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The Donor–Acceptor Complex between 4,6,8-Trimethylazulene and Picric Acid

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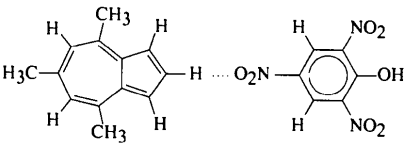
Abstract

Slow cooling of an equimolar mixture of 4,6,8-trimethylazulene and picric acid (2,4,6-trinitrophenol) in ethanol yields crystals of an 1:1 donor–acceptor complex, $C_{13}H_{14}.C_6H_3N_3O_7$, the structure of which has been determined by X-ray diffraction at 200 K. The donor and acceptor molecules alternate in mixed stacks along the [001] direction. All geometric parameters of the donor as well as the acceptor molecules are comparable to those in isolated 4,6,8-trimethylazulene and picric acid.

Comment

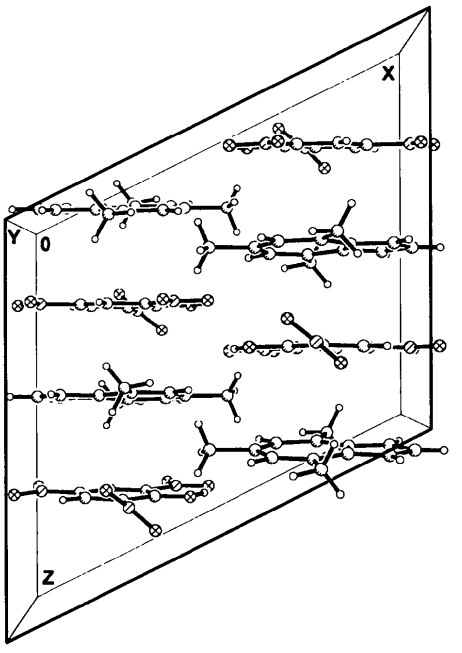
The structure of the title compound, (I), has been determined as part of a study of geometric perturbations on the formation of electron donor–acceptor complexes (Bock, Sievert, Schödel & Kleine, 1996; Bock, Ziemer, Näther, Schödel, Kleine & Sievert, 1996; Bock, Seitz, Sievert, Kleine & Bats, 1996; Bock, Rauschenbach, Näther, Kleine & Bats, 1996). In addition, the sodium metal reduction of azulene has been investigated (Bock, Arad, Näther & Göbel, 1996). 4,6,8-Trimethylazulene was selected for co-crystallization with picric acid because azulene tends to be disordered in the solid state (Kovats, Günthard & Plattner, 1955; Robertson, Shearer, Sim & Watson, 1962) even in its molecular complexes (Hanson, 1965).



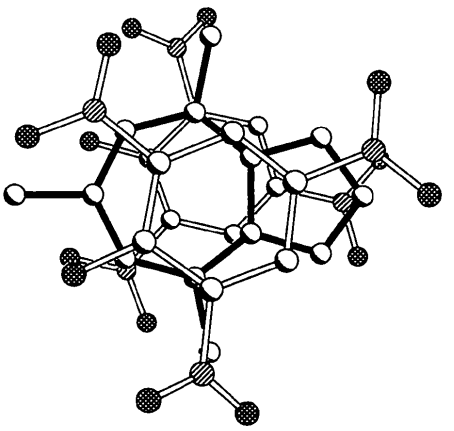
(I)

The crystal structure of the title complex contains mixed stacks of alternating donor and acceptor molecules, which are often observed in π-molecular complexes such as picric acid:anthracene (Herbstein & Kaftory, 1976) or picric acid:naphthalene (Banerjee & Brown, 1985; Yamaguchi, Goto, Takayanagi & Ogura, 1988). Between the stacks, which are oriented parallel to [001], short intermolecular contacts of 2.500 (2) Å are observed between the H5 atom of 4,6,8-trimethylazulene and the O4 atom of the picric acid. Each molecule is enclosed in a quasi-hexagonal environment. The angles between the molecular mean planes of the 4,6,8-trimethylazulene and picric acid molecules are 4.38 (3) and 9.44 (3)°, however, due to the non-parallel arrangement, the interplanar distances need additional specification. The calculated distances between the reference plane of the 4,6,8-trimethylazulene molecule and the centroid of the six-membered ring of picric acid are 3.35 (1) [interplanar angle = 4.38 (1)°] and 3.50 (1) Å [interplanar angle = 9.44 (12)°], and indicate only a weak 'molecule pairing' within the stacks, in which the orientation of picric acid alternates with a periodicity of about 14 Å. It has been shown (Herbstein, 1971; Herbstein & Kaftory, 1975) that equimolar π-molecular complexes with stack-axis lengths of about 7 Å can be sorted into groups of quasi-isomorphous structures. In addition, only a few compounds exhibit periodicities of about 14 Å, *e.g.* pyrene:picryl chloride, triphenylene:picryl chloride and triphenylene:picryl bromide (Herbstein & Kaftory, 1975). The title complex represents another example of this structure type.

Neither the donor 4,6,8-trimethylazulene nor the acceptor picric acid exhibit significant distortions of their structures attributable to complex formation, presumably as a result of the relatively large donor and acceptor molecules. Smaller acceptor molecules such as bromine



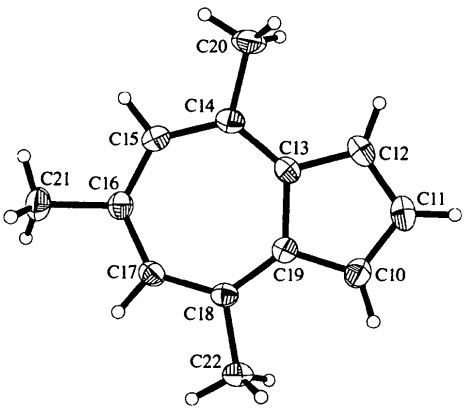
(*a*)



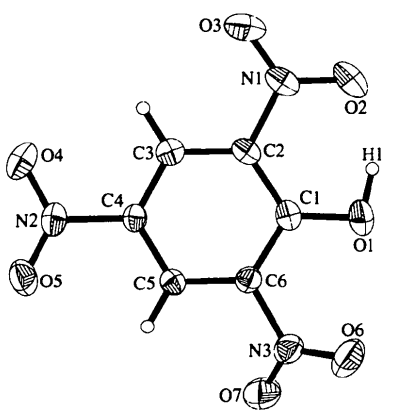
(*b*)

Fig. 1. Crystal structure of the 1:1 donor–acceptor complex between 4,6,8-trimethylazulene and picric acid (*a*) viewed along [010] and (*b*) showing the orientation of the molecules within the stacks, with 4,6,8-trimethylazulene projected onto the mean plane (hydrogen centres have been omitted).

display significantly larger distortions in donor–acceptor complexes (Bock, Havlas, Rauschenbach, Näther & Kleine, 1996). The geometry of 4,6,8-trimethylazulene in the title complex resembles that of the isolated molecule (Wong, So & Mak, 1984). The molecular skeleton is planar within experimental error, the largest deviation of a carbon centre from the mean plane being 0.036 (1) Å. The geometry of the picric acid in the title complex is also similar to that of the isolated molecule (Duesler, Engelmann, Curtin & Paul, 1978; Soriano-Garcia, Srikrishan & Parthasarathy, 1978, 1980). Two of the three nitro groups are planar with the six-membered ring [ω(O2—N1—C2—C1) 1.0 (1) and ω(O4—N2—C4—C3) 1.1 (2)°], whereas the other one is twisted out of the ring plane by 40.1 (2)°. The hydroxyl O1—H1 group forms an intramolecular hydrogen bond with the O2 atom of the nitro group, with distances H1···O2 of 1.71 (1) Å and O1···O2 of 2.570 (2) Å, and an O1—H1···O2 angle of 153 (3)°.



(*a*)



(*b*)

Fig. 2. The molecular structure of (*a*) 4,6,8-trimethylazulene and (*b*) picric acid with the labelling of the centres (displacement ellipsoids are drawn at the 50% probability level).

Experimental

Picric acid (2,4,6-trinitrophenol) and 4,6,8-trimethylazulene are commercially available. Crystals of the title compound were grown by slow cooling of an equimolar mixture of trimethylazulene and picric acid in ethanol.

Crystal data

$C_{13}H_{14}.C_6H_3N_3O_7$ — Mo $K\alpha$ radiation
M_r = 399.36 — λ = 0.71073 Å

Monoclinic
$P2_1/c$
a = 14.996 (2) Å
b = 9.8324 (12) Å
c = 13.461 (2) Å
β = 116.609 (6)°
V = 1774.6 (4) Å^3
Z = 4
D_x = 1.495 Mg m^{-3}
D_m not measured

Cell parameters from 44 reflections
θ = 10–15°
μ = 0.116 mm^{-1}
T = 200 (2) K
Block
0.6 × 0.5 × 0.4 mm
Dark red

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
6157 measured reflections
5124 independent reflections
3999 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0186

θ_{max} = 30.99°
$h = -21 \rightarrow 19$
$k = -14 \rightarrow 1$
$l = -1 \rightarrow 17$
4 standard reflections
monitored every 100 reflections
intensity decay: negligible

Refinement

Refinement on F^2
$R(F)$ = 0.0459
$wR(F^2)$ = 0.1334
S = 1.025
5124 reflections
269 parameters
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.4917P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.427 e Å^{-3}
$\Delta\rho_{min}$ = −0.217 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.42592 (7)	0.08698 (13)	0.40918 (9)	0.0379 (3)
O2	0.47266 (8)	0.33996 (14)	0.42125 (10)	0.0447 (3)
O3	0.35868 (10)	0.49589 (12)	0.36271 (10)	0.0457 (3)
O4	0.01335 (9)	0.38791 (12)	0.19549 (10)	0.0425 (3)
O5	−0.03572 (8)	0.17797 (13)	0.17935 (10)	0.0463 (3)
O6	0.34160 (9)	−0.14088 (12)	0.43573 (10)	0.0457 (3)
O7	0.22081 (10)	−0.18227 (12)	0.27289 (12)	0.0536 (3)
N1	0.38385 (9)	0.37721 (13)	0.37886 (10)	0.0324 (3)
N2	0.02928 (8)	0.26488 (13)	0.20805 (9)	0.0294 (2)
N3	0.27379 (9)	−0.10490 (12)	0.34677 (11)	0.0327 (3)
C1	0.33292 (9)	0.13453 (14)	0.36406 (10)	0.0254 (2)
C2	0.30653 (9)	0.27302 (13)	0.34606 (10)	0.0248 (2)
C3	0.20800 (9)	0.31655 (13)	0.29616 (10)	0.0250 (2)
C4	0.13347 (8)	0.21988 (13)	0.26127 (10)	0.0233 (2)
C5	0.15405 (9)	0.08164 (13)	0.27548 (11)	0.0248 (2)
C6	0.25294 (9)	0.04166 (13)	0.32790 (11)	0.0251 (2)
C10	0.08984 (10)	0.39206 (14)	0.47870 (11)	0.0300 (3)
C11	0.02251 (10)	0.2838 (2)	0.45181 (12)	0.0339 (3)
C12	0.07507 (10)	0.16182 (15)	0.48527 (11)	0.0303 (3)
C13	0.17831 (8)	0.18992 (12)	0.53538 (10)	0.0224 (2)
C14	0.25370 (9)	0.09201 (12)	0.58077 (10)	0.0245 (2)
C15	0.35685 (9)	0.11710 (13)	0.62905 (10)	0.0257 (2)
C16	0.41029 (9)	0.23830 (13)	0.64477 (10)	0.0245 (2)
C17	0.37267 (9)	0.37041 (13)	0.61440 (10)	0.0247 (2)
C18	0.27448 (9)	0.41907 (12)	0.56365 (10)	0.0234 (2)
C19	0.18783 (9)	0.34061 (12)	0.52978 (10)	0.0227 (2)
C20	0.22225 (12)	−0.05500 (14)	0.57986 (14)	0.0360 (3)
C21	0.52290 (10)	0.2265 (2)	0.70120 (13)	0.0353 (3)
C22	0.26238 (11)	0.57051 (13)	0.54219 (13)	0.0341 (3)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.332 (2)	C5—C6	1.383 (2)
O2—N1	1.246 (2)	C10—C11	1.398 (2)
O3—N1	1.216 (2)	C10—C19	1.408 (2)
O4—N2	1.230 (2)	C11—C12	1.395 (2)
O5—N2	1.222 (2)	C12—C13	1.412 (2)
O6—N3	1.226 (2)	C13—C14	1.400 (2)
O7—N3	1.221 (2)	C13—C19	1.494 (2)
N1—C2	1.459 (2)	C14—C15	1.405 (2)
N2—C4	1.466 (2)	C14—C20	1.519 (2)
N3—C6	1.472 (2)	C15—C16	1.398 (2)
C1—C2	1.408 (2)	C16—C17	1.402 (2)
C1—C6	1.409 (2)	C16—C21	1.514 (2)
C2—C3	1.389 (2)	C17—C18	1.401 (2)
C3—C4	1.380 (2)	C18—C19	1.400 (2)
C4—C5	1.388 (2)	C18—C22	1.512 (2)
O3—N1—O2	123.13 (12)	C1—C6—N3	119.50 (11)
O3—N1—C2	118.60 (12)	C11—C10—C19	109.13 (12)
O2—N1—C2	118.26 (13)	C12—C11—C10	109.44 (12)
O5—N2—O4	124.49 (12)	C11—C12—C13	109.04 (12)
O5—N2—C4	117.93 (12)	C14—C13—C12	124.92 (12)
O4—N2—C4	117.59 (12)	C14—C13—C19	128.86 (11)
O7—N3—O6	124.63 (13)	C12—C13—C19	106.21 (11)
O7—N3—C6	117.31 (12)	C13—C14—C15	125.98 (11)
O6—N3—C6	118.05 (12)	C13—C14—C20	117.63 (12)
O1—C1—C2	125.03 (12)	C15—C14—C20	116.38 (12)
O1—C1—C6	119.04 (13)	C16—C15—C14	131.08 (12)
C2—C1—C6	115.91 (11)	C15—C16—C17	128.09 (11)
C3—C2—C1	122.50 (11)	C15—C16—C21	116.45 (11)
C3—C2—N1	117.32 (12)	C17—C16—C21	115.46 (11)
C1—C2—N1	120.18 (11)	C18—C17—C16	131.02 (11)
C4—C3—C2	118.46 (12)	C19—C18—C17	126.15 (12)
C3—C4—C5	122.11 (11)	C19—C18—C22	117.76 (11)
C3—C4—N2	118.83 (11)	C17—C18—C22	116.07 (11)
C5—C4—N2	119.06 (11)	C18—C19—C10	125.05 (12)
C6—C5—C4	118.03 (11)	C18—C19—C13	128.74 (11)
C5—C6—C1	122.96 (12)	C10—C19—C13	106.18 (11)
C5—C6—N3	117.54 (11)		

The C-, O- and N-atom positions were refined with anisotropic displacement parameters. The hydrogen centres were located from a difference map, positioned with idealized geometry and refined with fixed isotropic displacement parameters [U_{iso} = 1.2U_{eq} (for aromatic C) and 1.5U_{eq} (for methyl C)], using a riding model with the parameters C—H(aromatic) = 0.95 Å and C—H(methyl) = 0.98 Å. The H atom bound to O1 was refined with free coordinates and a free isotropic displacement parameter.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990*b*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1217). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N,N'-Bis(4-methylbenzoyl)-*p*-phenylenediamine at 200 K

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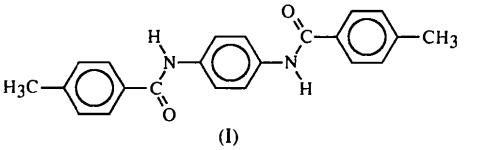
Abstract

The title compound, *N,N'*-*p*-phenylenebis(4-methylbenzamide), $C_{22}H_{20}N_2O_2$, crystallizes with an almost linear arrangement of the three benzene units, but both outer benzene ring planes are twisted relative to the plane of the central ring by 58.03 (6)°. N—H···O=C hydrogen bonds perpendicular to the long axis of the molecules connect them into ribbons parallel to the *a* axis.

Comment

The structure of the title compound, (I), has been determined as part of a study on the structures and properties of *N,N'*-di- and *N,N,N',N'*-tetrasubstituted *p*-phenylenediamines (Bock, Göbel, Näther, Havlas, Gavezzotti & Filippini, 1993; Bock, Meuret, Näther & Krynitz, 1994). The derivative *N,N'*-ditosyl-*p*-phenylenediamine, with two sulfonamide instead of two amide subunits, has the ability to include a large variety of solvents on crystallization. The inclusion compounds with one molecular equivalent of acetone, cyclopentanone, cyclopent-2-en-1-one, tetrahydrofuran, 2,5-dihydrofuran and dioxolane are isostructural, whereas a second type of isostructural inclusion compound includes one molar equivalent of a less polar solvent such as benzene or furan (Nagel, 1993; Näther, 1994). In addition, hydrogen-bonded 2:1 adducts crystallize from solutions containing strong hydrogen-bond acceptors such as dimethyl sulfoxide (DMSO) (Nagel, Näther & Bock, 1995) and *N,N*-dimethylformamide (DMF). In both types of isostructural inclusion compound, only one O atom of each sulfonamide group is involved in hydrogen bonding. We therefore became interested in the inclusion properties of (I).



(I)

Crystallization experiments on (I), however, proved it to be almost insoluble in most organic solvents and no solvates could be crystallized. Solvent-free crystals suitable for single-crystal X-ray structure analysis were obtained from DMF. The compound crystallizes in space group $P\bar{1}$ with half a molecule in the asymmetric unit. The geometric parameters correspond to values found in similar compounds (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1994). The molecules are located around crystallographic centres of inversion and their conformation can thus be characterized by the torsion along the three bonds C1—N1, N1—C4 and C4—C10 (Fig. 1). The torsion angles ω(C2—C1—N1—C4) of −30.7 (2), ω(C1—N1—C4—C10) of 179.29 (13) and ω(N1—C4—C10—C11) of −29.1 (2)° confirm that the H1N—N1—C4=O1 amide subunit is fixed in an antiperiplanar conformation and that the H1N and O1 atoms are both twisted out of the planes of their adjacent benzene subunits by about 30°. The position of the refined hydrogen bound to N1 indicates that the substituted nitrogen centre is almost planar, in contrast to the analogous compound with sulfonamide subunits,