

4-Nitro-9,10-dihydrophenanthrene
and a polymorphic form of 4-nitro-
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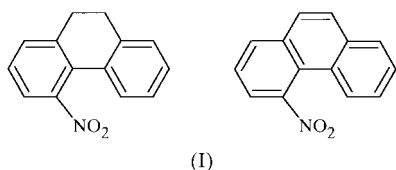
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The crystal structures of 4-nitro-9,10-dihydrophenanthrene, C₁₄H₁₁NO₂, (I), and 4-nitrophenanthrene, C₁₄H₉NO₂, (II), the latter having two crystallographically independent molecules, show that the molecules are not planar. The dihedral angles between the phenyl rings of the biphenyl skeletons are 28.64 (8)° for (I), and 10.34 (15) and 11.75 (13)° for the two molecules of (II). The differences in the dihedral angles have an effect on the photochemical reactivity of the molecules.

Comment

New triplet species for 2-nitrobiphenyl and 2,2'-dinitrobiphenyl were detected by electron paramagnetic resonance (EPR) after UV irradiation in ethanol glass with an He–Xe lamp at 77 K (Tanigaki *et al.*, 1988). The structures of the two molecules are twisted around the central C–C bonds, the dihedral angles of the two rings being 63.1 (3) and 62.6 (3)° for 2-nitro- and 2,2'-dinitrobiphenyl, respectively (Sekine *et al.*, 1994). The relationship between the nature of the triplet species and the molecular conformation has been discussed previously (Higuchi *et al.*, 1995, 1999). In order to examine this relationship more precisely, the title compounds, *i.e.* 4-nitro-9,10-dihydrophenanthrene, (I), and 4-nitrophenanthrene, (II), in which the two rings are connected by a –CH₂–CH₂– group in (I) and by a –CH=CH– group in (II), were analyzed by X-ray diffraction. The molecular structures of (I) and (II) are shown in Fig. 1 and 2, respectively.



There are two independent molecules of (II) in the crystal; however, the structural differences between the two molecules

are minor. The dihedral angles between the phenyl rings of the biphenyl skeleton are 28.64 (8)° in (I), and 10.34 (15) and 11.75 (13)° in the two molecules of (II). These values are much smaller than that found in 2-nitrobiphenyl, (III) (Sekine *et al.*, 1994), of 63.1 (3)° because (III) has no intramolecular

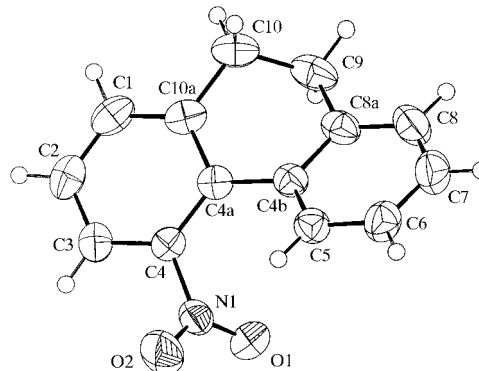


Figure 1

The molecular structure of (I), showing the atom labeling. Displacement ellipsoids are shown at the 50% probability level.

restriction between the two phenyl rings. The dihedral angles between the NO₂ groups and the phenyl rings to which they are bonded are 56.5 (1)° in (I), 70.3 (2) and 67.4 (2)° in (II), and 44.7 (4)° in (III).

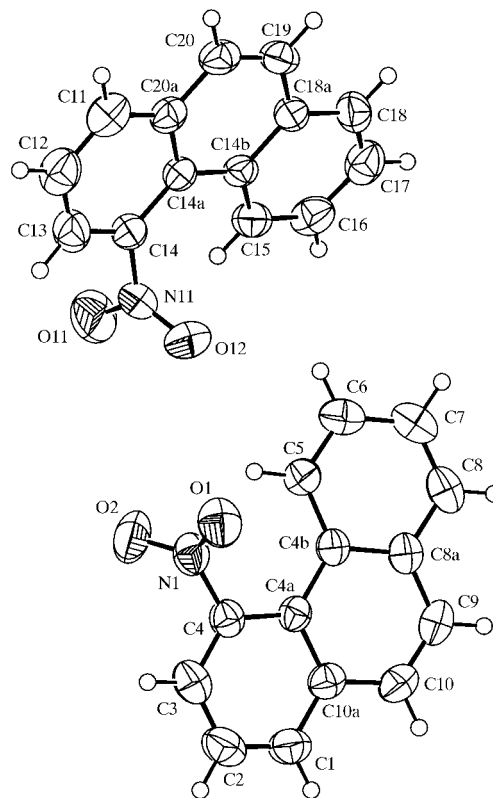


Figure 2

The molecular structures of the two independent molecules of (II), showing the atom labeling. Displacement ellipsoids are shown at the 50% probability level.

The biphenyl skeleton of (II) is nearly coplanar due to the strongly conjugated system, while that of (I) is not coplanar because of the bulky *o*-*o'*-linkage. Assuming that the molecular structure at the lowest excited triplet state is not different from its ground-state structure, the difference in the EPR signals of these compounds would be due to the differences in the molecular structures, *i.e.* the angles between the two phenyl rings.

The crystal structure of 4-nitrophenanthrene, (II), has also been reported by Taylor & Thompson (2001) in a different (polymorphic) form [TT form, $P2_1/c$, $Z = 4$, $a = 8.061$ (2), $b = 12.449$ (3), $c = 11.32$ (3) Å and $\beta = 109.73$ (1)°]. As the TT form was measured at the lower temperature of 168 (2) K, there is a possibility of a phase change from the room temperature form of this study. It is interesting that the two forms have the same space group and unit-cell dimensions, except for a halving of the *a* cell length for the TT form, and very similar molecular packing. In both structures, dimeric pairs of molecules are related by an inversion center, show a herring-bone motif and make a sheet structure parallel to the (011) face. In our new form, the two independent molecules have slightly different orientations, however, they make similar sheet structures, stacking alternately.

In both forms, the molecular dimensions show no significant differences when the difference in temperature of the structure determinations is considered. The dihedral angles are also comparable; the NO₂-phenyl and biphenyl skeleton dihedral angles are 72.7 (7) and 10.40 (8)°, respectively, in the TT form.

Experimental

Compound (I) was synthesized according to the method of Krueger & Mosettig (1939). Light-yellow crystals were obtained by recrystallization from a hexane solution (yield 10.5%). Compound (II) was obtained by modifying the dehydrogenation reported by Boekelheide & Hylton (1970). A solution of compound (I) and 2,3-dichloro-5,6-dicyanoquinone in *o*-dichlorobenzene was stirred in the dark at 473 K for 24 h. Yellow crystals were obtained by recrystallization from a hexane solution (yield 81.6%).

Compound (I)

Crystal data

$C_{14}H_{11}NO_2$	$D_x = 1.343 \text{ Mg m}^{-3}$
$M_r = 225.24$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 3 reflections
$a = 8.6710$ (5) Å	$\theta = 55.0\text{--}60.0^\circ$
$b = 16.4284$ (8) Å	$\mu = 0.74 \text{ mm}^{-1}$
$c = 7.8287$ (7) Å	$T = 296$ (2) K
$\beta = 92.542$ (6)°	Prismatic, light yellow
$V = 1114.11$ (13) Å ³	$0.5 \times 0.3 \times 0.3 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.014$
θ - 2θ scans	$\theta_{\text{max}} = 62.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968).	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.643$, $T_{\text{max}} = 0.802$	$k = 0 \rightarrow 18$
1966 measured reflections	$l = 0 \rightarrow 8$
1763 independent reflections	3 standard reflections
1476 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 2.0%

Refinement

Refinement on F^2	$w = 1/[s^2(F_o^2) + (0.0417P)^2 + 0.1823P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$
1762 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
154 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °) for (I).

O1—N1	1.220 (2)	C4—C3	1.379 (2)
O2—N1	1.217 (2)	C4—C4a	1.397 (2)
N1—C4	1.474 (2)	C4a—C4b	1.482 (2)
O1—N1—O2	124.09 (15)	C3—C4—C4a	123.88 (14)
O1—N1—C4	117.66 (13)	C3—C4—N1	114.97 (14)
O2—N1—C4	118.20 (14)	C4a—C4—N1	121.00 (13)

Compound (II)

Crystal data

$C_{14}H_9NO_2$	$D_x = 1.393 \text{ Mg m}^{-3}$
$M_r = 223.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 15.934$ (7) Å	$\theta = 55.0\text{--}60.0^\circ$
$b = 12.471$ (5) Å	$\mu = 0.09 \text{ mm}^{-1}$
$c = 11.436$ (5) Å	$T = 296$ (2) K
$\beta = 110.48$ (5)°	Prismatic, yellow
$V = 2129.0$ (16) Å ³	$0.4 \times 0.3 \times 0.3 \text{ mm}$
$Z = 8$	

Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.030$
θ - 2θ scans	$\theta_{\text{max}} = 24.1^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968).	$h = -18 \rightarrow 17$
$T_{\text{min}} = 0.797$, $T_{\text{max}} = 0.972$	$k = 0 \rightarrow 14$
3583 measured reflections	$l = 0 \rightarrow 13$
3398 independent reflections	3 standard reflections
2240 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: 0.2%

Refinement

Refinement on F^2	$w = 1/[s^2(F_o^2) + (0.0868P)^2 + 0.2279P]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.163$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
3398 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
307 parameters	
H-atom parameters constrained	

Table 2

Selected geometric parameters (Å, °) for (II).

N1—O1	1.213 (3)	N11—O11	1.223 (4)
N1—O2	1.230 (3)	N11—O12	1.217 (3)
N1—C4	1.468 (4)	N11—C14	1.471 (4)
C4—C3	1.371 (4)	C14—C13	1.363 (4)
C4—C4a	1.427 (4)	C14—C14a	1.418 (4)
C4a—C4b	1.460 (4)	C14b—C14a	1.464 (4)
O1—N1—O2	123.6 (3)	O12—N11—O11	123.4 (3)
O1—N1—C4	118.9 (2)	O12—N11—C14	118.2 (3)
O2—N1—C4	117.4 (2)	O11—N11—C14	118.3 (3)
C3—C4—C4a	123.9 (3)	C13—C14—C14a	124.0 (3)
C3—C4—N1	114.1 (3)	C13—C14—N11	113.6 (3)
C4a—C4—N1	121.9 (2)	C14a—C14—N11	122.3 (2)

H atoms were refined as riding, with C—H distances of 0.93 and 0.97 Å for (I) and 0.93 Å for (II).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1338). Services for accessing these data are described at the back of the journal.

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