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Structure of 1,3,5-Triisopropyl-2-nitrobenzene

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Abstract

The nitro group in 1,3,5-triisopropyl-2-nitrobenzene is almost perpendicular to the aromatic ring. The crystal structure is disordered, which is indicated by the large U_{eq} values of the atoms of the four substituent groups. The C—C distances in the isopropyl groups lie within the range 1.30–1.55 Å.

Comment

Sterically hindered nitrobenzenes of the type 1,3,5-tri-*R*-2-nitrobenzene (with *R* = Me, Et, ^{i}Pr, ^{t}Bu), bearing bulky alkyl substituents in positions *ortho* to the nitro group, are mostly resistant to light-induced hydrogen abstraction from external sources. Rather, reductive processes initiated by intramolecular hydrogen abstraction predominate if *R* = Et, ^{i}Pr, ^{t}Bu (Döpp & Müller, 1979; Kitaura & Matsuura, 1971). The present crystal-structure determination was undertaken to obtain a better insight into the geometry of the nitro group.

The crystals were of poor quality. The atoms of the isopropyl and nitro groups have high U_{eq} values and e.s.d.'s, indicating disorder. This is reflected in the lower accuracy of the corresponding bond distances and angles. The maximum distance of a ring atom from the best plane through the benzene ring is 0.03 (3) Å. The nitro group is rotated 84 (1)° out of the aromatic plane. In nitromesitylene (*R* = Me), the nitro group is tilted 66° out of the plane of the aromatic ring (Trotter, 1959). In the title compound and in nitromesitylene, the endocyclic angles of the benzene ring show the same behaviour: an increase in the endocyclic angle at the substituent site carrying the nitro group and a decrease (on average) at the substituent sites carrying the alkyl groups. These observations are in agreement with the investigations of Domenicano & Murray-Rust (1979).

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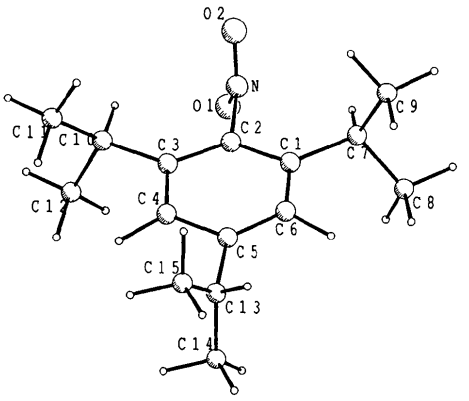

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing showing the numbering system of the title compound. The H atoms are shown but not labelled.

Experimental

Crystal data

$C_{15}H_{23}NO_2$
M_r = 249.35
Monoclinic
Ia
a = 10.851 (2) Å
b = 14.057 (2) Å
c = 11.350 (2) Å
β = 114.80 (1)°
V = 1571.6 (5) Å^3
Z = 4
D_x = 1.054 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 23 reflections
θ = 29.9–33.9°
μ = 5.16 cm^{-1}
T = 253 K
Rod
0.8 × 0.25 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3160 measured reflections
1489 independent reflections
800 observed reflections [$I > 2.5\sigma(I)$]
θ_{max} = 69.91°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 17$
$l = -13 \rightarrow 0$
2 standard reflections
frequency: 60 min
intensity variation: 5.8%

Refinement

Refinement on F
Final R = 0.074
wR = 0.096
S = 0.284
800 reflections
179 parameters
H-atom parameters not refined; methyl H atoms restrained
$w = 1/(6.72 + F_o + 0.0062F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.427
$\Delta\rho_{max}$ = 0.137 e Å^{-3}
$\Delta\rho_{min}$ = −0.227 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: g = 3 (2) × 10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	U_{eq}
C1	0.703 (2)	0.7750 (9)	0.589 (2)	0.065 (8)
C2	0.596 (2)	0.8210 (4)	0.600 (2)	0.064 (4)
C3	0.492 (2)	0.7751 (8)	0.623 (2)	0.065 (8)
C4	0.496 (2)	0.674 (1)	0.624 (2)	0.069 (7)
C5	0.602 (3)	0.6281 (5)	0.606 (2)	0.078 (5)
C6	0.700 (2)	0.6788 (9)	0.590 (2)	0.069 (8)
C7	0.812 (2)	0.832 (1)	0.565 (3)	0.10 (1)
C8	0.832 (2)	0.800 (1)	0.450 (2)	0.12 (1)
C9	0.946 (2)	0.820 (1)	0.688 (2)	0.12 (1)
C10	0.375 (2)	0.827 (1)	0.634 (2)	0.071 (8)
C11	0.359 (2)	0.792 (1)	0.757 (2)	0.11 (1)
C12	0.245 (2)	0.817 (1)	0.517 (2)	0.14 (2)
C13	0.586 (4)	0.5195 (6)	0.606 (3)	0.12 (1)
C14	0.512 (2)	0.4799 (9)	0.481 (2)	0.18 (2)
C15	0.586 (2)	0.475 (1)	0.705 (2)	0.17 (2)
N	0.607 (2)	0.9265 (5)	0.607 (3)	0.086 (5)
O1	0.522 (2)	0.9657 (7)	0.501 (2)	0.15 (1)
O2	0.659 (2)	0.966 (1)	0.702 (2)	0.14 (1)

Table 2. *Geometric parameters* (Å, °)

C1—C2	1.38 (3)	C5—C13	1.54 (1)
C1—C6	1.35 (2)	C7—C8	1.47 (4)
C1—C7	1.55 (3)	C7—C9	1.54 (3)
C2—C3	1.41 (3)	C10—C11	1.55 (3)
C2—N	1.488 (9)	C10—C12	1.49 (3)
C3—C4	1.42 (2)	C13—C14	1.42 (3)
C3—C10	1.51 (3)	C13—C15	1.30 (4)
C4—C5	1.41 (4)	N—O1	1.29 (3)
C5—C6	1.35 (3)	N—O2	1.14 (3)
C2—C1—C6	116 (2)	C1—C7—C8	114 (2)
C2—C1—C7	121 (1)	C1—C7—C9	106 (2)
C6—C1—C7	123 (2)	C8—C7—C9	110 (2)
C1—C2—C3	125 (1)	C3—C10—C11	110 (1)
C1—C2—N	115 (2)	C3—C10—C12	113 (2)
C3—C2—N	120 (2)	C3—C10—H10	108 (7)
C2—C3—C4	116 (2)	C11—C10—C12	110 (2)
C2—C3—C10	124 (1)	C5—C13—C14	114 (2)
C4—C3—C10	120 (2)	C5—C13—C15	122 (3)
C3—C4—C5	119 (2)	C14—C13—C15	118 (2)
C4—C5—C6	121 (1)	C2—N—O1	111 (2)
C4—C5—C13	111 (2)	C2—N—O2	122 (2)
C6—C5—C13	128 (3)	O1—N—O2	124 (1)
C1—C6—C5	123 (2)		

The compound was synthesized according to literature procedures (Newton, 1943). Absent reflections *hkl*, $h + k + l = 2n + 1$ and *h*0*l*, $h = 2n + 1$, indicated the non-standard space group *Ia* [No. 9, standard setting *Cc*, *International Tables for X-ray Crystallography* (1965, Vol. I)]. The structure was solved by direct methods (*SIMPEL*; Schenk & Hall, 1990) and refined by full-matrix least-squares calculations with anisotropic temperature factors for the non-H atoms and isotropic temperature factors for the H atoms kept fixed at 0.08 Å^2. The H atoms were positioned geometrically and included as riding atoms in the structure-factor calculations. Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CELCON* program comparable to *Xtal LATCON* (Hall & Stewart, 1990). Data reduction: *Xtal ADDREF*. Program(s) used to solve structure: *Xtal SIMPEL*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *Xtal BONDLA*, *CIFIO*.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71333 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1053]

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Structure of 6-*tert*-Butyl-3,3-dimethyl-3*H*-indolium-1-oxide

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Abstract

Crystallographic characterization of 6-*tert*-butyl-3,3-dimethyl-3*H*-indolium-1-oxide has shown that the bicyclic ring moiety is almost planar. The N—O bond of 1.29 (1) Å has mainly single-bond character.

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