Data collection: *XDS98* (Kabsch, 1993). Cell refinement: *XDS98*. Data reduction: *XDS98*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *CRYSTAN88* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *SHELXL97* and local software.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1343). Services for accessing these data are described at the back of the journal.

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Mixed stacking and stoichiometry in a π-molecular complex between fluorene and 1,3,5-trinitrobenzene

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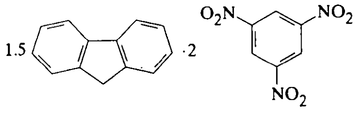
Abstract

The crystal structure of the title complex, fluorene–1,3,5-trinitrobenzene (1.5/2) ($1.5C_{13}H_{10} \cdot 2C_6H_3N_3O_6$) has been determined at room temperature. The molecule crystallizes in a triclinic cell and in the $P\bar{1}$ space group. One of the three fluorene molecules in the unit cell is located at a special position and adopts two different orientations that are related by an inversion center. Therefore, the asymmetric unit contains 1.5 fluorene molecules and two molecules of 1,3,5-trinitrobenzene. Acceptor and donor molecules are arranged in mixed stacks, one with 1:1 and the other with 2:1 trinitrobenzene:fluorene stoichiometries. This mixed arrangement and the composition of the asymmetric unit explains the global 4:3 stoichiometry. These two independent stacking directions are parallel to the *c* and *a* axes, respectively.

Comment

Trinitrobenzolates are charge–transfer compounds formed by donors groups and 1,3,5-trinitrobenzene (TNB) as the acceptor group (Rao, 1970). Usually, these molecular compounds have an integer acceptor–donor ratio, but in this case the observed ratio is 4:3. Herbstein *et al.* (1976) have studied crystals of the fluorene–TNB compound, (I), and reported triclinic yellow plates, $a = 27.63$, $b = 7.563$, $c = 7.264$ Å, $\alpha = 91.2$, $\beta = 92.85$, $\gamma = 98.2°$, $D_x = 1.495\ \mathrm{g\ cm^{-3}}$ and a composition of $(\text{fluorene})_3(\text{TNB})_4$ per unit cell. They suggested that the space group could be $P1$ or $P\bar{1}$, but did not report a structure determination. We have solved the structure and determined that the space group is $P\bar{1}$. There are two independent TNB molecules [(1) and (2)] and two independent fluorene molecules [(3) and (4)] in the asymmetric unit. Fluorene-(4), is situated on a special position and the composition of the asymmetric unit is $(\text{fluorene})_{1.5}(\text{TNB})_2$. The crystal structure also demonstrates that fluorene-(4) is capable of assuming two half-occupied alternative orientations as shown in Fig. 2.



(I)

Both independent fluorene molecules are planar. The maximum absolute deviation from the mean plane is 0.038 (3) Å for C31 and C34 in fluorene-(3) and 0.045 (15) Å for C411 in fluorene-(4). As previously observed (Bar & Bernstein, 1981), the nitro groups belonging to the TNB molecules twist out of the plane of the benzene nucleus. The maximum dihedral angle reported between the least-squares planes of the nitro group and the benzene ring was 15° (Bar & Bernstein, 1981). In the present structure, the maximum angle is 5.0 (3)° for the O13—N12—O14 nitro group of TNB-(1) and 22.5 (2)° for the O21—N21—O22 group of TNB-(2). All bond distances and angles take the expected values for these kinds of compounds.

Fluorene and TNB molecules are arranged in mixed stacks. Two different and independent stacking directions are observed. Each fluorene-(3) molecule packs

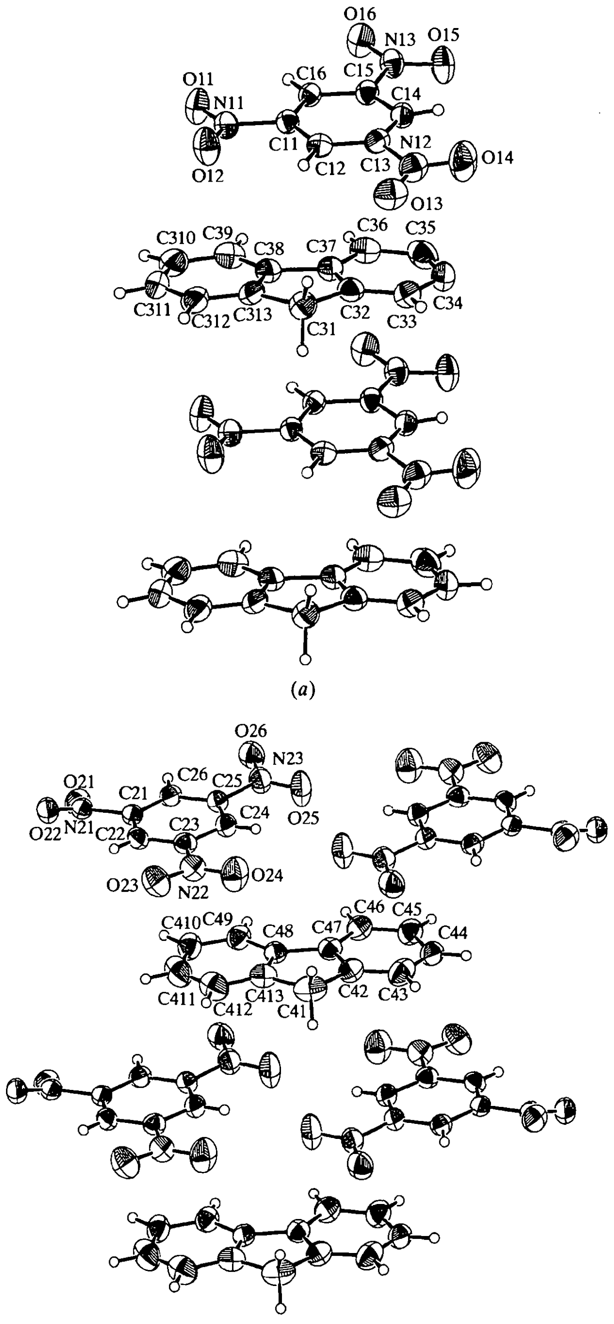


Fig. 1. Drawing showing both independent stacking arrangements of the title compound; (*a*) stacking of fluorene-(3) and TNB-(1) molecules, and (*b*) stacking of fluorene-(4) and TNB-(2) molecules. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as spheres of an arbitrary radius.

in the vicinity of two translationally equivalent TNB-(1) molecules. In the same way, as seen in Fig. 1(*a*), each TNB-(1) molecule packs between two fluorene-(3) molecules, leading to 1:1 acceptor–donor ratio. This molecular arrangement is equivalent to that observed in the complex between 4-methylchrysene and TNB (Zacharias *et al.*, 1991) that has also a 1:1 ratio. On the other hand, each fluorene-(4) molecule is layered between two pairs of equivalent TNB-(2) molecules, leading to a 2:1 acceptor–donor ratio, as it is shown in Fig. 1(*b*). The compound 1-methylchrysene:TNB-(2) (Zacharias *et al.*, 1991) stacks in an equivalent arrangement. The average perpendicular distances between the centroids of the benzene rings of the TNB molecules and the least-squares plane of the five-membered ring of the

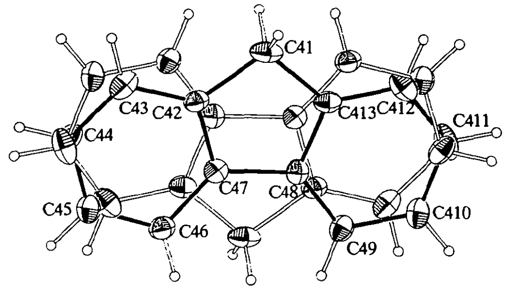


Fig. 2. Drawing showing the two possible orientations of fluorene-(4) placed at a center of symmetry. All displacement ellipsoids are drawn at an arbitrary probability level.

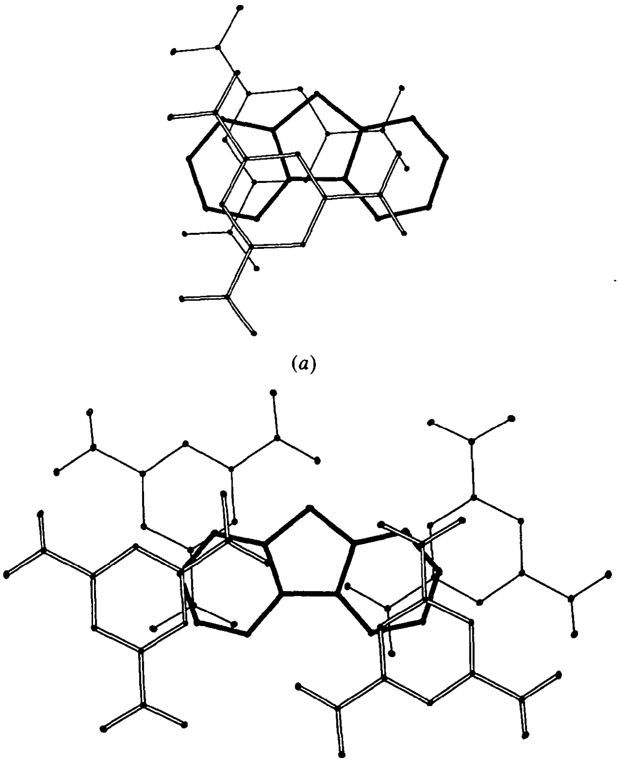
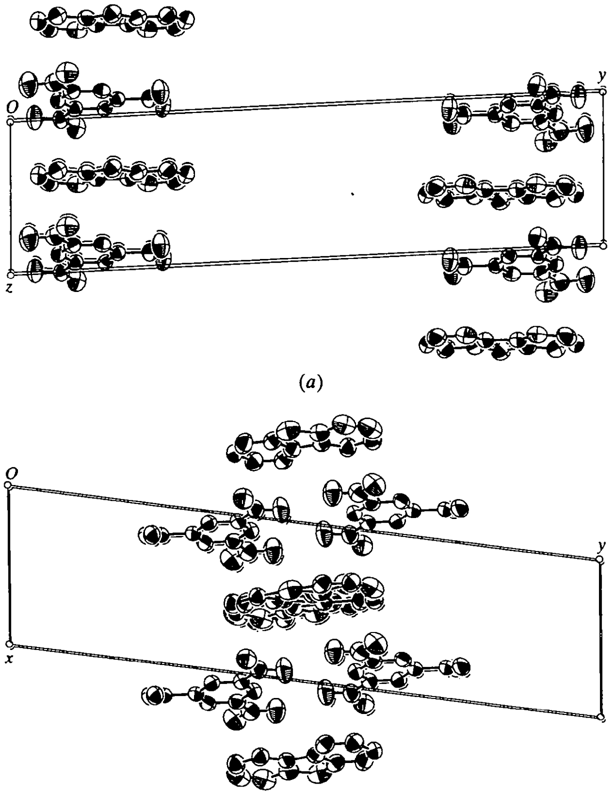


Fig. 3. Drawing showing the TNB molecules projected onto the least-squares plane of the fluorene molecule; (*a*) fluorene-(3) and TNB-(1) molecules, and (*b*) fluorene-(4) and TNB-(2) molecules. H atoms have been omitted for clarity.

fluorene molecule are 3.42 Å for fluorene-(3)–TNB-(1) and 3.46 Å for fluorene-(4)–TNB-(2). The interplanar spacing is virtually the same in both cases but the relative position of the TNB molecules with respect to the fluorene molecule is clearly different as seen in Fig. 3. There is a more marked overlap between the donor and acceptor molecules in the first case.

Diagrams of the crystal packing showing both arrangements and the unit cell are shown in Fig. 4. The 1:1 stacking is arranged in the direction of the c axis while the 2:1 stacking lies in the direction of the a axis. Both arrangements are combined in the packing.



(a)

(b)

Fig. 4. (a) View of the unit cell down the x axis showing the 1:1 stacking arranged along the z axis, and (b) view of the unit cell down the z axis showing the 2:1 stacking arranged along the x axis.

Experimental

The title compound was synthesized by mixing equimolar solutions of fluorene and 1,3,5-trinitrobenzene in benzene/petroleum ether (60:80). The reaction mixture was heated in a water bath and allowed to react for 10 min (Rahman & Tombesi, 1966). Crystals were obtained by slow cooling and purified by recrystallization in the same solvents. Crystals suitable for diffraction were recrystallized from methanol at room temperature.

Crystal data

$1.5C_{13}H_{10}\cdot 2C_6H_3N_3O_6$
$M_r = 675.54$
Triclinic
$P\overline{1}$
$a = 7.596\,(7)$ Å
$b = 27.69\,(2)$ Å
$c = 7.276\,(11)$ Å
$\alpha = 93.117\,(9)^\circ$
$\beta = 91.114\,(11)^\circ$
$\gamma = 82.374\,(8)^\circ$
$V = 1514\,(3)$ Å^3
$Z = 2$
$D_x = 1.482$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 35.30$–38.65°
$\mu = 0.117$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.25 × 0.20 × 0.10 mm
Yellow

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1993)
$T_{\min} = 0.971$, $T_{\max} = 0.988$
7492 measured reflections
6960 independent reflections

3845 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 27.50^\circ$
$h = 0 \rightarrow 9$
$k = -35 \rightarrow 35$
$l = -9 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: 4.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.184$
$S = 1.046$
6960 reflections
568 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0964P)^2 + 0.1305P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.482$ e Å^{-3}
$\Delta\rho_{\min} = -0.243$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.016 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Direct methods were used to solve the structure in the $P1$ space group, since no interpretable Fourier maps could be derived in space group $P\overline{1}$. All non-H atoms except those belonging to the positionally disordered fluorene molecule were found in the initial map. Atoms for this fluorene molecule were located in difference Fourier maps by fitting one rigid fluorene molecule with half occupancy and then locating atoms of the equivalent fluorene in successive ΔF maps. After detection of an inversion center, the coordinates were transformed to comply with space group $P\overline{1}$. The H atoms of the potentially disordered fluorene molecule were placed in calculated positions and refined riding. All the others were located on ΔF maps and freely refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1080). Services for accessing these data are described at the back of the journal.

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Bis(2,2-dimethylaziridinyl)phosphinic amide

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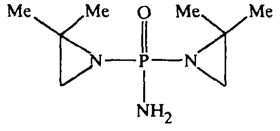
Abstract

The asymmetric unit of the title compound, $C_8H_{18}N_3OP$, contains one bis(2,2-dimethylaziridinyl)phosphinic amide molecule. The crystal structure is characterized by hydrogen bonds from the amide-N atom, which involve both H atoms of the amino group, to the phosphinic-O atom in two different molecules, thus forming infinite double-stranded chains along the base vector [100], and by hydrophobic contacts between these chains.

Comment

Bis(2,2-dimethylaziridinyl)phosphinic amide, (I), was synthesized as a member of a series of antitumour agents incorporating a bis(2,2-dimethylaziridinyl) phosphinoyl moiety (MacDiarmid *et al.*, 1985). These compounds are significantly different from conventional aziridine-type chemical alkylating agents, and have demonstrated tumour regression activity in a variety of neoplasms (Belgrad & Wampler, 1982). An amino-substituted derivative of the title compound is currently being developed as a treatment for œsophageal cancer and multiple myeloma, and the title compound itself is scheduled to be tested in the 60-panel human tumour screen of the National Cancer Institute of USA in the near future (Dunn, 1998).



(I)

The molecular structure of (I) is presented in Fig. 1. Normals to the two planes through the aziridinyl rings intersect at an angle of 68.1 (2)°. The bond lengths and angles of the aziridinyl rings are similar to those in 5-(1-aziridinyl)-2,4-dinitrobenzamide (Iball *et al.*, 1975), and 1-(1-aziridinyl)-2,4,6-trinitrobenzene (Barnes *et al.*, 1977). The aziridinyl moieties are, within experimental error, equilateral triangles. Significant shortening of the C—C single bond of the aziridinyl rings displayed in this structure [1.484 (3) and 1.475 (4) Å] is also found in other compounds which contain strained three-membered rings, such as the two cited above, *meso*-1,4-diaziridinyl-2,3-butanediol (Gould & Pasternak, 1961) and aziridine borane (Ringertz, 1969). Even shorter distances were observed in 5-(1-aziridinyl)-3-nitro-1-(3-oxo-1-butyl)-1,2,4-triazole [1.445 (4) Å; McKenna *et al.*, 1988] and in 2,5-diaziridinyl-3-phenyl-*p*-benzoquinone [1.462 (6) and 1.467 (6) Å; Hargreaves *et al.*, 1997]. Distances from atom P1 to atoms O2, N3, N4 and N9 are 1.481 (2), 1.623 (2), 1.654 (2) and 1.662 (2) Å,

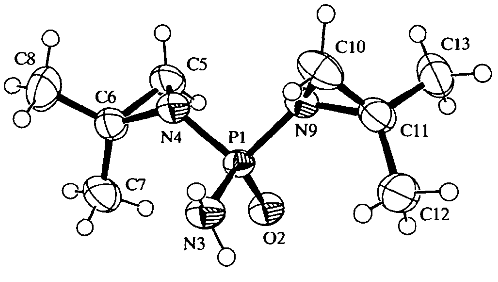


Fig. 1. *ORTEP*-3 (Farrugia, 1997) view of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small circles of an arbitrary radius.