (5)	99 (3)
C(15)	8011 (7)	392 (4)	6020 (5)	86 (2)
C(16)	2903 (6)	9668 (3)	4728 (4)	67 (2)
C(17)	3070 (8)	-510 (3)	6185 (4)	81 (2)
C(18)	7780 (7)	569 (3)	4486 (5)	87 (2)
C(21)	332 (6)	181 (3)	9623 (3)	55 (1)
C(22)	-601 (9)	723 (3)	9023 (4)	82 (2)
C(23)	258 (14)	1087 (4)	8245 (4)	107 (3)
C(24)	1923 (15)	838 (6)	8208 (5)	121 (4)
C(25)	2833 (12)	308 (7)	8779 (7)	131 (4)
C(26)	7905 (8)	38 (4)	513 (5)	91 (2)
C(27)	-2247 (12)	901 (4)	9197 (6)	105 (3)
C(28)	3000 (8)	-615 (5)	10131 (6)	91 (3)
C(31)	5455 (6)	5182 (3)	4656 (3)	57 (1)
C(32)	4706 (11)	5296 (4)	3859 (4)	97 (3)
C(33)	5650 (20)	5671 (7)	3179 (6)	163 (6)
C(34)	7240 (22)	5914 (8)	3344 (10)	197 (9)
C(35)	8027 (14)	5819 (6)	4087 (10)	157 (5)
C(36)	7084 (8)	5445 (4)	4759 (6)	96 (3)
C(37)	3030 (15)	5028 (6)	3842 (8)	130 (5)
C(38)	7809 (11)	5325 (6)	5568 (9)	134 (6)
C(51)	9815 (6)	2144 (3)	10985 (3)	59 (1)
C(52)	10952 (6)	2266 (3)	10339 (4)	61 (2)
C(53)	10523 (8)	2706 (4)	9562 (4)	72 (2)
C(54)	8948 (7)	3017 (3)	9425 (3)	57 (1)
C(55)	7783 (7)	2937 (3)	10026 (3)	53 (1)
C(56)	8218 (6)	2498 (3)	10776 (3)	52 (1)
C(57)	10247 (9)	1723 (4)	11846 (4)	82 (2)
N(58)	12698 (7)	1933 (4)	10444 (4)	96 (2)
O(59)	12971 (5)	1262 (4)	10948 (3)	121 (2)
O(60)	13739 (5)	2293 (3)	10009 (4)	142 (2)
N(61)	8473 (8)	3466 (3)	8599 (3)	83 (2)
O(62)	9550 (6)	3545 (3)	8073 (3)	121 (2)
O(63)	7033 (7)	3726 (3)	8497 (3)	114 (2)
N(64)	6849 (5)	2407 (3)	11396 (3)	67 (1)
O(65)	5885 (5)	3048 (3)	11411 (2)	91 (1)
O(66)	6724 (5)	1683 (3)	11826 (2)	97 (1)
C(71)	5233 (6)	7397 (3)	5695 (3)	57 (1)
C(72)	6273 (6)	7683 (3)	5039 (4)	62 (2)
C(73)	5790 (7)	7780 (3)	4239 (3)	66 (2)
C(74)	4213 (7)	7567 (3)	4074 (3)	60 (1)
C(75)	3121 (6)	7281 (3)	4677 (3)	57 (1)
C(76)	3648 (6)	7211 (3)	5469 (3)	51 (1)
C(77)	5755 (8)	7218 (5)	6597 (4)	96 (2)
N(78)	8010 (7)	7913 (3)	5181 (5)	105 (2)
O(79)	8334 (6)	8174 (3)	5826 (4)	154 (3)
O(80)	8982 (6)	7890 (4)	4637 (4)	162 (3)
N(81)	3651 (9)	7671 (3)	3203 (3)	97 (2)
O(82)	4706 (7)	7942 (3)	2675 (3)	134 (2)
O(83)	2244 (8)	7494 (3)	3092 (3)	136 (2)
N(84)	2366 (6)	6929 (3)	6082 (3)	79 (1)
O(85)	1383 (5)	6397 (3)	5932 (3)	117 (2)
O(86)	2263 (6)	7273 (3)	6697 (3)	119 (2)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Bond lengths with e.s.d.'s in parentheses

Pyrene	Molecule 1	Molecule 2	Molecule 3	Molecule 4	*
C(1)-C(2)	1.413 (6)	1.425 (6)	1.396 (7)	1.437 (8)	c 1.412
C(2)-C(3)	1.403 (7)	1.383 (9)	1.492 (10)	1.407 (14)	b 1.399
C(3)-C(4)	1.348 (8)	1.353 (12)	1.379 (16)	1.386 (24)	a 1.387
C(4)-C(5)	1.372 (7)	1.385 (11)	1.349 (14)	1.372 (23)	a
C(5)-C(6)	1.397 (6)	1.458 (9)	1.346 (10)	1.397 (16)	b
C(6)-C(1)	1.407 (6)	1.410 (9)	1.463 (10)	1.405 (8)	c
C(2)-C(7)	1.425 (7)	1.438 (9)	1.374 (12)	1.427 (15)	d 1.429
C(6)-C(8)	1.441 (6)	1.402 (9)	1.456 (10)	1.445 (17)	d
C(7)-C(8')	1.320 (7)	1.322 (9)	1.282 (10)	1.243 (15)	f 1.360
C(1)-C(1')	1.431 (7)	1.387 (9)	1.392 (8)	1.396 (15)	e 1.423

Molecule 1 has atoms C(*n*), molecule 2 has atoms C(10 + *n*), molecule 3 has atoms C(20 + *n*), molecule 4 has atoms C(30 + *n*).

Trinitrotoluene

	Molecule 1	Molecule 2	Molecule 1†	Molecule 2†
C(1)-C(2)	1.388 (7)	1.385 (7)	1.390	1.395
C(2)-C(3)	1.395 (8)	1.363 (8)	1.364	1.383
C(3)-C(4)	1.344 (8)	1.363 (8)	1.415	1.344
C(4)-C(5)	1.347 (7)	1.352 (7)	1.375	1.373
C(5)-C(6)	1.358 (6)	1.364 (7)	1.372	1.387
C(6)-C(1)	1.399 (7)	1.384 (7)	1.408	1.379
C(1)-C(7)	1.507 (8)	1.532 (8)	1.505	1.507
C(2)-N(8)	1.476 (7)	1.485 (7)	1.496	1.459
N(8)-O(9)	1.229 (8)	1.216 (10)	1.210	1.177
N(8)-O(10)	1.192 (8)	1.181 (7)	1.214	1.232
C(4)-N(11)	1.479 (7)	1.492 (7)	1.443	1.482
N(11)-O(12)	1.211 (7)	1.245 (8)	1.215	1.232
N(11)-O(13)	1.213 (8)	1.197 (10)	1.195	1.214
C(6)-N(14)	1.487 (6)	1.465 (7)	1.449	1.494
N(14)-O(15)	1.216 (6)	1.203 (7)	1.217	1.179
N(14)-O(16)	1.221 (6)	1.197 (7)	1.252	1.236

Molecule 1 has atoms C, N, O (50 + *n*), molecule 2 has atoms C, N, O (70 + *n*).

* Neutron diffraction study by Hazell *et al.* (1972) (equivalent values averaged).

† X-ray study by Carper *et al.* (1982).

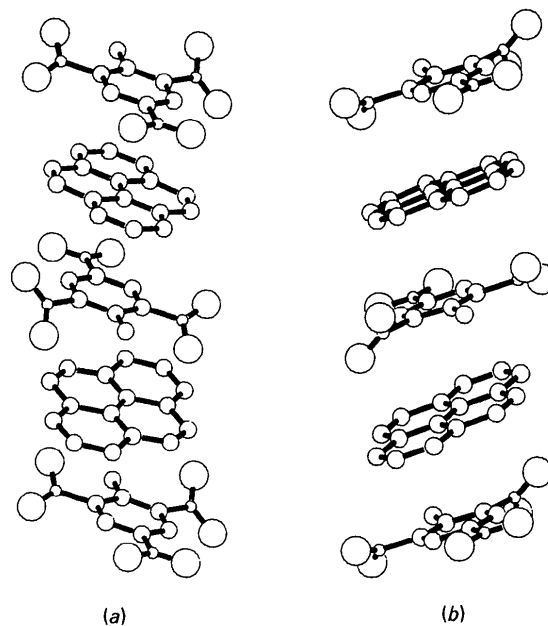


Fig. 1 (a). Pyrene-2,4,6-trinitrotoluene complex, stack I. (b) Stack II.

Fig. 2 shows the four unique overlap diagrams [acceptor projected on to the plane of the donor (Prout & Kamemar, 1973)] for the complex. Each pattern is different but none is unusual in the relationship of acceptor to donor. In each case the TNT molecule is sufficiently displaced from the centre of inversion of the pyrene (seen in projection) that the benzene rings of the TNT above and below the pyrene do not overlap. Some aspects of the intra- and intermolecular geometry of the complex are given in Table 3.

When viewed projected onto the plane of the TNT molecule the centres of the two independent pyrene

Table 3. *Inter- and intramolecular geometry*

	Stack I	Stack II
Average distances between ring atoms within stacks (Å)		
Pyrene (A)—Pyrene (B)	6.751 (16)	6.826 (12)
Pyrene (A)—TNT	3.461 (8)	3.499 (9)
Pyrene (B)—TNT	3.486 (11)	3.489 (12)
Angles between normals to planes (°)		
Within stacks		
Pyrene (A)—Pyrene (B)	11.4 (1)	7.8 (1)
Pyrene (A)—TNT	3.3 (1)	3.7 (2)
Pyrene (B)—TNT	8.1 (1)	6.0 (2)
2-NO ₂ Group to TNT ring	28.1 (2)	25.2 (1)
4-NO ₂ Group to TNT ring	1.7 (1)	1.5 (2)
6-NO ₂ Group to TNT ring	42.3 (1)	38.2 (1)
Between stacks		
Pyrene (A)—Pyrene (A)		40.6 (1)
Pyrene (A)—Pyrene (B)		34.4 (2)
Pyrene (B)—Pyrene (A)		44.5 (2)
Pyrene (B)—Pyrene (B)		37.0 (2)
TNT (1)—TNT (2)		34.4 (1)

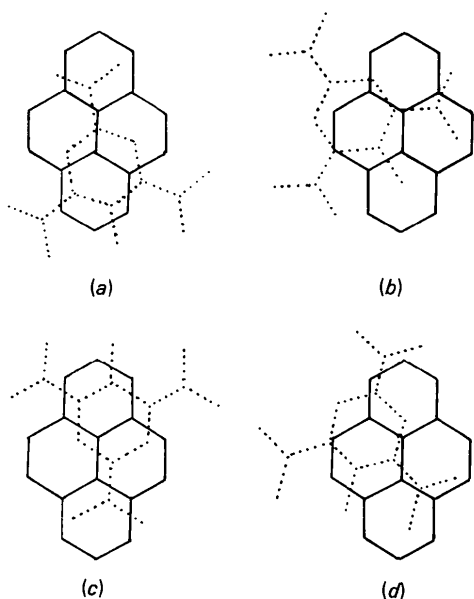


Fig. 2. Overlap diagrams showing projection of the acceptor molecule on to the plane of the donor. (a) Stack I. Molecule 5 on to Molecule 1. (b) Stack I. Molecule 5 on to Molecule 3. (c) Stack II. Molecule 6 on to Molecule 2. (d) Stack II. Molecule 6 on to Molecule 4.

molecules in stack I are displaced from each other by 2.737 (10) Å. In this projection the C(1)—C(1') vectors make an angle of 26 (1)°. The corresponding values for stack II are 2.312 (9) Å and 73 (1)°. In each stack the angle between the ring plane of the TNT and that of one pyrene is 3.5 (2)°. For the second pyrene the corresponding angle is 7.0 (1)°. Each TNT molecule has one nitro group not overlapping either adjacent pyrene molecule. In stack I this is the 6-NO₂ group [N(64)] but in stack II the 4-NO₂ group [N(81)] is uncovered. The great similarity in the twist angles for the nitro groups in the two molecules in spite of the different environment shows that in this case forces within the stack have very little influence on the equilibrium position of these rotatable groups. This can be correlated with the interplanar spacing between donor and acceptor. In the present compound this ranges from 3.461 (8) to 3.499 (9) Å. These values lie between those for the complex pyrene-1,3,5-trinitrobenzene (Prout & Tickle, 1973), where an interplanar spacing of 3.38 Å is accompanied by nitro-group twist angles of 6.0, 2.6 and 6.3°, and those for pyrene-2,4,6-trinitroanisole (Barnes *et al.*, 1984) where the interplanar spacing is 3.79 Å and the nitro-group twist angles 41.0, 2.7 and 20.7° are very similar to those in the present complex. Although the increased separation in the 2,4,6-trinitroanisole complex does not lead to further twisting of the nitro groups, it may allow the disorder of the pyrene molecules found in that structure but not in the complexes with TNT or 1,3,5-trinitrobenzene.

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