

## The Crystal Structure of the 1:1 Molecular Complex between 1,3,7,9-Tetramethyluric Acid and Pyrene

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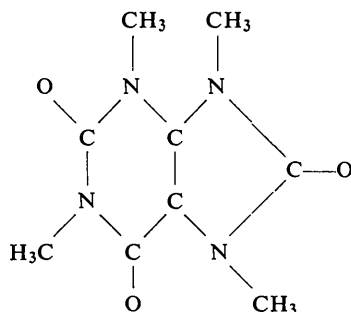
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Crystals of the 1:1 molecular complex between 1,3,7,9-tetramethyluric acid (TMU) and pyrene are monoclinic, space group *Pc*, with  $a = 9.71 \pm 0.02$ ,  $b = 8.00 \pm 0.02$ ,  $c = 15.04 \pm 0.02$  Å,  $\beta = 117^\circ 00' \pm 12'$ ,  $Z = 2$ . The crystal structure has been determined by means of optical Fourier transform and Patterson methods and then refined by three-dimensional Fourier synthesis and several cycles of Booth's differential synthesis. The structure is characterized by a plane to plane alternate stacking of TMU and pyrene molecules in infinite columns parallel to the *b* axis. The molecular planes are almost exactly parallel (the angle between them being  $4^\circ$  only). The sum of the perpendicular distances from the origin to the two least-squares planes through the TMU and pyrene molecules is 3.48 Å. This characteristic molecular geometry of the complex indicates that intermolecular binding forces are due to 'polarization bonding' and to van der Waals interactions.

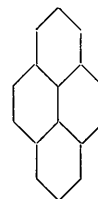
### Introduction

The solubilization of polycyclic aromatic hydrocarbons in water solutions of several purines, as well as the formation of crystalline complexes between purines and aromatic hydrocarbons from organic solvents, was first described by Weil-Malherbe (1946). Recently the ability of aqueous solutions of deoxyribonucleic acid to solubilize aromatic hydrocarbons has been reported (Liquori, Ascoli & Botrè, 1962); (Liquori, de Lerma, Ascoli, Botrè & Trasciatti, 1962). The great biological interest of the interaction between aromatic hydrocarbons and nucleic acids led us to undertake crystal structure analysis of the 1:1 molecular complex of 1,3,7,9-tetramethyluric acid (TMU) with pyrene and of the 2:1 complexes of TMU with 3,4-benzpyrene and coronene in order to investigate the arrangement of purine and aromatic molecules in these complexes and to obtain some indication on the main binding forces responsible for their stability.

A preliminary account of the crystal structure of the 1:1 complex between TMU



and pyrene



has been previously reported (De Santis, Giglio, Liquori & Ripamonti, 1961). Here we wish to describe the results of a much more detailed structure analysis, carried out in three dimensions.

### Experimental

Crystals of the 1:1 molecular complex of TMU with pyrene prepared from benzene according to Weil-Malherbe (1946) were used in the previous X-ray studies. However when X-ray three-dimensional data were collected from such crystals it became apparent that only about one quarter of the 2400 possible reflexions (Cu *K* $\alpha$  radiation) could be recorded and therefore it became necessary to improve the quality of the crystals after various attempts. Suitable crystals were grown from ethanol. 71% of the total accessible reflexions were thus recorded with a Wiebenga integrating Weissenberg camera.

The *h0l*, *h1l*, ... *h7l* and *0kl* reflexions were collected and their integrated intensities, estimated visually with a set of standard strips, were corrected for Lorentz and polarization factors and were put on a common scale with the aid of the *0kl* intensity data. No absorption corrections were applied.

### Crystal data

$C_{16}H_{10} \cdot C_9N_4O_3H_{12}$ ,  $M = 426.5$ . Colourless crystals, monoclinic,  $a = 9.71 \pm 0.02$ ,  $b = 8.00 \pm 0.02$ ,  $c = 15.04$

$\pm 0.02 \text{ \AA}$ ,  $\beta = 117^\circ 00' \pm 12'$ ,  $U = 1041 \text{ \AA}^3$ ,  $F(000) = 448$ ,  $\lambda_{\text{Cu } K\alpha} = 1.542 \text{ \AA}$ .

Absent spectra:  $h0l$  when  $l$  odd.

Space group  $P2/c$  or  $Pc$ . Positive piezoelectric test indicates  $Pc$  to be the space group.

The theoretical density is  $1.351 \text{ g.cm}^{-3}$ .

### Three-dimensional refinement of the structure

The phases of a sufficiently large fraction of the observed reflexions on (010) and (100) were established through a combination of optical Fourier transform and Patterson methods. A refinement was then carried out with reiterated cycles of structure factor calculations and Fourier difference syntheses. The final  $R$  indices were:  $R_{hol} = 0.21$  and  $R_{0kl} = 0.19$ . At this stage, starting with the atomic coordinates and isotropic temperature parameters, derived from the two-dimensional analysis, a three-dimensional Fourier synthesis was calculated with 525 independent reflexions.

The refinement of the positional parameters was carried out first by the block-diagonal least-squares method and later by several cycles of Fourier differential synthesis using all the available reflexions. Anisotropic temperature factors and the contribution of the hydrogen atoms were introduced in the last cycles. The hydrogen atoms were put at expected positions, assuming  $\text{C-H} = 1.08 \text{ \AA}$ , with the same isotropic temperature factors of  $6.0 \text{ \AA}^2$ . The  $R$  index dropped from 0.341 to 0.174. Although this value is rather high for a three-dimensional refinement, we feel that it is an

adequate representation of the complexity of the structure. In fact the pronounced thermal anisotropy, in addition to the possible action of inverse overlap (Srinivasan, 1961; Rae & Maslen, 1963), due to the presence of a group of atoms with a centre of symmetry in a non-centrosymmetric structure, might severely limit the precision of the positional parameters of these atoms. The refinement was considered complete when the coordinate shifts were less than the corresponding standard deviations, except for the carbon atom C(5), which has two coordinates with standard deviations slightly smaller than the shifts.

The final fractional atomic coordinates and their corresponding standard deviations are reported in Table 1. For the numbering of atoms see Fig. 1, where bond lengths and bond angles are also indicated.

Fig. 2(a) shows a composite projection, along the  $b$  axis, of the final electron density distribution calculated through sections containing the atoms of a pyrene molecule. Fig. 2(b) shows a similar composite projection for the TMU molecule. Fig. 3 shows a composite projection of the complex along the  $a$  axis.

The initial disagreement between observed and calculated curvatures of the electron density at the atomic positions indicated a pronounced thermal anisotropy for all the atoms. Approximate  $b_{ij}$  coefficients were found for the temperature factor expression  $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{13}hl)]$ . No quantitative analysis of thermal parameters was made but, as expected, the directions of maximum vibration of the atoms were

Table 1. Final fractional atomic coordinates, and their standard deviations ( $\text{\AA}$ )

	$x/a$	$y/b$	$z/c$	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0.0813	0.5244	0.1589	0.024	0.014	0.014
C(2)	0.2030	0.4659	0.1585	0.026	0.018	0.016
C(3)	0.2123	0.3817	0.0757	0.014	0.014	0.017
C(4)	0.3474	0.3200	0.0665	0.021	0.025	0.033
C(5)	0.3209	0.2300	-0.0173	0.017	0.020	0.032
C(6)	0.1773	0.1974	-0.1008	0.016	0.021	0.018
C(7)	0.0475	0.2486	-0.0955	0.012	0.013	0.011
C(8)	-0.1183	0.2249	-0.1723	0.016	0.013	0.012
C(9)	-0.2388	0.2795	-0.1687	0.020	0.017	0.018
C(10)	-0.2173	0.3651	-0.0822	0.014	0.018	0.019
C(11)	-0.3464	0.4305	-0.0725	0.017	0.020	0.022
C(12)	-0.3252	0.5050	0.0065	0.019	0.024	0.026
C(13)	-0.1928	0.5456	0.0845	0.020	0.019	0.017
C(14)	-0.0642	0.4874	0.0794	0.012	0.013	0.011
C(15)	-0.0737	0.3997	-0.0052	0.007	0.008	0.008
C(16)	0.0693	0.3425	-0.0024	0.008	0.009	0.008
C(17)	0.3146	-0.1729	0.0630	0.008	0.009	0.008
C(18)	0.2331	-0.2904	-0.1042	0.014	0.016	0.013
C(19)	0.0501	-0.1745	-0.0362	0.008	0.009	0.008
C(20)	-0.1380	-0.2871	-0.2047	0.015	0.017	0.012
C(21)	-0.2162	-0.1346	-0.0845	0.011	0.015	0.015
C(22)	-0.2947	-0.0044	0.0273	0.012	0.021	0.014
C(23)	-0.0216	-0.0350	0.0836	0.009	0.011	0.011
C(24)	0.0902	-0.1017	0.0573	0.007	0.008	0.008
C(25)	0.3512	-0.0339	0.2170	0.010	0.012	0.009
N(26)	0.1876	-0.2210	-0.0311	0.007	0.007	0.006
N(27)	-0.0967	-0.2011	-0.1071	0.008	0.008	0.008
N(28)	-0.1720	-0.0657	0.0056	0.008	0.009	0.008
N(29)	0.2527	-0.1009	0.1185	0.006	0.007	0.006
O(30)	0.4494	-0.2065	0.0857	0.007	0.011	0.009
O(31)	-0.3527	-0.1559	-0.1498	0.010	0.011	0.012
O(32)	0.0068	0.0303	0.1650	0.008	0.010	0.008

found to lie in the molecular planes. Furthermore the carbon atoms of pyrene have larger  $b_{ij}$  values than those of the TMU molecule. It also appears that the  $b_{ij}$  values increase with the distances of the atoms from

the centre of the molecule. This effect explains the lower electron density of a pyrene molecule with respect to a TMU molecule [see Fig. 2(a) and (b)] and may be interpreted in terms of a rigid body oscillation about

Table 2. Final temperature factors in the form  $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{13}hl)]$

	$b_{11}$	$b_{13}$	$b_{22}$	$b_{33}$
C(1)	0.0310	0.0125	0.0115	0.0100
C(2)	0.0300	0.0070	0.0210	0.0085
C(3)	0.0220	0.0135	0.0140	0.0127
C(4)	0.0270	0.0090	0.0255	0.0130
C(5)	0.0285	0.0195	0.0235	0.0130
C(6)	0.0300	0.0230	0.0260	0.0130
C(7)	0.0260	0.0195	0.0175	0.0092
C(8)	0.0300	0.0150	0.0124	0.0088
C(9)	0.0270	0.0147	0.0178	0.0124
C(10)	0.0235	0.0170	0.0195	0.0138
C(11)	0.0235	0.0120	0.0260	0.0120
C(12)	0.0300	0.0185	0.0290	0.0135
C(13)	0.0300	0.0210	0.0218	0.0120
C(14)	0.0255	0.0210	0.0150	0.0110
C(15)	0.0144	0.0103	0.0064	0.0066
C(16)	0.0144	0.0103	0.0065	0.0060
C(17)	0.0140	0.0048	0.0088	0.0055
C(18)	0.0255	0.0170	0.0190	0.0095
C(19)	0.0156	0.0082	0.0070	0.0062
C(20)	0.0264	0.0117	0.0236	0.0066
C(21)	0.0160	0.0110	0.0170	0.0118
C(22)	0.0195	0.0125	0.0307	0.0087
C(23)	0.0156	0.0120	0.0129	0.0095
C(24)	0.0147	0.0113	0.0055	0.0081
C(25)	0.0186	0.0100	0.0177	0.0064
N(26)	0.0161	0.0088	0.0098	0.0050
N(27)	0.0163	0.0085	0.0104	0.0075
N(28)	0.0168	0.0096	0.0162	0.0074
N(29)	0.0116	0.0066	0.0077	0.0056
O(30)	0.0165	0.0120	0.0248	0.0092
O(31)	0.0210	0.0106	0.0208	0.0110
O(32)	0.0215	0.0165	0.0228	0.0095

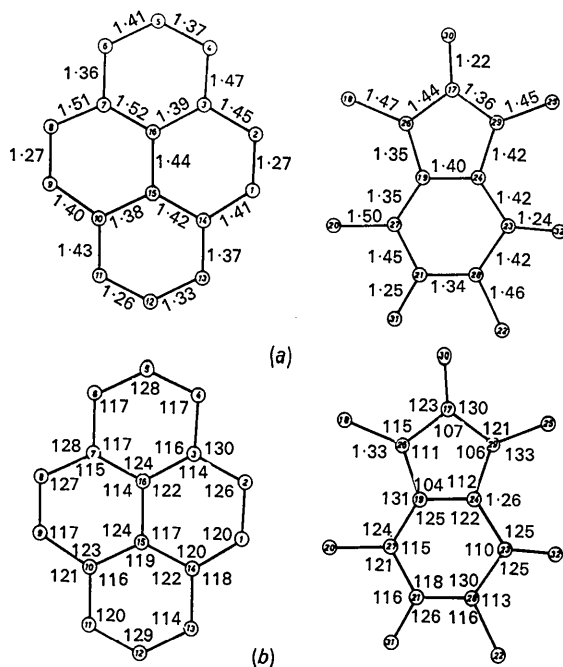


Fig. 1. (a) Atomic numbering and bond lengths. (b) Bond angles.

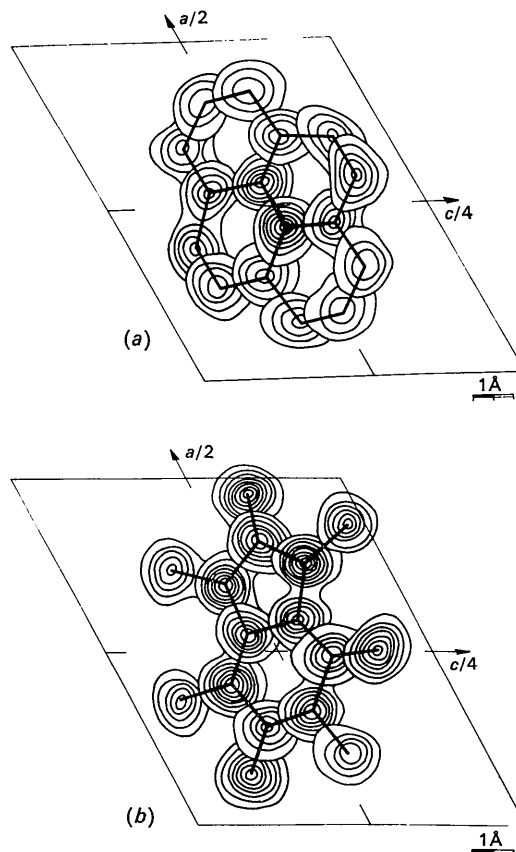


Fig. 2. Composite drawing of the final electron-density series, viewed along the  $b$  axis. Contours are at intervals of  $1 \text{ e.}\text{\AA}^{-3}$  starting with  $1 \text{ e.}\text{\AA}^{-3}$ . (a) Pyrene. (b) TMU.

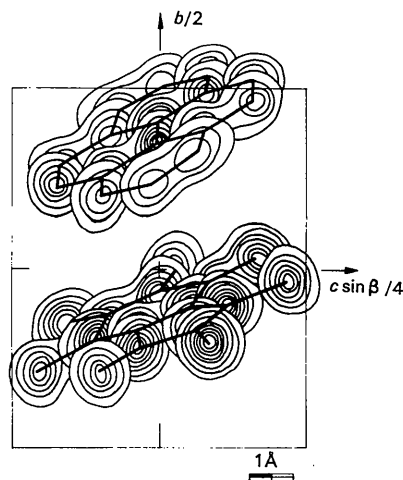


Fig. 3. Composite drawing of the final electron-density series, viewed along the  $a$  axis. Contours are at intervals of  $1 \text{ e.}\text{\AA}^{-3}$  starting with  $1 \text{ e.}\text{\AA}^{-3}$ .

the centre of the pyrene molecule. The final  $b_{ij}$  values are reported in Table 2, but they must be considered only as additional parameters for improving the agreement index.

The accuracy of the atomic coordinates was estimated by applying Cruickshank's (1949) formulae but the corresponding standard deviations appear to be rather optimistic. The e.s.d.'s for the bond lengths and angles (Cruickshank & Robertson, 1953) are collected in Tables 3 and 4. The comparison between observed and calculated peak heights is given in Table 5. The e.s.d.'s of the electron density and of its first derivatives are:

$$\begin{aligned}\sigma(\rho) &= 0.18 \text{ e.}\text{\AA}^{-3}; & \sigma(A_h) &= 0.45, \\ \sigma(A_k) &= 0.49, & \sigma(A_l) &= 0.44 \text{ e.}\text{\AA}^{-4}.\end{aligned}$$

Table 6 shows final values of the observed and calculated structure factors. The atomic scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, N and O and of McWeeny (1951) for H. The calculations were performed on an IBM 1620 computer with the programs of Van der Helm (1961*a, b*) for structure

Table 3. *Estimated standard deviations for the bond lengths (Å)*

C(1)–C(2)	0.026	C(15)–C(16)	0.011
C(2)–C(3)	0.025	C(17)–O(30)	0.012
C(3)–C(4)	0.030	C(17)–N(26)	0.011
C(4)–C(5)	0.035	C(17)–N(29)	0.010
C(5)–C(6)	0.029	C(18)–N(26)	0.016
C(6)–C(7)	0.022	C(19)–N(26)	0.011
C(7)–C(8)	0.018	C(19)–C(24)	0.012
C(8)–C(9)	0.023	C(19)–N(27)	0.012
C(9)–C(10)	0.025	C(20)–N(27)	0.017
C(10)–C(11)	0.026	C(21)–N(27)	0.016
C(11)–C(12)	0.030	C(21)–O(31)	0.017
C(12)–C(13)	0.030	C(21)–N(28)	0.016
C(13)–C(14)	0.022	C(22)–N(28)	0.018
C(1)–C(14)	0.021	C(23)–N(28)	0.013
C(3)–C(16)	0.017	C(23)–O(32)	0.014
C(7)–C(16)	0.015	C(23)–C(24)	0.013
C(10)–C(15)	0.019	C(24)–N(29)	0.010
C(14)–C(15)	0.014	C(25)–N(29)	0.012

factors, least-squares and Fourier syntheses, and those of Damiani, De Santis, Giglio & Ripamonti (1963) for differential synthesis.

### Discussion

The least-squares planes of the pyrene and TMU molecules, calculated according to Schomaker, Waser, Marsh & Bergman (1959) with a unitary weight for all the C, N and O atoms, are respectively:

$$\begin{aligned}1.025x + 2.667y - 2.979z &= 1 \\ -2.613x - 7.835y + 7.547z &= 1.\end{aligned}$$

These equations are referred to the crystal axes and  $x, y, z$  are fractional coordinates. The distances of the least-squares planes from the origin of the crystal cell are 2.576 and  $-0.908 \text{ \AA}$  respectively.

The pyrene and TMU molecules are nearly parallel, the angle between the two molecular planes being only  $3^\circ 35'$ . The individual atomic deviations from the least-squares planes are reported in Table 7. In the pyrene molecule only the C(2) atom deviates more than  $0.03 \text{ \AA}$  from its least-squares plane, whereas the individual atomic deviations from the TMU plane are larger also with respect to those found in the TMU crystal struc-

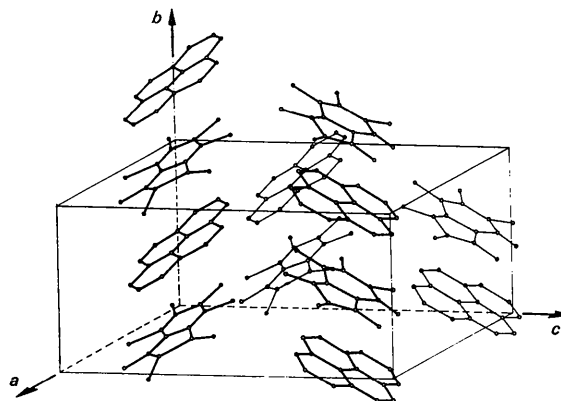


Fig. 4. Clinographic view of the structure.

Table 4. *Estimated standard deviations for the bond angles*

C(2)–C(1)–C(14)	1° 38'	C(13)–C(14)–C(15)	1° 12'	N(29)–C(24)–C(19)	41'
C(1)–C(2)–C(3)	1° 48'	C(13)–C(14)–C(1)	1° 21'	C(23)–C(24)–C(19)	47'
C(2)–C(3)–C(16)	1° 20'	C(1)–C(14)–C(15)	1° 08'	C(23)–C(24)–N(29)	45'
C(4)–C(3)–C(16)	1° 29'	C(10)–C(15)–C(14)	1° 01'	C(17)–N(29)–C(24)	38'
C(2)–C(3)–C(4)	1° 41'	C(10)–C(15)–C(16)	58'	C(24)–N(29)–C(25)	42'
C(3)–C(4)–C(5)	2° 08'	C(14)–C(15)–C(16)	47'	C(17)–N(29)–C(25)	42'
C(4)–C(5)–C(6)	2° 08'	C(3)–C(16)–C(7)	58'	C(19)–N(27)–C(21)	51'
C(5)–C(6)–C(7)	1° 40'	C(7)–C(16)–C(15)	46'	C(19)–N(27)–C(20)	53'
C(6)–C(7)–C(16)	1° 11'	C(3)–C(16)–C(15)	54'	C(20)–N(27)–C(21)	57'
C(6)–C(7)–C(8)	1° 17'	N(26)–C(17)–N(29)	40'	N(27)–C(21)–N(28)	1° 04'
C(8)–C(7)–C(16)	59'	N(26)–C(17)–O(30)	48'	N(27)–C(21)–O(31)	1° 08'
C(7)–C(8)–C(9)	1° 24'	N(29)–C(17)–O(30)	50'	N(28)–C(21)–O(31)	1° 13'
C(8)–C(9)–C(10)	1° 39'	C(17)–N(26)–C(19)	40'	C(21)–N(28)–C(23)	57'
C(9)–C(10)–C(15)	1° 29'	C(17)–N(26)–C(18)	47'	C(21)–N(28)–C(22)	1° 02'
C(9)–C(10)–C(11)	1° 38'	C(19)–N(26)–C(18)	49'	C(22)–N(28)–C(23)	56'
C(11)–C(10)–C(15)	1° 28'	N(26)–C(19)–C(24)	42'	C(24)–C(23)–N(28)	50'
C(10)–C(11)–C(12)	1° 56'	C(24)–C(19)–N(27)	47'	C(24)–C(23)–O(32)	57'
C(11)–C(12)–C(13)	2° 12'	N(26)–C(19)–N(27)	47'	N(28)–C(23)–O(32)	57'
C(12)–C(13)–C(14)	1° 44'				

Table 5. Peak heights and curvatures

Values in parentheses are from  $F_c$  differential synthesis

	$Q$ (e.Å <sup>-3</sup> )	$-A_{hh}$ (e.Å <sup>-5</sup> )	$-A_{kk}$ (e.Å <sup>-5</sup> )	$-A_{ll}$ (e.Å <sup>-5</sup> )	$A_{kk}$ (e.Å <sup>-5</sup> )	$A_{hl}$ (e.Å <sup>-5</sup> )	$A_{kl}$ (e.Å <sup>-5</sup> )
C(1)	4.50 (5.05)	18.7 (22.7)	36.5 (36.1)	31.5 (30.2)	-0.5 (-0.4)	10.3 (9.6)	0.7 (0.9)
C(2)	4.58 (4.74)	17.4 (20.8)	27.3 (28.0)	27.5 (28.1)	-7.3 (-3.0)	5.7 (7.3)	5.7 (2.5)
C(3)	5.02 (5.12)	31.9 (32.0)	34.2 (34.4)	26.3 (27.5)	-3.5 (2.0)	10.9 (11.4)	4.1 (0.6)
C(4)	3.82 (4.01)	21.1 (20.7)	20.1 (20.7)	13.4 (18.1)	-2.4 (-1.2)	6.1 (6.3)	6.1 (1.6)
C(5)	4.05 (4.39)	26.8 (25.8)	25.2 (25.8)	14.0 (20.2)	-0.4 (0.0)	11.8 (11.1)	4.3 (0.1)
C(6)	4.23 (4.42)	27.5 (27.8)	23.9 (24.6)	24.3 (26.2)	-2.8 (-2.4)	16.8 (15.9)	4.7 (2.4)
C(7)	5.50 (5.67)	35.8 (36.7)	37.9 (37.9)	40.0 (40.7)	-0.9 (-1.5)	22.5 (21.5)	3.8 (2.5)
C(8)	5.40 (5.43)	27.4 (29.6)	36.7 (36.9)	38.1 (38.3)	-2.7 (-0.7)	15.6 (16.3)	1.7 (2.2)
C(9)	4.55 (4.65)	21.8 (22.3)	29.0 (28.8)	24.5 (25.1)	-3.5 (-1.9)	7.6 (8.0)	4.3 (1.8)
C(10)	4.75 (4.73)	31.6 (30.7)	27.4 (27.4)	23.2 (23.8)	-4.0 (-2.6)	10.4 (10.8)	5.5 (2.1)
C(11)	4.21 (4.43)	26.5 (24.7)	24.6 (25.4)	19.8 (22.0)	-3.9 (-1.5)	8.8 (9.1)	6.7 (2.8)
C(12)	3.90 (4.23)	23.1 (24.1)	20.2 (22.9)	17.3 (20.7)	0.2 (0.2)	10.5 (10.6)	2.4 (0.8)
C(13)	4.10 (4.47)	22.8 (26.1)	26.1 (26.6)	26.4 (26.8)	-1.9 (-1.6)	14.7 (14.6)	4.6 (3.0)
C(14)	5.49 (5.60)	38.2 (37.7)	37.4 (36.8)	39.5 (38.2)	1.0 (0.3)	22.9 (21.2)	4.1 (1.3)
C(15)	7.74 (7.85)	60.2 (61.7)	58.9 (58.6)	59.0 (60.4)	-3.2 (-2.4)	29.7 (29.9)	5.4 (1.5)
C(16)	7.52 (7.61)	59.5 (60.9)	55.3 (56.0)	57.5 (58.9)	-3.4 (-2.5)	29.3 (29.7)	3.2 (0.9)
C(17)	7.63 (7.55)	57.6 (58.4)	54.3 (54.8)	56.0 (56.6)	-0.2 (-0.2)	25.0 (25.3)	0.2 (1.3)
C(18)	5.22 (5.32)	32.1 (33.2)	31.9 (31.8)	35.0 (35.8)	2.2 (0.2)	17.3 (17.3)	-1.9 (-0.7)
C(19)	7.46 (7.54)	56.3 (58.0)	55.0 (55.4)	54.6 (55.9)	-0.5 (-0.4)	23.5 (24.6)	0.5 (-0.1)
C(20)	5.20 (5.22)	29.2 (29.6)	29.1 (28.9)	38.4 (38.3)	-3.8 (-2.2)	14.7 (14.6)	1.4 (0.3)
C(21)	5.40 (5.52)	40.3 (40.7)	34.1 (34.7)	30.3 (31.0)	0.0 (-0.1)	14.6 (14.9)	5.7 (2.2)
C(22)	5.06 (5.03)	35.8 (36.4)	23.6 (23.9)	32.8 (33.1)	0.2 (-0.2)	16.1 (16.0)	3.1 (1.0)
C(23)	6.20 (6.42)	49.3 (49.5)	44.1 (43.8)	41.9 (43.0)	1.6 (0.4)	21.9 (21.6)	2.7 (1.0)
C(24)	7.28 (7.49)	59.8 (61.5)	60.9 (60.8)	52.5 (53.5)	-0.8 (-0.8)	27.9 (28.5)	2.7 (1.3)
C(25)	6.48 (6.42)	45.5 (44.6)	40.5 (40.3)	47.6 (47.7)	1.6 (0.8)	21.8 (22.3)	-2.7 (-0.3)
N(26)	9.09 (9.23)	66.8 (67.7)	66.3 (66.1)	72.1 (73.8)	-2.0 (-2.0)	33.1 (33.4)	2.9 (1.7)
N(27)	7.99 (8.18)	56.3 (57.1)	60.3 (60.1)	53.5 (54.1)	-3.5 (-3.4)	23.4 (23.0)	7.1 (3.5)
N(28)	7.73 (7.86)	57.5 (56.6)	52.5 (52.7)	53.9 (54.6)	0.2 (0.4)	25.9 (26.0)	7.2 (3.1)
N(29)	9.48 (9.51)	76.0 (76.5)	70.8 (72.0)	71.3 (72.1)	-3.1 (-0.6)	31.3 (32.7)	1.2 (0.7)
O(30)	8.18 (8.19)	62.0 (62.4)	45.8 (47.5)	50.5 (51.6)	2.2 (1.6)	25.7 (26.4)	1.3 (0.2)
O(31)	7.25 (7.25)	46.1 (47.2)	44.3 (44.6)	37.4 (39.3)	-0.2 (0.1)	15.2 (16.3)	3.6 (1.2)
O(32)	7.95 (8.03)	53.0 (53.8)	48.5 (48.7)	55.8 (54.3)	2.8 (1.2)	29.7 (28.2)	0.0 (-0.3)

Table 6. Comparison between final observed and calculated structure factors  
Values are multiplied by 10.

Table with columns: F, L, FOBS, FCAL, H, K, L, FOBS, FCAL, H, K, L, FOBS, FCAL, H, K, L, FOBS, FCAL. The table contains multiple rows of numerical data representing structure factors for various reflections.



ture refined by Sutor (1963a). Although this effect might be ascribed to the lower accuracy of our results, it seems that intermolecular contacts are likely to be important in this respect. A view of the arrangement of the molecules in the crystal is shown in Fig. 4. Two infinite columns of alternate TMU and pyrene molecules run through the unit cell and are related to each other by a glide plane.

Table 7. Atomic deviations (Å) from the least-squares planes of the pyrene and TMU molecules

C(1)	0.022	C(17)	-0.007
C(2)	-0.056	C(18)	0.109
C(3)	0.026	C(19)	0.033
C(4)	0.029	C(20)	-0.059
C(5)	-0.016	C(21)	0.016
C(6)	0.022	C(22)	-0.010
C(7)	-0.010	C(23)	0.035
C(8)	-0.021	C(24)	0.006
C(9)	0.008	C(25)	0.013
C(10)	-0.011	N(26)	-0.006
C(11)	0.023	N(27)	-0.018
C(12)	-0.016	N(28)	-0.006
C(13)	0.014	N(29)	-0.022
C(14)	-0.007	O(30)	-0.082
C(15)	0.015	O(31)	-0.012
C(16)	-0.022	O(32)	0.009

All intermolecular distances within a column agree well with the normal van der Waals separations, as can be seen in Table 8, where intermolecular distances less than 3.80 Å are reported. A methyl-oxygen distance between TMU molecules of adjacent columns is only 3.06 Å. A methyl-oxygen intermolecular approach as short as 3.00 Å has also been found by Sutor (1963a) in the TMU crystal and this shortening of the van der Waals separation has been ascribed to hydrogen bond formation (Sutor, 1963b). The difficulty of

locating the atoms has been mentioned above, and the bond lengths and angles reflect this situation. The TMU bond lengths and angles agree rather well with those found by Sutor (1963a). The greatest discrepancies occur in the bonds C(19)-C(24) and N(27)-C(21), which differ by about 0.06 Å from Sutor's values. However, the C(19)-C(24) bond length agrees better with the value of 1.37 Å found in theophylline (Sutor, 1958) and in adenine hydrochloride (Cochran, 1951). The N(27)-C(21) bond length of 1.45 Å is very close to those of the N(26)-C(17) and N(28)-C(23) bonds.

Although some bond distances of the pyrene molecule show considerable deviations from the calculated and measured values reported by Robertson (1948), there is a general qualitative resemblance which appears to be more than fortuitous. The accuracy of the structure, however, is such that a comparison of the bond lengths of the constituent molecules in their own crystals with respect to those in the complex would be inappropriate. On the other hand the most important feature of the structure, represented by the molecular geometry of the TMU-pyrene complex, is determined by the mode of packing of the constituents.

The characteristic plane-to-plane alternate stacking of TMU and pyrene molecules indicates that the intermolecular attraction is due to 'polarization bonding' between the components (Wallwork, 1961). The relative orientation of the components (see Fig. 5, where the projection of three molecules, TMU-pyrene-TMU, of the same stack along the normal to the least-squares plane of the pyrene is illustrated) shows a rather small degree of overlap, which seems to indicate that charge transfer forces, if any, must be weak. This is also supported by the spectroscopic properties of the complex in solution and in the solid state (Van Duuren, 1964). It seems therefore that electrostatic interactions be-

Table 8. Intermolecular contacts (Å) less than 3.8 Å

Superscripts refer to the molecules:					
( <sup>1</sup> )	( <sup>2</sup> )	( <sup>3</sup> )	( <sup>4</sup> )	( <sup>5</sup> )	( <sup>6</sup> )
( <sup>1</sup> ) (x, 1+y, z);	( <sup>2</sup> ) (x, -y, ½+z);	( <sup>3</sup> ) (1+x, y, z);	( <sup>4</sup> ) (1+x, y-1, z);	( <sup>5</sup> ) (1+x, -y, ½+z).	
C(4) ... C(25)	3.61	C(16) ... C(23)	3.55	C(16) ... N(26')	3.76
C(4) ... N(29)	3.67	C(16) ... C(24)	3.65	C(10) ... N(27')	3.74
C(5) ... C(17)	3.45	C(16) ... O(32)	3.79	C(14) ... N(27')	3.66
C(5) ... N(29)	3.58	C(2) ... C(17')	3.61	C(15) ... N(27')	3.51
C(5) ... O(30)	3.79	C(3) ... C(17')	3.73	C(12) ... N(28')	3.75
C(6) ... C(17)	3.69	C(1) ... C(19')	3.70	C(13) ... N(28')	3.37
C(6) ... C(19)	3.52	C(14) ... C(19')	3.65	C(14) ... N(28')	3.75
C(6) ... C(24)	3.73	C(15) ... C(19')	3.71	C(1) ... N(29')	3.61
C(6) ... N(26)	3.50	C(9) ... C(20')	3.71	C(2) ... N(29')	3.59
C(7) ... C(19)	3.50	C(10) ... C(20')	3.61	C(11) ... O(31')	3.50
C(7) ... C(24)	3.53	C(15) ... C(20')	3.74	C(12) ... O(31')	3.52
C(8) ... C(19)	3.75	C(11) ... C(21')	3.73	O(32) ... C(6'')	3.63
C(8) ... C(21)	3.47	C(12) ... C(21')	3.55	O(32) ... C(8'')	3.79
C(8) ... N(27)	3.53	C(13) ... C(21')	3.54	C(1) ... C(18'')	3.69
C(8) ... N(28)	3.76	C(14) ... C(21')	3.75	C(2) ... C(18'')	3.72
C(9) ... C(21)	3.52	C(13) ... C(22')	3.73	O(32) ... C(18'')	3.78
C(9) ... N(28)	3.66	C(1) ... C(23')	3.70	C(13) ... C(20'')	3.62
C(9) ... O(31)	3.70	C(13) ... C(23')	3.75	O(32) ... C(20'')	3.54
C(10) ... C(22)	3.62	C(1) ... C(24')	3.38	O(30) ... C(22'')	3.40
C(10) ... N(28)	3.65	C(2) ... C(24')	3.74	O(30) ... C(12 <sup>iv</sup> )	3.73
C(11) ... C(22)	3.73	C(14) ... C(24')	3.69	O(30) ... C(9 <sup>v</sup> )	3.61
C(15) ... C(23)	3.68	C(2) ... N(26')	3.75	C(25) ... O(31 <sup>v</sup> )	3.06
C(15) ... O(32)	3.75	C(3) ... N(26')	3.52		



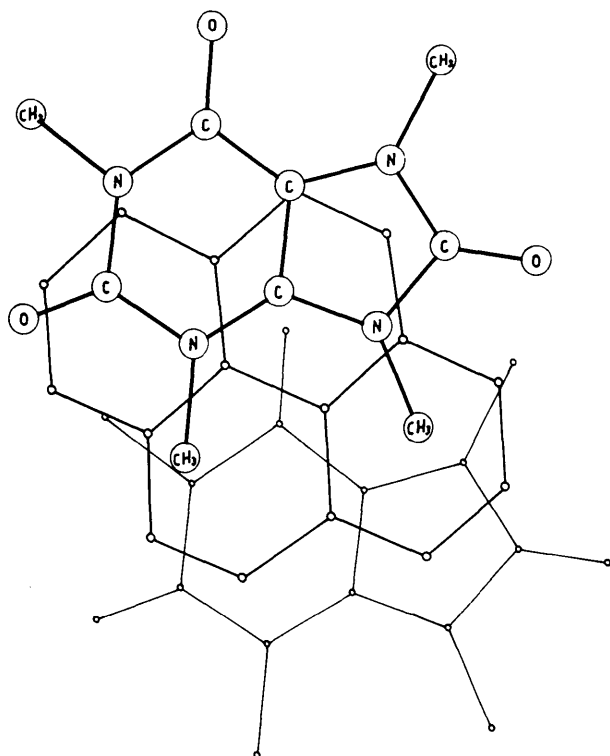


Fig. 5. Projection of three molecules of the same stack on to the pyrene least-squares plane.

tween the polar purine and the polarizable aromatic hydrocarbon together with van der Waals interactions have the determining influence on the molecular orientation and that they make the main contribution to the stability of this complex.

Perpendicular interactions are also the main feature of the structures of the 2:1 molecular complexes between TMU and 3,4-benzopyrene (Damiani, De Santis, Giglio, Liquori & Ripamonti, to be published) and coronene (Damiani, De Santis, Giglio, Liquori, Puliti & Ripamonti, to be published). These structures, which are being refined in our laboratory, are characterized by a sandwich-like arrangement of the aromatic hydro-

carbons between two TMU molecules. The same forces which determine the plane-to-plane packing of the aromatic hydrocarbons and the purine in these crystals may be responsible for the solubilization ability of purine water solutions toward aromatic hydrocarbons observed by Weil-Malherbe (1946). This type of perpendicular interaction may therefore also account for the mechanism of solubilization of aromatic hydrocarbons in aqueous deoxyribonucleic acid solutions in terms of insertion of these molecules in the empty spaces between neighbouring paired bases in the stretched conformations of deoxyribonucleic acid as proposed by Liquori, Ascoli & Botrè (1962).

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