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COMPLEXES OF PYRENE WITH 2,4,6-TRINITROANISOLE. STUDIES OF ASSOCIATION IN SOLUTION AND THE CRYSTAL STRUCTURE OF THE 1:1 COMPLEX

J. C. BARNES, J. A. CHUDEK, R. FOSTER*, F. JARRETT, F. MACKIE, J. PATON and D. R. TWISELTON

Chemistry Department, University of Dundee, Dundee DD1 4HN, Scotland

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Abstract—Cyclohexane solutions of 2,4,6-trinitroanisole (A) containing excess pyrene (D) can be described in terms of a double equilibrium involving complexes DA and D_2A. Formation constants for these complexes from A and from DA respectively from three independent experiments are in good agreement, the average values being $K_1 = 9.7\,kg\,mol^{-1}$ and $K_2 = 1.8\,kg\,mol^{-1}$ at 33.5°.

The crystalline complex was obtained by gel diffusion. The mw ($C_{23}H_{15}N_3O_7$) corresponds to 1:1 stoichiometry $C_{16}H_{10}$, $C_7H_5N_3O_7$, X-ray structure data: $P2_1/c$, a = 10.633(7), b = 16.336(8), c = 11.683(7) Å, $\beta = 94.62(12)°$, V = 2023 Å^3, $F_{000} = 924$, $\mu(CuK\alpha) = 8.3\,cm^{-1}$, Z = 4. R = 0.091 for 1572 reflexions. The crystal contains extended stacks ADADA, parallel to (101). The pyrene molecules are disordered by rotation over two sites. The majority site has an occupancy factor of 0.544(2). The angle between the normals to the mean planes of A and D is 7.0(4)°, allowing the nitro groups of A to twist out of the plane of the benzene ring by 41.0(1.0), 2.7(5) and 20.7(8)°.

The stoichiometry of crystalline electron–donor–acceptor (EDA) complexes between neutral planar π-donors (D) and neutral planar π^*-acceptors (A) is generally simple–usually 1:1.[1] By contrast, it has been suggested that for many such interactions in solution a simple *overall* stoichiometry does not obtain.[2,3] That is not to say that there are no 1:1 associations in these solutions but that the behaviour cannot be explained in terms of only 1:1 associations. For example under the usual concentration condition $[D] \gg [A]$ a satisfactory interpretation of optical and NMR properties can be given if a double equilibrium is postulated in which complexes DA and D_2A are formed thus:[2-4]

$$D + A \rightleftharpoons DA \qquad K_1 = [DA]/[D][A] \qquad (1)$$

$$DA + D \rightleftharpoons D_2A \qquad K_2 = [D_2A]/[DA][D]. \qquad (2)$$

In order to test further the suggestion that the stoichiometry in the crystalline phase does not wholly determine the stoichiometry in solution we have studied the π-π^* EDA system pyrene-2,4,6-trinitroanisole in the solid state and in solution in cyclohexane.

Solution experiments. Cyclohexane was chosen as solvent as it shows one of the lowest solvent–solute interactions amongst the common solvents. A result of this choice is that we were constrained to the experimental condition $[D]_0 \gg [A]_0$ (the subscripts denote the total, free and complexed, concentration of the species). Under these conditions we have assumed that the solution behaviour is as described in eqns (1) and (2).

Sufficient information must be obtained[5] to evaluate the four parameters implied by eqns (1) and (2): namely K_1, K_2 and, in the case of optical experiments ϵ_1, ϵ_2 (absorption coefficients of DA and D_2A respectively at the wavelength of measurement); or in the case of NMR shift experiments $\Delta_0(1)$ and $\Delta_0(2)$ (chemical shifts of the measured nuclei in the A moiety of DA and D_2A respectively relative to the shift of the same nucleus in free A). To this end the range of the fraction of A complexed (i.e. $\{[DA] + [D_2A]\}/[A]_0$), often termed the saturation fraction, *s*, should be large.[5] We have been able to fulfil this condition in the present set of experiments. Incidentally, this condition has ruled out the possibility of effective experiments being carried out under the condition $[D]_0 = [A]_0$. There, not only is the practical range of *s* very much smaller, but the information criterion is also higher because for such solutions consideration should be made of a third equilibrium involving DA_2 thereby extending the problem to one of evaluating six parameters.

Two methods have been used to study the equilibria. (a) The dependence of the ^1H NMR chemical shift of a given nucleus in A as a function of $[D]_0$.[3] From the shifts of the singlet from the ring protons of 2,4,6-trinitroanisole and of the singlet from the methyl group, two sets of values of K_1, K_2 have been obtained. The method has been previously described.[3,4] A further subroutine corrects for the initial approximation $[D]_0 \doteq [D]$. (b) An established spectrophotometric method[3,5] yields a further independent set of K_1, K_2 values.

EXPERIMENTAL

Pyrene was recrystallised three times from ethanol m.p. 149°, lit[6] m.p. 149–150°. 2,4,6-Trinitroanisole (TNA) was prepared by the nitration of anisic acid, recrystallised three times from methanol, m.p. 68°, lit[7] m.p. 67–8°. Cyclohexane was BDH "pure for spectroscopy". All solutions were made up by weight. All concentrations have been expressed in moles per kg of solution and all *K* values are in units $mol\,kg^{-1}$.

Proton chemical shift measurements were made using a Bruker HX90 c.w. spectrometer operating at 90 MHz. The solvent ^1H signal was used as internal reference. The use of an internal reference for this type of experiment has been justified.[8]

Optical measurements were made using a Varian Cary 219 spectrophotometer. Because of overlapping absorptions of the complexed species with those of free A and free D, measurements of absorbance were made at 450 nm which does not correspond to λ_{max} for DA or D_2A. All measurements were made at 33.5°.

Concentration, measured chemical shift (Δ), optical absorbance (A), and saturation-fraction (s) ranges are listed in Table 1.†

Crystal structure. Crystals of the complex were grown by gel diffusion using the Sephadex LH20-methanol toluene gel suggested by Desiraju *et al.*[10]

After preliminary oscillation photographs, data were collected by equi-inclination Weissenberg photography for crystals mounted on the axes of the centred space group $B2_1/c$. Data were collected for layers (0-2)kl, h0l and hk(0-12) of this setting. Intensities were obtained from the SERC Microdensitometer Service and merged to give 1736 unique reflexions.

The data were re-indexed into the standard space group $P2_1/c$ before attempting to solve the structure. All calculations were carried out using SHELX 76 and XANADU.[11,12] After inclusion of 1787 unobserved reflexions (with $I = 0.5\,I\,\min$) the direct methods routine EEES gave a model showing all non hydrogen atoms of the anisole and 6 atoms of pyrene. Refinement of this fragment gave R 0.26 and a Fourier map showed the remaining C atoms of pyrene. The model refined to R 0.19 with all atoms having isotropic thermal parameters and to R 0.14 with all non hydrogen atoms anisotropic. At this point a difference Fourier map showed an alternative position for the pyrene molecule. In all remaining calculations the pyrene molecule was considered to be partially occupying both sites, with the site occupancy factor allowed to refine. Since some of the observed bond lengths in the pyrene molecules were unacceptable both molecules were idealised as rigid bodies using the dimensions from the neutron diffraction study by Hazell *et al.*[13] The oxygen atoms of the nitro groups were also ill-defined. In this case it proved that a model with anisotropic thermal parameters for ordered oxygen atoms (R 0.122 for 217 parameters) was preferable to one with isotropic thermal parameters and disordered oxygen atoms (R 0.129 for 245 parameters). Refinement continued with the inclusion of all hydrogen atoms on calculated positions with isotropic thermal parameters and all non hydrogen atoms anisotropic to convergence at R 0.091 for 390 parameters after the exclusion of 164 weak reflexions for which $|F_o| > 2|F_c|$. The largest peaks on the final difference Fourier map where 0.4 e/Å^3 in the region of the TNA ring.

†A list of the experimental data for both optical and NMR experiments has been deposited with the National Lending Library, Boston Spa.

RESULTS AND DISCUSSION

The results of the solution experiments are summarised in Table 2.

The close agreement of the values of K_1 and K_2 from the three independent determinations justifies the interpretation of the solution equilibria in terms of eqns (1) and (2). It must be recognised however, that we can only conclude that the solution behaviour is *equivalent* to the equilibria of eqns (1) and (2). There will be an essentially infinite array of possible D–A orientations so that to think in terms of a precise geometry, or precise stoichiometry, is meaningless. Any expression of the relative orientation(s) of the donor molecule(s) with an acceptor molecule and the stoichiometric ratio(s) that are used in such a description must involve the weighted average of the near-continuum of orientations. The association-dissociation processes for D–A interactions in solution are very fast.[14] The NMR method therefore measures the effects as a dynamically averaged spectrum. The observation that $\Delta_0(1)$ and $\Delta_0(2)$ values of the aromatic protons of TNA have larger upfield values than the corresponding values for the methyl protons of TNA (Table 2) suggests that the ring protons are more within the shielding cone of one (or more) D molecules than is the methyl group of TNA. This might be expected if the preferred configuration(s) involves the overlap of the HOMO of D with the LEMO of A where the D and A molecules lie in parallel planes as anticipated in

Table 1. Experimental details of solution measurements

Method	$[A]_o$[a] /mol kg^{-1}	$[D]_o$[a] /mol kg^{-1}	n[b]	s-range[c]	Δ[d] range /p.p.m.	A[e] range
optical (λ = 450 nm)	1.00×10^{-3}	0.006 - 0.16	88	0.05 - 0.7		0.01 - 0.22
n.m.r. (aromatic ^{1}H)	3.00×10^{-3}	0.01 - 0.08	28	0.09 - 0.51	0.127 - 0.609	
(methyl ^{1}H)	3.00×10^{-3}	0.01 - 0.2	41	0.09 - 0.73	0.069 - 0.341	

[a] concentrations in moles per kg of solution.

[b] n = number of solutions measured.

[c] s = saturation fraction, see text.

[d] Δ = chemical shift of measured nucleus in A in equilibrium mixture relative to the corresponding shift in A in a solution in which $[D]_o = 0$.

[e] A = optical absorbance.

Table 2. Parameters[a] for equilibria in cyclohexane solution at 33.5°

Method	K_1[b]/kg mol^{-1}	K_2[b]/kg mol^{-1}	Δ_o[c](1)/p.p.m	Δ_o[c](2)/p.p.m.	ϵ_1[d]/dm^3 mol^{-1} cm^{-1}	ϵ_2[d]/dm^3 mol^{-1} cm^{-1}
N.m.r. (Ar-proton)	9.7 ± 0.6	1.6 ± 0.2	1.14 ± 0.12	2.27 ± 0.33	-	-
N.mr. (Me-proton)	9.5 ± 0.5	1.8 ± 0.2	0.62 ± 0.07	1.61 ± 0.16	-	-
Optical	9.8 ± 1.0	1.7 ± 0.9	-	-	315 ± 20	402 ± 150

[a] Errors at 95% confidence level.

[b] In kg solution per mole

[c] Upfield chemical shifts in DA(1) and D_2A(2) of measured nuclei relative to the corresponding shifts in A.

[d] Molar absorption coefficients for DA(1) and D_2A(2) at the wavelength of measurement (450 nm).

Mulliken's description[15] of π-donor-π*-acceptor interactions. However, until detailed MO calculations on populations of structures of the type described can be made, such conclusions cannot be drawn with a reasonable degree of certainty.

By contrast, the orientation of D molecules with respect to A molecules in the solid crystal lattice have been determined with precision. Atomic coordinates and thermal parameters are given in Table 3.†

Figure 1 shows the bond lengths and angles in TNA. These contain no surprises. C8 is 0.907(2) Å out of the plane of the ring C1–C6. The normals to the planes of the nitro groups make angles to the normal to the ring of 41.0° (N9), 2.7° (N12) and 20.7° (N15). Since literature[13] dimensions were used for the pyrene molecule they are not quoted here. The relationship between the two pyrene positions is shown in Fig. 2. The rotation angle separating them is 15.3° with an angle between the normals to the pyrene planes of 1.4(5)°. This can be compared with the pyrene–pyromellitic dianhydride complex where a very similar disorder appears with a rotation angle of ~23°.[14]

Figure 3 shows the overlap of TNA with the two pyrene positions, viewed normal to the plane of TNA. With the minor pyrene position the long axis C22B...C27B is almost parallel to C2...C5 of the anisole to give a symmetrical arrangement of C3–C4 and C6–C1 over the centres of the pyrene rings. This symmetry is largely lost with the major position of the pyrene.

The crystal structure determination shows the simple 1:1 stoichiometry for this complex. It also establishes the essential relationship between the two molecular species, namely extended DADADA stacks in which the planes of adjacent molecules are close to parallel (Fig. 4). The pyrene molecules make angles of 6.5(8) and 7.6(8)° to the trinitroanisole plane,

†A list of observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW.

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (× 10^3) with ESD's in parentheses for the non-hydrogen atoms of the pyrene-2,4,6-trinitroanisole complex

	X/A	Y/B	Z/C	U_{Eq}
C1	1437(4)	2028(3)	643(4)	34(1)
C2	2478(5)	1965(3)	-26(4)	36(1)
C3	3098(5)	2626(3)	-429(4)	40(1)
C4	2654(5)	3401(3)	-203(4)	36(1)
C5	1604(5)	3511(3)	403(4)	40(1)
C6	1024(4)	2832(3)	826(4)	34(1)
O7	1000(3)	1364(2)	1126(3)	43(1)
C8	-254(5)	1079(3)	759(5)	51(1)
N9	2914(4)	1145(2)	-326(4)	48(1)
O10	4061(4)	1057(3)	-309(5)	82(1)
O11	2135(4)	624(2)	-615(5)	71(1)
N12	3314(5)	4125(3)	-600(4)	48(1)
O13	2921(5)	4790(2)	-370(4)	73(1)
O14	4234(5)	3989(3)	-1135(4)	79(1)
N15	-33(4)	3027(3)	1534(4)	46(1)
O16	-334(4)	2514(3)	2200(4)	77(1)
O17	-511(4)	3691(3)	1442(4)	70(1)
C21	1918(3)	3300(2)	3827(3)	63(1)
C22	2212(3)	4094(2)	3521(3)	59(1)
C23	3197(3)	4379(2)	2923(3)	61(1)
C24	5061(3)	3917(2)	2045(3)	49(1)
C25	5927(3)	3346(2)	1820(3)	39(1)
C26	6571(3)	1843(2)	1750(3)	60(1)
C27	6272(3)	1047(2)	2048(3)	57(1)
C28	5253(3)	789(2)	2620(3)	68(1)
C29	3379(3)	1236(2)	3520(3)	53(1)
C30	2582(3)	1821(2)	3826(3)	34(1)
C31	3973(3)	3722(2)	2648(3)	38(1)
C32	5777(3)	2486(2)	2048(3)	51(1)
C33	4467(3)	1439(2)	2922(3)	37(1)
C34	2751(3)	2672(2)	3553(3)	29(1)
C35	3828(3)	2885(2)	2964(3)	36(1)
C36	4680(3)	2269(2)	2620(3)	30(1)
C21B	2109(4)	3726(2)	3576(4)	46(1)
C22B	2740(4)	4374(2)	3124(4)	55(1)
C23B	3807(4)	4451(2)	2532(4)	62(1)
C24B	5564(4)	3610(2)	1838(4)	42(1)
C25B	6154(4)	2884(2)	1761(4)	50(1)
C26B	6325(4)	1393(2)	2016(4)	70(1)
C27B	5717(4)	725(2)	2447(4)	62(1)
C28B	4669(4)	688(2)	3079(4)	71(1)
C29B	2883(4)	1500(2)	3779(4)	43(1)
C30B	2330(4)	2238(2)	3840(4)	47(1)
C31B	4414(4)	3694(2)	2397(4)	36(1)
C32B	5659(4)	2129(2)	2170(4)	38(1)
C33B	4012(4)	1431(2)	3189(4)	27(1)
C34B	2786(4)	2996(2)	3403(4)	36(1)
C35B	3920(4)	2950(2)	2830(4)	25(1)
C36B	4515(4)	2165(2)	2738(4)	29(1)

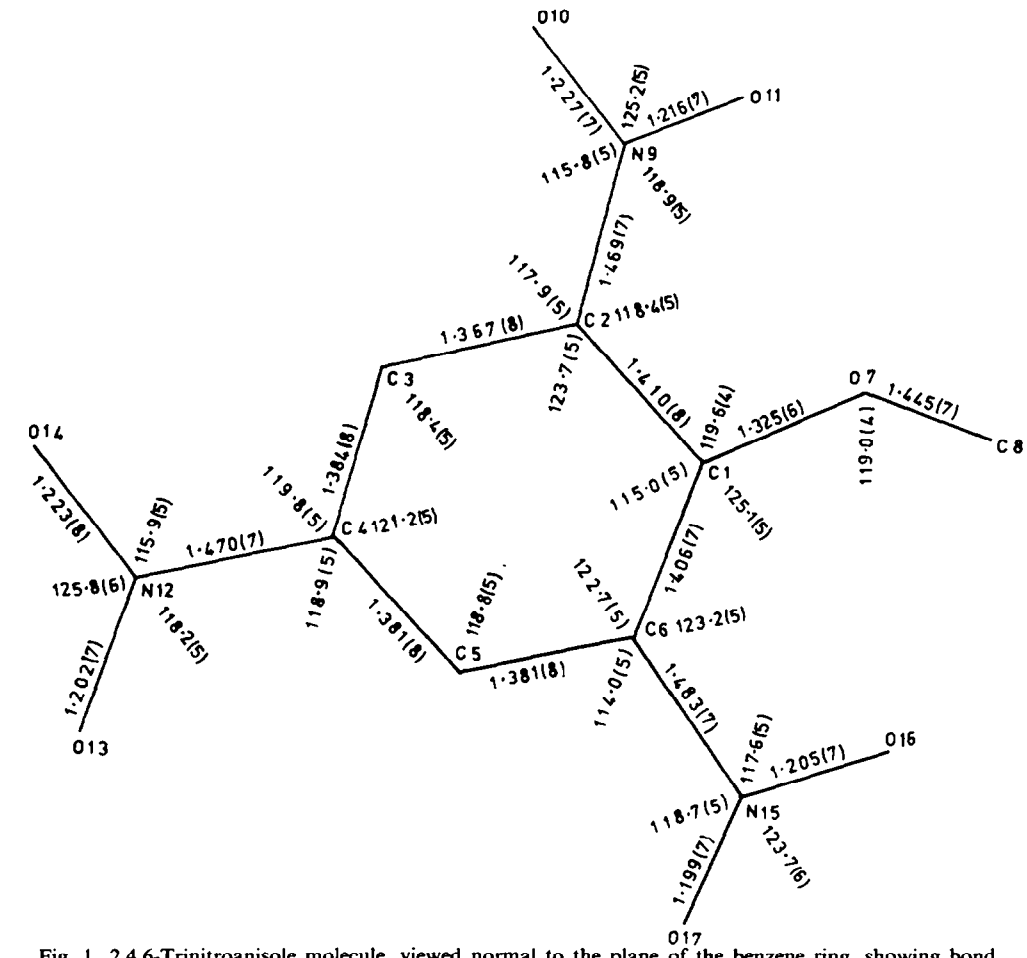

Fig. 1. 2,4,6-Trinitroanisole molecule, viewed normal to the plane of the benzene ring, showing bond lengths (Å) and angles (°).

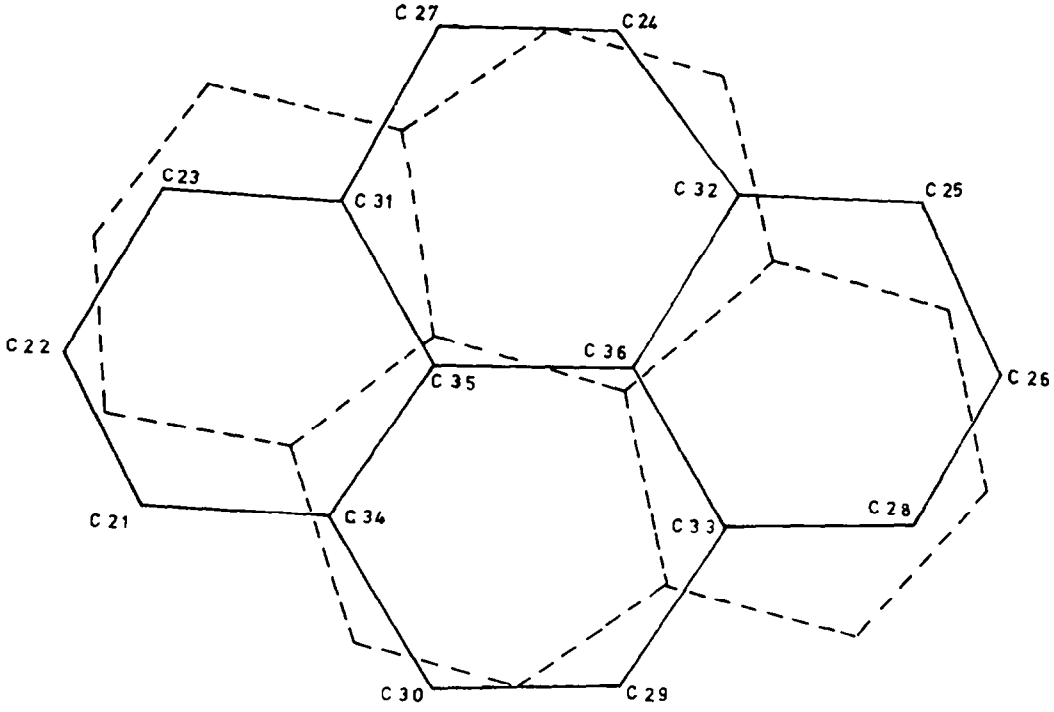

Fig. 2. The pyrene molecules viewed normal to the plane of the major component. The minor component has bonds dotted.

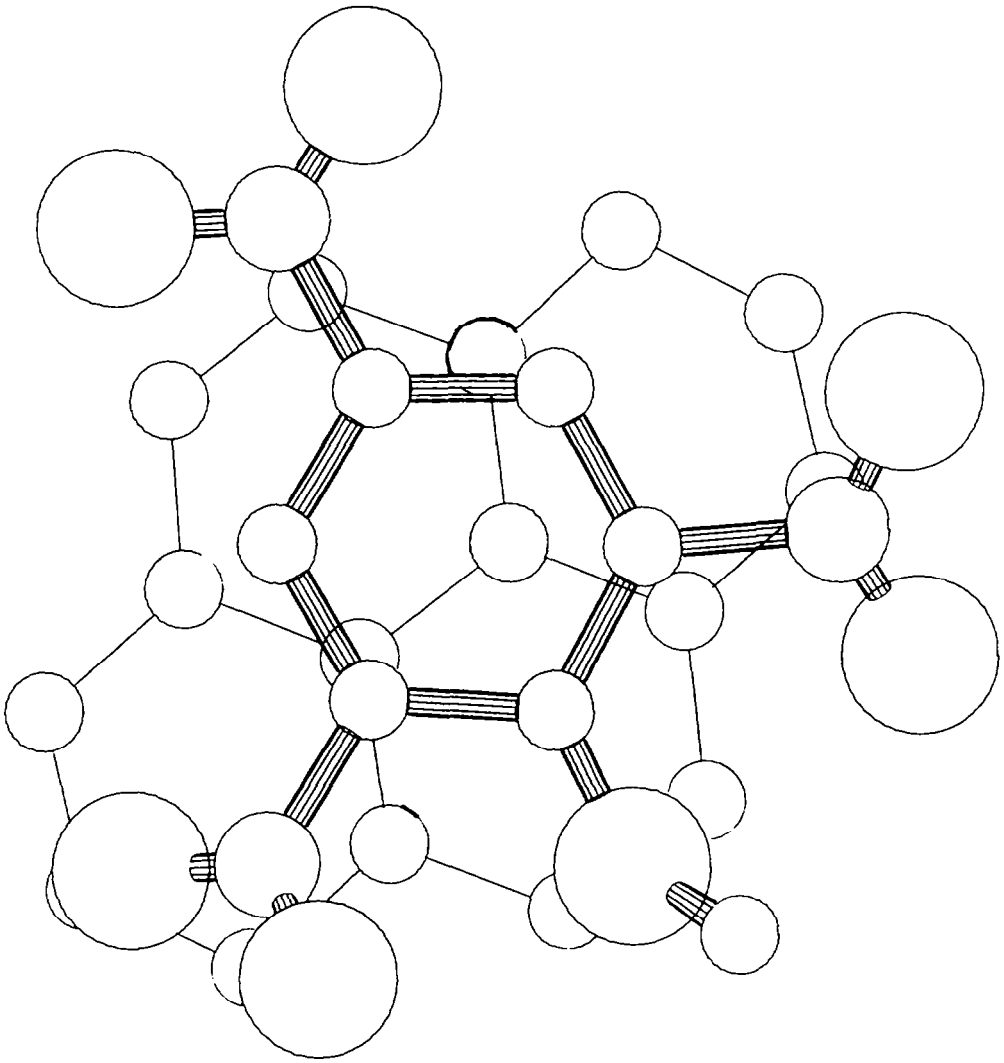

Fig. 3(a).

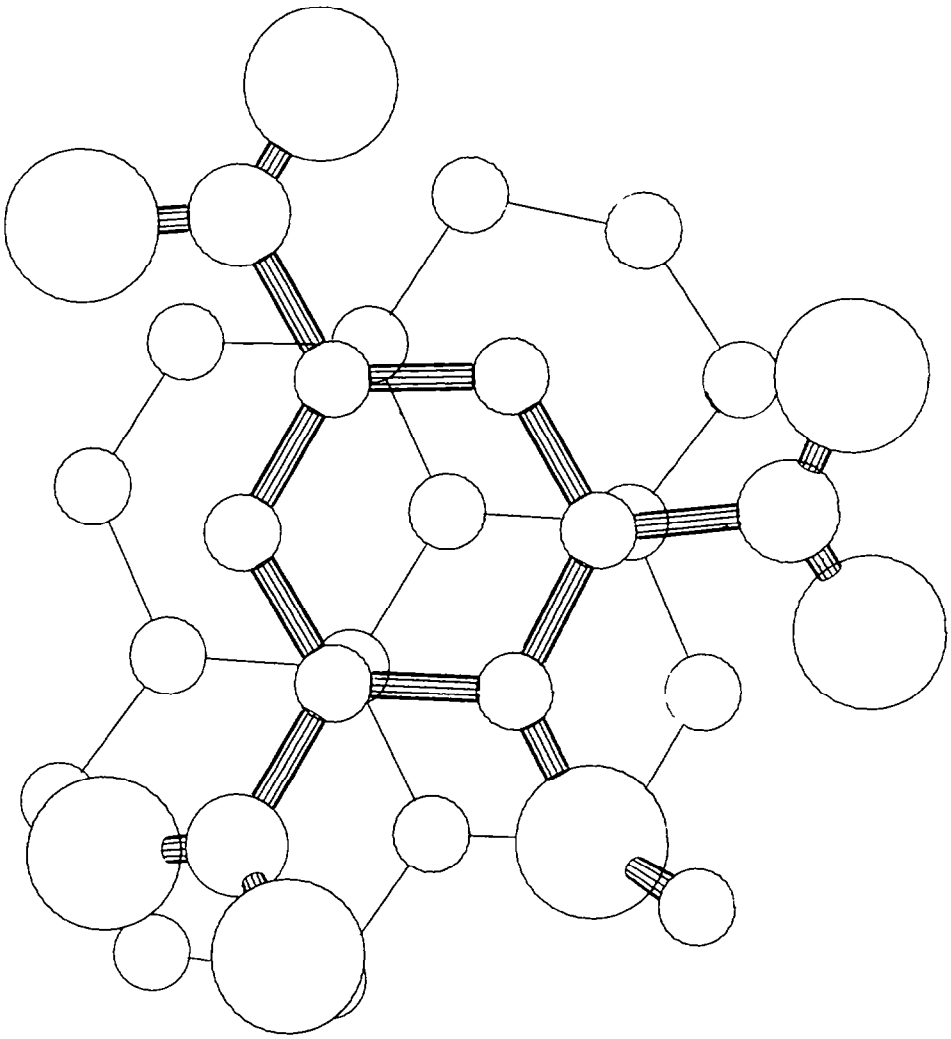

Fig. 3(b).

Fig. 3. View normal to the plane of the ring of the 2,4,6-trinitroanisole molecule showing the relation to (a) the majority position of the pyrene molecule; (b) the minority position of the pyrene molecule.

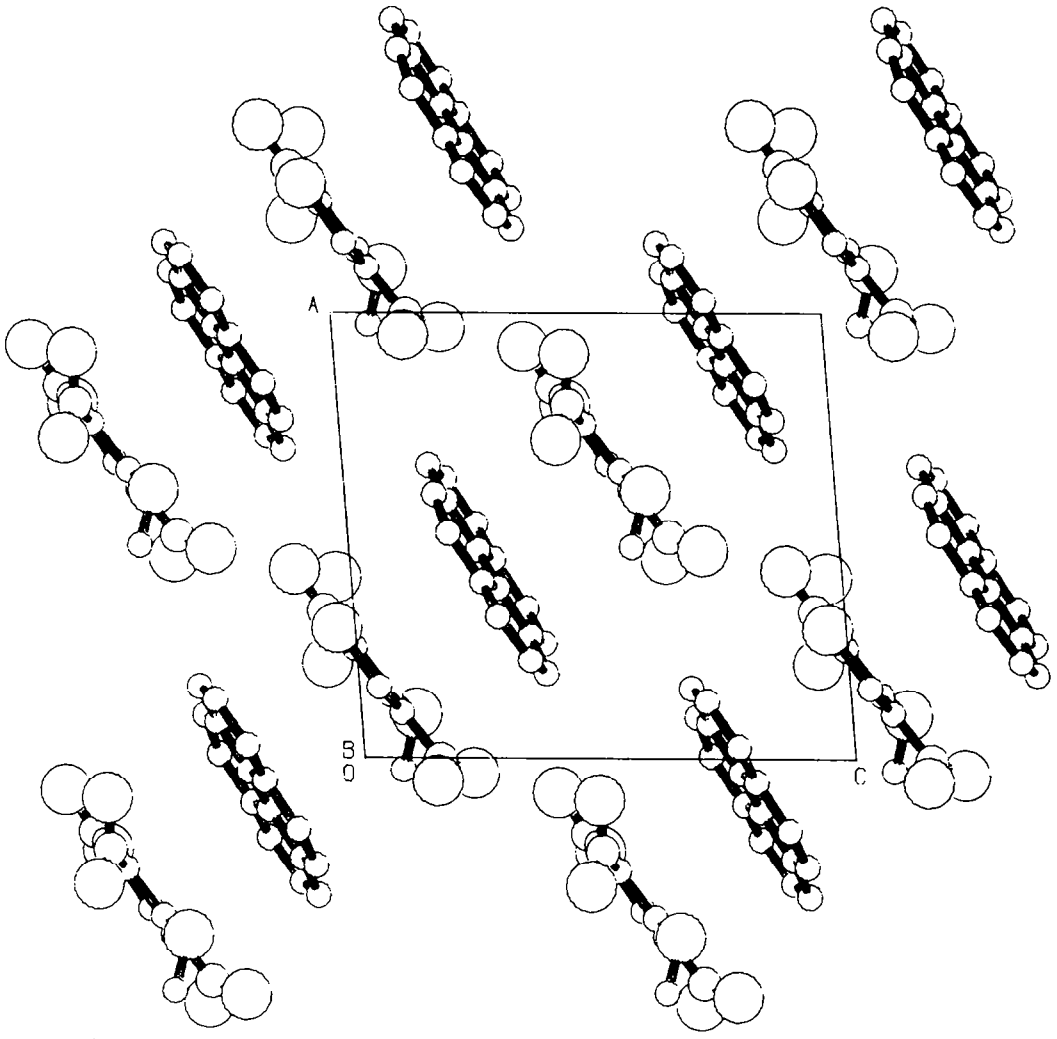

Fig. 4. Packing diagram viewed down *b*, including one half of the cell contents in the *b* direction.

providing a wedge-shaped cavity for the anisole which allows for the 41° twist of (N9, 010, 011) away from the plane of the ring and for the methoxy group. The average anisole to pyrene distance is 3.79 Å and there are no contacts under 3.5 Å.

Whilst it is not possible, for the reasons stated above, to determine the average orientation of D molecules with respect to A molecules in their association in solution from the present NMR data, the observed values of $\Delta_0(1)$ and $\Delta_0(2)$ for the ring protons and methyl protons of the TNA moiety are not inconsistent with the D–A arrangement observed in the crystal lattice. The average structures of DA pairs and DAD triplets in solution might on such a basis be considered to correspond to DA and DAD fragments in the extended stacks observed in the crystal.

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