Program used for data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Programs used for data reduction and structure resolution: *SDP* software (Frenz, 1978) *via* direct methods *MULTAN* (Main *et al.*, 1980), completed by difference Fourier synthesis.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: PA1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,5-Di-*tert*-butyl-2,4-dinitrobenzene, $C_{14}H_{20}N_2O_4$

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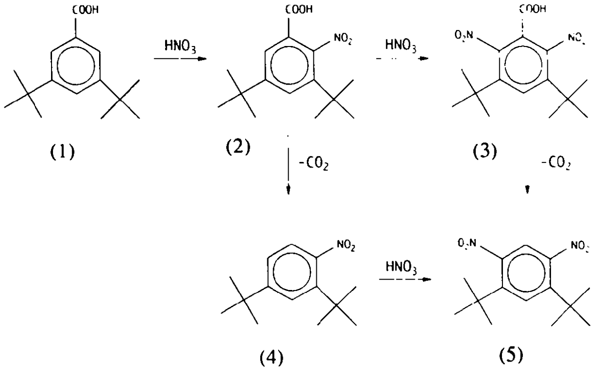
Abstract

The present crystal study was undertaken to gain a better insight into the geometry of the nitro group. The nitro groups in 1,5-di-*tert*-butyl-2,4-dinitrobenzene are rotated by approximately 65° out of the plane of the aromatic ring.

Comment

Crystals suitable for X-ray diffraction were grown *in vacuo* at 473 K by sublimation of a crude sample of 3,5-di-*tert*-butyl-2-nitrobenzoic acid (2) prepared according to Franck & Leser (1970); this crude sample probably also contained compound (3). The m.p. of the title compound (5) was 432–433 K (*cf.* 436.5–437 K; Knoester, De Konig, Verkade & Wepster, 1967). The crystals were of poor quality.



The maximum distance of a ring atom from the best plane through the benzene ring is 0.019 (5) Å. The nitro groups are tilted by 63.0 (2) and 68.0 (2)° out of the plane of the aromatic ring, whereas an average of 35 (2)° is reported for a set of nitrobenzenes with only one *ortho* substituent (De Ridder, 1992). In the title compound, the endocyclic angles are increased at the substituent sites carrying the nitro groups and decreased at the sites carrying the alkyl groups, in accordance with the observations of Domenicano & Murray-Rust (1979).

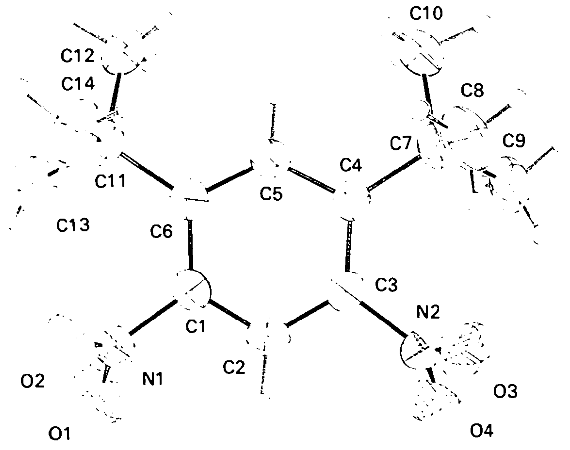


Fig. 1. *PLATON* (Spek, 1990) drawing showing the numbering system for the title compound. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are shown but not labelled.

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Experimental

Crystal data

$C_{14}H_{20}N_2O_4$
$M_r = 280.32$
Monoclinic
$P2_1/n$
$a = 9.446$ (1) Å
$b = 10.817$ (3) Å
$c = 15.100$ (2) Å
$\beta = 101.16$ (1)°
$V = 1513.7$ (5) Å^3
$Z = 4$
$D_x = 1.23$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 40.21$–43.74°
$\mu = 0.71$ mm^{-1}
$T = 247$ K
Block
0.63 × 0.43 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.47$, $T_{\max} = 1.00$
2719 measured reflections
2565 independent reflections

2026 observed reflections [$I > 2.5\sigma(I)$]
$\theta_{\max} = 64.91°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -17 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.070$
$wR = 0.087$
$S = 0.235$
2026 reflections
262 parameters
All H-atom parameters refined
$w = 1/(6.06 + 0.0037F^2)$
$(\Delta/\sigma)_{\max} = 0.048$

$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 228 (102)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

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

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

	x	y	z	$U_{\rm eq}$
C1	0.0620 (3)	0.4255 (3)	0.1766 (2)	0.038 (1)
C2	−0.0579 (3)	0.3550 (3)	0.1420 (2)	0.041 (1)
C3	−0.1274 (3)	0.2939 (3)	0.2011 (2)	0.037 (1)
C4	−0.0792 (3)	0.2946 (3)	0.2945 (2)	0.038 (1)
C5	0.0451 (3)	0.3647 (3)	0.3231 (2)	0.040 (1)
C6	0.1201 (3)	0.4322 (3)	0.2682 (2)	0.037 (1)
C7	−0.1517 (4)	0.2292 (3)	0.3647 (2)	0.046 (2)
C8	−0.2719 (6)	0.3120 (5)	0.3857 (4)	0.077 (3)
C9	−0.2143 (5)	0.1021 (4)	0.3327 (3)	0.066 (2)
C10	−0.0424 (6)	0.2055 (6)	0.4521 (3)	0.082 (3)
C11	0.2573 (3)	0.5047 (3)	0.3113 (2)	0.045 (2)
C12	0.3270 (5)	0.4481 (5)	0.4021 (3)	0.074 (3)
C13	0.3729 (4)	0.5017 (5)	0.2525 (3)	0.070 (3)
C14	0.2144 (5)	0.6384 (4)	0.3270 (4)	0.075 (3)
N1	0.1178 (3)	0.4957 (3)	0.1070 (2)	0.051 (2)
N2	−0.2590 (3)	0.2295 (3)	0.1561 (2)	0.052 (2)
O1	0.1597 (3)	0.4372 (3)	0.0485 (2)	0.078 (2)
O2	0.1136 (3)	0.6075 (3)	0.1088 (2)	0.075 (2)
O3	−0.3754 (3)	0.2703 (3)	0.1680 (2)	0.078 (2)
O4	−0.2470 (3)	0.1435 (3)	0.1073 (2)	0.081 (2)

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

C1—C2	1.381 (4)	C7—C8	1.527 (7)
C1—C6	1.387 (4)	C7—C9	1.536 (5)
C1—N1	1.475 (4)	C7—C10	1.532 (5)
C2—C3	1.375 (5)	C11—C12	1.528 (5)
C3—C4	1.396 (4)	C11—C13	1.535 (6)
C3—N2	1.471 (4)	C11—C14	1.533 (6)
C4—C5	1.394 (4)	N1—O1	1.213 (5)
C4—C7	1.541 (5)	N1—O2	1.211 (4)
C5—C6	1.396 (5)	N2—O3	1.229 (4)
C6—C11	1.547 (4)	N2—O4	1.206 (4)
C2—C1—C6	122.9 (3)	C4—C7—C10	110.7 (3)
C2—C1—N1	113.2 (3)	C8—C7—C9	109.5 (3)
C6—C1—N1	123.8 (3)	C8—C7—C10	108.9 (4)
C1—C2—C3	118.6 (3)	C9—C7—C10	106.0 (3)
C2—C3—C4	123.3 (3)	C6—C11—C12	110.8 (3)
C2—C3—N2	113.3 (3)	C6—C11—C13	112.2 (3)
C4—C3—N2	123.4 (3)	C6—C11—C14	108.6 (3)
C3—C4—C5	113.9 (3)	C12—C11—C13	106.2 (3)
C3—C4—C7	126.2 (3)	C12—C11—C14	108.7 (4)
C5—C4—C7	119.8 (3)	C13—C11—C14	110.4 (4)
C4—C5—C6	126.5 (3)	C1—N1—O1	117.5 (3)
C1—C6—C5	114.6 (3)	C1—N1—O2	118.7 (3)
C1—C6—C11	125.7 (3)	O1—N1—O2	123.7 (3)
C5—C6—C11	119.7 (3)	C3—N2—O3	117.5 (3)
C4—C7—C8	108.7 (3)	C3—N2—O4	118.5 (3)
C4—C7—C9	113.0 (3)	O3—N2—O4	123.9 (3)

The structure was solved by direct methods (*Xtal*3.2 *SIMPEL*; Hall, Flack & Stewart, 1992) and refined by full-matrix least-squares calculations with anisotropic displacement factors for the non-H atoms and isotropic displacement factors for the H atoms. The H atoms were positioned geometrically and included as riding atoms in the structure-factor calculations.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1990). Cell refinement: *CELCON* (comparable to *Xtal*3.2 *LATCON*). Data reduction: *Xtal*3.2 *ADDREF*. Program(s) used to solve structure: *Xtal*3.2 *SIMPEL*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *Xtal*3.2 *BONDLA*, *CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 262–265

Novel *N*-Acyl α-Azidopyrrolidines (*N*-Acyliminium-Ion Precursors)

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(*Received* 11 *March* 1994; *accepted* 23 *May* 1994)

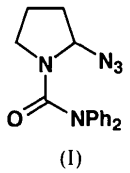
Abstract

As an alternative to the electrochemical procedure [Shono (1984). *Tetrahedron*, **40**, 811–850], *N*-acyliminium-ion precursors may be generated utilizing novel hypervalent iodine chemistry. The crystal structures of 2-azido-*N*,*N*-diphenylpyrrolidine-1-carboxamide, $C_{17}H_{17}N_5O$, and 2,5-diazido-*N*-(3,4,5-trimethoxybenzoyl)pyrrolidine, $C_{14}H_{17}N_7O_4$, are reported. In both instances the pyrrolidine ring is found in the half-chair conformation. The azido groups are non-linear with an average bond angle of 172.9 (1)°.

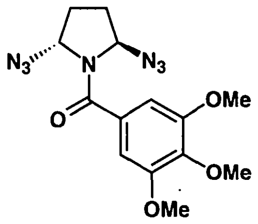
Comment

The oxidation of amides leading to the generation of *N*-acyliminium-ion precursors is a transformation which has broad synthetic utility. This reactive intermediate has found applications in many fields including alkaloid synthesis and lactam-based peptide mimetics (Hiemstra & Speckamp, 1988; Hart, 1988; Baldwin, Hulme, Edwards, Schofield & Parkes, 1993; Wong & Moeller, 1993). We have reported recently the oxidation of amides, carbamates and ureas using iodosobenzene $(PhIO)_n$ or *o*-iodosobenzoic acid with trimethylsilylazide ($TMSN_3$) in dichloromethane (Magnus, Hulme & Weber, 1994), to give *N*-acyliminium-ion precursors with an α-azido substituent (Clauss, Grimm & Prossel, 1974). Interestingly, there are no reports of crystal structures having the α-azidopyrrolidine moiety in the Cambridge Structural Database (1993).

The pyrrolidine rings each have the half-chair conformation in 2-azido-*N*,*N*-diphenylpyrrolidine-1-carboxamide, (I), and 2,5-diazido-*N*-(3,4,5-trimethoxybenzoyl)pyrrolidine, (II). The azido groups are decidedly non-linear. The angle at the central N atom of the azide group in (I) is 171.7 (2)° and those in (II) are 173.9 (3) and 173.1 (3)°. For (I), the geometry around the pyrrolidinic N atom is slightly pyramidalized with N1 being 0.132 (2) Å from the plane through C2, C5 and C9. The carbonyl-C9-to-N-atom bond length is slightly shorter for the pyrrolidinic N atom [1.369 (3) Å] than for the amino N atom [1.403 (2) Å].



(I)



(II) ,

For (II), N1 is only 0.041 (2) Å from the plane through C2, C5 and C12, and the carbonyl group (N1, C12, O13, C14) is nearly orthogonal to the phenyl ring (C15–C19) forming a dihedral angle of 69.0 (1)°. The carbonyl-to-phenyl-ring C—C bond length is

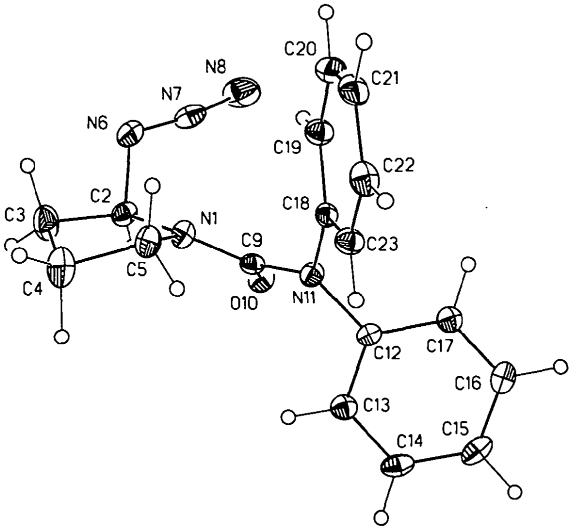


Fig. 1. Displacement ellipsoid plot of (I) showing the atom-labeling scheme; ellipsoids are scaled to the 30% probability level. H atoms are represented as spheres of arbitrary radii.

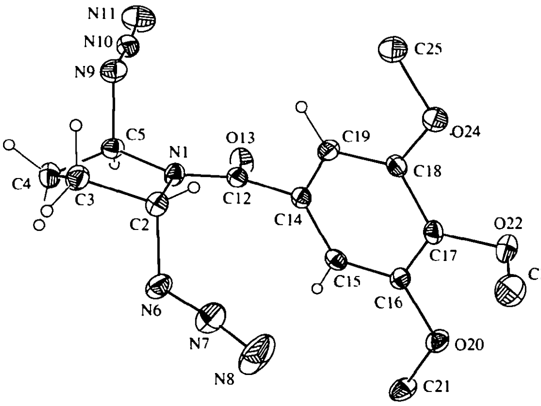


Fig. 2. Displacement ellipsoid plot of (II) showing the atom-labeling scheme; ellipsoids are scaled to the 30% probability level. H atoms are represented as spheres of arbitrary radii.

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