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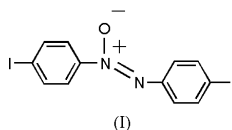
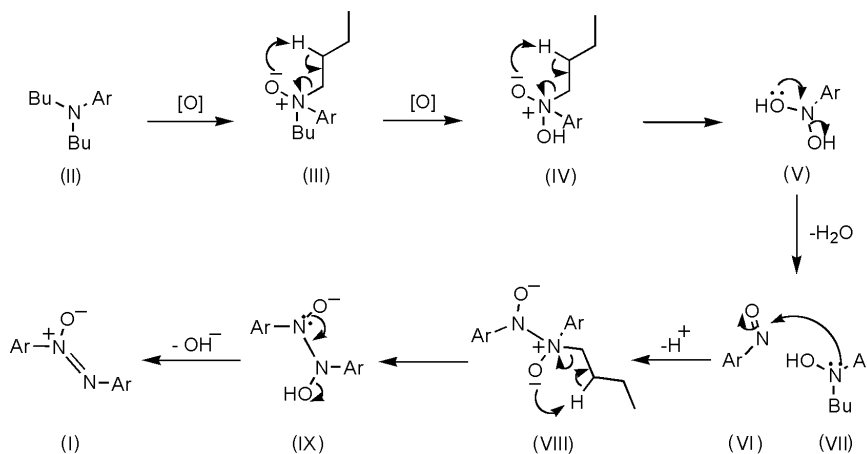
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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.055
wR factor = 0.105
Data-to-parameter ratio = 9.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*N,N'*-Bis(4-iodophenyl)diazene *N*-oxideThe title compound, $\text{C}_{12}\text{H}_8\text{I}_2\text{N}_2\text{O}$, was obtained as an unexpected product while attempting to protect *N,N*-dibutyl-4-iodoaniline as the *N*-oxide. It crystallizes as a layer structure.Received 4 June 2003
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Comment

The title compound, (I), was obtained in 10% yield as an unexpected product while attempting to convert *N,N*-dibutyl-4-iodoaniline into its *N*-oxide with hydrogen peroxide (Demir & Shaw, 1987), and was identified crystallographically.To the best of our knowledge, the direct transformation of a tertiary amine into a diazo compound is unprecedented. Compound (I) has previously been prepared by several routes (*e.g.* Gabriel, 1876; Wang *et al.*, 1999); the melting point, NMR data and mass spectrum of our product confirmed its identity. A possible mechanism for the formation of this compound is shown in the Scheme below.Oxidation of (II) by hydrogen peroxide gives the *N*-oxide (III). This eliminates butene *via* a Cope reaction (Adams & Kovacic, 1974) before being oxidized again [to give (IV)] and undergoing a second elimination [to give (V)]. Di(hydroxyl)-amine (V) then eliminates water to give nitrosamine (VI). From this point, it is likely that the mechanism is similar to that of the reaction between nitrosobenzene and phenylhydroxylamine (Becker & Sternson, 1980) [a radical mechanism is also seen in the presence of base (Russell *et al.*,

1967)]. Nucleophilic attack by the species that has undergone one elimination (VII) forms dimer (VIII). This undergoes a further elimination (to give IX), followed by displacement of OH^- by the lone pair of the adjacent N atom to give (I). (I) crystallizes as an inversion twin [Flack (Flack & Bernardinelli, 1999, 2000) parameter = 0.46 (9)]. The whole molecule is also disordered with an image of itself in the ratio 4:1. The image can be regarded as being due either to a local pseudo-centre of symmetry, or a stacking fault with translation of approximately $\frac{1}{4}$ along z . This is the preferred description, since the structure consists of layers of molecules perpendicular to c , with a layer distance of $z/4$. The minimum $\text{I} \cdots \text{I}$ distances between layers is 4.05 Å. The bond lengths and angles are comparable to similar azoxy compounds. Short intramolecular contacts occur between O1 and H41 (2.04 Å), and between O1 and H101 (2.31 Å); both of these are shorter than the sum of the van der Waals radii (2.68 Å; Rowland & Taylor, 1996).

Experimental

A mixture of *N,N*-dibutyl-4-iodoaniline (1.3 g, 3.93 mmol), chloroform (2.5 ml), methanol (2.5 ml) and hydrogen peroxide (35% w/w in water, 2.5 ml) was heated to reflux. Starting material was still present after 24 h, as shown by thin-layer chromatography (silica, 9:1 60–80 petroleum ether–DCM, $R_F = 0.78$). Further additions of hydrogen peroxide (35% w/w in water, 2.5 ml) were made every 24 h for 4 d until the starting material had been consumed. The product was then isolated by extraction into chloroform followed by crystallization (DCM/60–80 petroleum ether), to give colourless crystals (180 mg, 10%). M.p. 471 K. Crystals were grown by slow evaporation of a solution in CDCl_3 . (λ_{max} (CH_2Cl_2)/nm log (ϵ): 239 (4.08), 343 (4.13) m/z (TOF MS ES⁺): 454.54 ($[M + 4H]^+$), 330.07 ($[M - I + 4H]^+$, 100%), 327.17 ($[M - I + H]^+$), 217.01 ($[M - I + \text{C}_6\text{H}_4\text{NO}]^+$), 201.07 ($[M - I + 3H]^+$).

Crystal data

| | |
|-------------------------------------------------------|---------------------------------------|
| $\text{C}_{12}\text{H}_8\text{I}_2\text{N}_2\text{O}$ | Mo $K\alpha$ radiation |
| $M_r = 450.02$ | Cell parameters from 1542 reflections |
| Orthorhombic, $I2cb$ | $\theta = 1\text{--}27^\circ$ |
| $a = 6.0119$ (1) Å | $\mu = 4.90$ mm ⁻¹ |
| $b = 7.2082$ (2) Å | $T = 150$ K |
| $c = 59.0233$ (18) Å | Plate, white |
| $V = 2557.77$ (11) Å ³ | 0.20 × 0.19 × 0.01 mm |
| $Z = 8$ | |
| $D_x = 2.337$ Mg m ⁻³ | |

Data collection

| | |
|---------------------------------------------------------------------------------------------------|-----------------------------------------|
| Nonius KappaCCD diffractometer | 2682 independent reflections |
| ω scans | 2681 reflections with $I > 10\sigma(I)$ |
| Absorption correction: multi-scan (<i>DENZO</i> and <i>SCALEPACK</i> ; Otwinowski & Minor, 1997) | $R_{\text{int}} = 0.029$ |
| $T_{\text{min}} = 0.39$, $T_{\text{max}} = 0.95$ | $\theta_{\text{max}} = 27.5^\circ$ |
| 2815 measured reflections | $h = -7 \rightarrow 7$ |
| | $k = -9 \rightarrow 9$ |
| | $l = -74 \rightarrow 75$ |

Refinement

| | |
|----------------------------------------------------|----------------------------------------------------------------------------|
| Refinement on F^2 | $(\Delta/\sigma)_{\text{max}} = 0.003$ |
| $R(F) = 0.055$ | $\Delta\rho_{\text{max}} = 1.78$ e Å ⁻³ |
| $wR(F^2) = 0.105$ | $\Delta\rho_{\text{min}} = -1.70$ e Å ⁻³ |
| $S = 0.98$ | Absolute structure: Flack & Bernardinelli (1999, 2000), 1226 Friedel pairs |
| 2681 reflections | Flack parameter = 0.46 (9) |
| 296 parameters | |
| H-atom parameters not refined | |
| $w = 1/[\sigma^2(F^2) + (0.032p)^2 + 33]$ | |
| where $p = 0.33\text{Max}(0, F_o^2) + (0.67F_c^2)$ | |

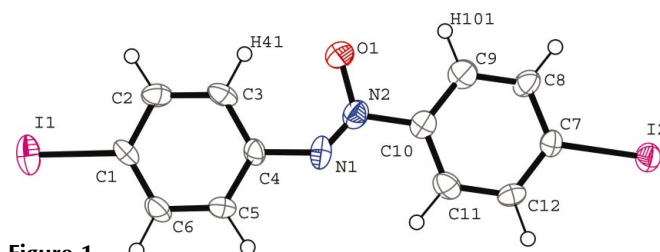


Figure 1

Plot showing the atomic numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

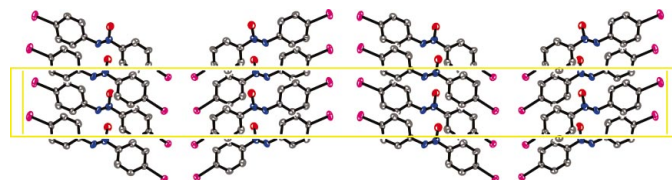


Figure 2

The unit cell of (I), viewed normal to the b axis, showing all N–O groups pointing in the same direction.

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|----------------|-------------|
| I1–C1 | 2.095 (6) | I202–C207 | 2.083 (9) |
| I2–C7 | 2.098 (6) | O201–N201 | 1.321 (9) |
| C1–C2 | 1.397 (7) | N201–N202 | 1.090 (9) |
| C1–C6 | 1.390 (8) | N201–C204 | 1.438 (9) |
| C2–C3 | 1.407 (8) | N202–C210 | 1.433 (9) |
| C3–C4 | 1.405 (7) | C201–C202 | 1.391 (9) |
| C4–C5 | 1.377 (7) | C201–C206 | 1.393 (9) |
| C4–N1 | 1.417 (6) | C202–C203 | 1.396 (9) |
| C5–C6 | 1.376 (7) | C203–C204 | 1.393 (9) |
| C7–C8 | 1.391 (8) | C204–C205 | 1.389 (9) |
| C7–C12 | 1.394 (8) | C205–C206 | 1.392 (9) |
| C8–C9 | 1.380 (8) | C207–C208 | 1.389 (9) |
| C9–C10 | 1.372 (7) | C207–C212 | 1.392 (9) |
| C10–C11 | 1.406 (7) | C208–C209 | 1.387 (9) |
| C10–N2 | 1.459 (7) | C209–C210 | 1.387 (9) |
| C11–C12 | 1.400 (7) | C210–C211 | 1.398 (9) |
| N2–O1 | 1.322 (7) | C211–C212 | 1.393 (9) |
| I201–C201 | 2.088 (9) | | |
| I1–C1–C2 | 119.3 (6) | O201–N201–N202 | 115.0 (25) |
| I1–C1–C6 | 118.3 (6) | O201–N201–C204 | 115.1 (17) |
| C2–C1–C6 | 122.4 (7) | N202–N201–C204 | 129.8 (18) |
| C1–C2–C3 | 118.4 (7) | N201–N202–C210 | 136.8 (19) |
| C2–C3–C4 | 119.0 (5) | I201–C201–C202 | 119.0 (20) |
| C3–C4–C5 | 120.49 (13) | I201–C201–C206 | 119.2 (20) |
| C3–C4–N1 | 119.81 (9) | C202–C201–C206 | 121.8 (13) |
| C5–C4–N1 | 119.69 (9) | C201–C202–C203 | 118.7 (12) |
| C4–C5–C6 | 121.6 (5) | C202–C203–C204 | 120.0 (8) |
| C1–C6–C5 | 118.1 (7) | N201–C204–C203 | 119.8 (1) |
| I2–C7–C8 | 120.6 (6) | N201–C204–C205 | 119.8 (1) |
| I2–C7–C12 | 119.2 (6) | C203–C204–C205 | 120.49 (14) |
| C8–C7–C12 | 120.2 (7) | C204–C205–C206 | 120.2 (8) |
| C7–C8–C9 | 120.5 (7) | C201–C206–C205 | 118.8 (12) |
| C8–C9–C10 | 120.0 (6) | I202–C207–C208 | 119.1 (11) |
| C9–C10–C11 | 120.50 (13) | I202–C207–C212 | 119.3 (11) |
| C9–C10–N2 | 119.73 (9) | C208–C207–C212 | 121.6 (13) |
| C11–C10–N2 | 119.77 (9) | C207–C208–C209 | 119.1 (12) |
| C10–C11–C12 | 119.6 (5) | C208–C209–C210 | 120.2 (8) |
| C7–C12–C11 | 119.2 (7) | N202–C210–C209 | 119.7 (1) |
| C4–N1–N2 | 131.7 (7) | N202–C210–C211 | 119.8 (1) |
| C10–N2–N1 | 123.9 (6) | C209–C210–C211 | 120.49 (14) |
| C10–N2–O1 | 113.4 (5) | C210–C211–C212 | 119.7 (8) |
| N1–N2–O1 | 122.5 (8) | C207–C212–C211 | 118.9 (12) |

H atoms were placed geometrically after each cycle. The structure was solved for the major component using *SIR97* (Altomare *et al.*, 1994). The disorder was detected through the large anisotropic

displacement parameters (ADPs) and a residual peak near nitrogen of $2 \text{ e } \text{Å}^{-3}$. Because of the severe disorder, the structure was refined with similarity restraints between the two N_2O residues. The aromatic rings were refined with hexagonally restrained geometry and ADP similarity restraints. Almost-coincident atoms were restrained to have similar ADPs. The largest residual peak in the difference map was close to iodine, with a smaller peak near the disordered N_2O . The reflection 004 has $F_c = 68.5$, $F_o = -0.45$, and was omitted from the refinement. After averaging Friedel pairs there would be 1556 unique reflections.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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