

planar with a maximum deviation of 0.11 (6) Å from the least-squares plane, and the N(1) and C(16) atoms deviate from the plane by 0.53 (7) and 0.46 (7) Å, respectively. The C(13), C(14) and C(15) atoms of the propyl group, and the N(1) and C(17) atoms are planar within 0.05 Å. The two zigzag chains cross at the N(1) atom with a dihedral angle of 98.4 (5)°.

The molecular packing is illustrated in Fig. 2. The long hydrocarbon chains have an antiparallel arrangement forming a layer parallel to the (001) plane. The direction of the long-chain axis is approximately parallel to $[\bar{3}01]$. The chain packing may be expressed by a triclinic subcell with dimensions $a_s = 2.535$ (2), $b_s = 4.20$ (1), $c_s = 4.88$ (1) Å, $\alpha_s = 75.4$ (1), $\beta_s = 88.0$ (1), $\gamma_s = 63.2$ (1)°. These values are comparable with those of the triclinic subcells observed in other crystals (Abrahamsson, Dahlén, Löfgren & Pascher, 1978), and they agree well with $a_s = 2.54$, $b_s = 4.30$, $c_s = 4.45$ Å, $\alpha_s = 78$, $\beta_s = 90$, $\gamma_s = 72.5$ ° given for ideal packing of infinite hydrocarbon chains (Kitaigorodsky, 1973). The Br ions and water molecules are located between the hydrocarbon layers, held together by hydrogen bonds. The two Br ions and two water molecules form an isolated anionic group with a square shape. The Br...O hydrogen-bond distances are 3.326 (3) and 3.354 (4) Å, and the O...Br...O and Br...O...Br angles are 72.0 (1) and 108.0 (1)°. These values are in good agreement with those of a similar

group found in decamethylenehexamethyldiammonium dibromide monohydrate (Lonsdale, Milledge & Pant, 1965). The plane normal of the anionic group is parallel to $(\bar{2}03)$, and makes an angle of 28 (2)° with the long-chain axis. The anionic group is surrounded by ammonium groups with shortest Br...N distance 4.526 (5) Å and shortest O...N distance 4.221 (5) Å.

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Structure–Reactivity Correlations of Aromatic Nitro Compounds: Structures of 1-*tert*-Butyl-3,5-dimethyl-2,4,6-trinitrobenzene (I) and 1-*tert*-Butyl-3,4,5-trimethyl-2,6-dinitrobenzene (II)

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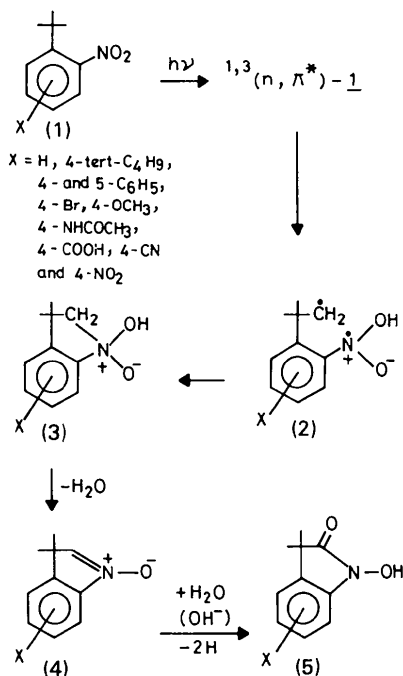
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Abstract. (I): $C_{12}H_{15}N_3O_6$, $M_r = 297.28$, monoclinic, $P2_1/a$, $a = 9.226$ (1), $b = 11.104$ (1), $c = 14.622$ (1) Å, $\beta = 107.79$ (1)°, $V = 1426.3$ (2) Å³, $Z = 4$, $D_m = 1.365$ (floatation in KI), $D_x = 1.384$ g cm⁻³, $\mu(\text{Mo } K\alpha)$, $\lambda = 0.7107$ Å) = 0.72 cm⁻¹, $F(000) = 624.0$, $T = 293$ K, $R = 5.0\%$ for 1591 significant reflections. (II): $C_{13}H_{18}N_2O_4$, $M_r = 266.30$, monoclinic, $P2_1/n$, $a = 9.610$ (1), $b = 14.619$ (1), $c = 11.006$ (1) Å, $\beta = 115.43$ (1)°, $V = 1396.3$ (1) Å³, $Z = 4$, $D_m = 1.243$

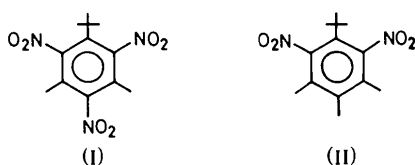
(floatation in KI), $D_x = 1.267$ g cm⁻³, $\mu(\text{Cu } K\alpha)$, $\lambda = 1.5418$ Å) = 6.99 cm⁻¹, $F(000) = 568.0$, $T = 293$ K, $R = 5.9\%$ for 1869 significant reflections. Both (I) and (II) crystallize in a common conformation for the *tert*-butyl group and the two *ortho* nitro groups, where the latter are almost perpendicular to the plane of the benzene ring. The solid-state photoreactivity of these compounds, in which the O of the nitro group intramolecularly abstracts an H from the *tert*-butyl

group, is explained in terms of the intramolecular geometry ($O\cdots H$, $C\cdots N$ distances and $C-H\cdots O$, $N-O\cdots H$ angles) and the intermolecular packing.

Introduction. Certain 1-*tert*-butyl-2-nitrobenzenes (I) upon $n\pi^*$ excitation by UV light ($\lambda \geq 280$ nm) undergo an intramolecular H-abstraction (Döpp, 1971*a,b*; Döpp & Brugger, 1979). This primary reaction initiates a sequence of events [(2)→(3)→(4)] leading to 3*H*-indole 1-oxides as the final products.



Owing to both their thermal and their photochemical instability, the *N*-oxides (4), however, have not been isolated. Instead, in most cases, hydroxamic acids (5), derived from the hydrates of (4) by dehydrogenation, are generally obtained along with products of deoxygenation or isomerization of (4). Solid representatives of (1) (Döpp, 1971*b,c*, and unpublished results) as well as compounds (I) and (II) have been successfully converted into hydroxamic acids (5) by irradiation of their crystals followed by alkaline oxidative work-up (Döpp & Sailer, 1975*a,b*).



(I) and (II) do not undergo intramolecular H-abstraction from the benzylic methyl groups, a normal photoreaction of *o*-nitrotoluenes (Morrison, 1969), to any measurable extent. Instead, intramolecular abstraction from the nonactivated β -position is clearly preferred. We have carried out X-ray crystallographic studies on (I) and (II) with the aim of deriving conclusions regarding the H that is being abstracted and the favourable directionality for the abstraction, as seen from the ground-state geometry of the molecule.

Experimental. Single crystals of (I) and (II) grown from ethyl acetate and benzene respectively by slow evaporation. Crystals approximately $0.31 \times 0.09 \times 0.09$ mm (I) and $0.12 \times 0.25 \times 0.24$ mm (II). Preliminary Weissenberg photographs indicated both crystals to be monoclinic. Nonius CAD-4 diffractometer. Lattice parameters refined by least-squares fit to settings of 25 accurately centred reflections in the range $13 < \theta < 20^\circ$ for (I) and $40 < \theta < 50^\circ$ for (II). Intensity data collected using graphite-monochromatized $\text{Mo K}\alpha$ radiation for (I), $\theta \leq 30^\circ$, and $\text{Cu K}\alpha$ radiation for (II), $\theta \leq 75^\circ$, scan speed 1° min^{-1} , $\omega/2\theta$ mode. For (I), three standard reflections ($\bar{1}\bar{2}8$, $\bar{3}\bar{2}\bar{5}$ and $\bar{3}\bar{4}4$) showed little or no decay throughout data collection. 4577 reflections collected, 1591 significant [$I \geq 2.25\sigma(I)$], where $\sigma^2(I) = T + 2B + [0.04(T-B)]^2$, T = total peak count, and B = time-averaged background. h 0 to 12, k 0 to 15, l -20 to 20. For (II), the standard reflections were $1\bar{9}2$, $0\bar{1}7$ and 404 . 2867 independent reflections, 1869 with $I \geq 3.0\sigma(I)$. h 0 to 12, k 0 to 18 and l -13 to 13. Data corrected for Lorentz and polarization factors, but not for absorption. Structures solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement was carried out for a scale factor, positional and anisotropic thermal parameters of nonhydrogen atoms and positional and isotropic thermal parameters of H atoms (located from a difference map). *SHELX76* (Sheldrick, 1976) was used for the full-matrix least-squares refinement. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1.5965/(\sigma^2|F| + 0.002|F|^2)$ for (I) and $w = 4.0125/(\sigma^2|F| + 0.000375|F|^2)$ for (II). At the end of the last cycle of refinement, $R = 0.050$, $wR = 0.071$, $S = 1.64$ for 1591 reflections, 250 variables for (I) and $R = 0.059$, $wR = 0.078$, $S = 4.91$ for 1869 reflections, 244 variables for (II). Max. Δ/σ for nonhydrogen atoms, 0.020 for (I) and 0.018 for (II). Final difference maps of both (I) and (II) were featureless. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Illustrations were made by *ORTEP* (Johnson, 1976) and *PLUTO78* (Motherwell & Clegg, 1978). All computations were carried out on the DEC-1090 system at the Indian Institute of Science.

Discussion. The final atomic parameters for compounds (I) and (II) are given in Tables 1 and 2 respectively and the numbering schemes are illustrated in Figs. 1 and 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42675 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^4$) for nonhydrogen atoms in compound (I) with their e.s.d.'s in parentheses

The temperature factor is of the form:

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	8129 (3)	425 (2)	7284 (2)	351 (8)
C(2)	7893 (3)	561 (2)	8182 (2)	361 (8)
C(3)	7835 (3)	1642 (2)	8659 (2)	404 (9)
C(4)	8010 (3)	2672 (2)	8161 (2)	397 (9)
C(5)	8265 (3)	2677 (2)	7285 (2)	391 (9)
C(6)	8307 (3)	1540 (2)	6877 (2)	368 (8)
C(7)	8129 (3)	-808 (2)	6778 (2)	431 (9)
C(8)	6502 (4)	-1045 (4)	6138 (3)	635 (13)
C(9)	9204 (4)	-826 (3)	6151 (3)	627 (12)
C(10)	8681 (6)	-1860 (3)	7480 (3)	774 (15)
C(11)	8471 (4)	3831 (3)	6782 (3)	583 (12)
C(12)	7586 (5)	1698 (3)	9626 (2)	584 (12)
N(13)	8504 (3)	1613 (2)	5914 (2)	492 (9)
N(14)	7586 (3)	-493 (2)	8713 (2)	497 (9)
N(15)	7881 (3)	3841 (2)	8604 (2)	505 (9)
O(13)	7363 (3)	1495 (2)	5217 (1)	646 (9)
O(14)	9770 (3)	1834 (2)	5859 (2)	683 (9)
O(15)	6295 (3)	-894 (2)	8459 (3)	668 (10)
2O(13)	8626 (3)	-861 (2)	9391 (2)	696 (9)
2O(14)	6661 (3)	4327 (2)	8367 (2)	932 (11)
2O(15)	8978 (3)	4248 (2)	9198 (2)	924 (11)

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^4$) for nonhydrogen atoms in compound (II) with their e.s.d.'s in parentheses

The temperature factor is of the form:

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	11205 (2)	1762 (1)	3964 (2)	487 (5)
C(2)	10886 (2)	967 (1)	3182 (2)	519 (5)
C(3)	9589 (2)	409 (1)	2817 (2)	579 (6)
C(4)	8500 (2)	638 (1)	3272 (2)	569 (6)
C(5)	8747 (2)	1395 (1)	4103 (2)	539 (5)
C(6)	10059 (2)	1918 (1)	4399 (2)	500 (5)
C(7)	12661 (2)	2373 (2)	4341 (2)	664 (6)
C(8)	12335 (4)	3399 (2)	4477 (3)	1030 (8)
C(9)	13289 (3)	2369 (2)	3262 (3)	958 (7)
C(10)	13926 (3)	2028 (2)	5660 (3)	1083 (7)
C(11)	7602 (3)	1645 (2)	4652 (2)	819 (7)
C(12)	7041 (3)	76 (2)	2865 (3)	926 (7)
C(13)	9370 (3)	-428 (2)	1946 (3)	910 (7)
N(14)	10188 (2)	2693 (1)	5303 (2)	733 (6)
N(15)	11980 (2)	634 (1)	2659 (2)	757 (6)
O(14)	10998 (3)	2584 (1)	6499 (2)	1016 (6)
2O(14)	9411 (3)	3376 (1)	4818 (2)	1085 (7)
O(15)	11685 (2)	784 (2)	1490 (2)	1061 (6)
2O(15)	13087 (2)	195 (2)	3436 (2)	1102 (7)

Structure-reactivity correlation

The results pertaining to compound (I) are discussed in detail whereas those pertaining to (II) are suitably highlighted.

On the basis of the observed O...H distances in (I), it may be concluded that eight possibilities involving the H atoms of the *tert*-butyl group which could be abstracted by the O atoms of the two *ortho* nitro groups exist (Table 3). Since this primary photoprocess involves the $n\pi^*$ excited state of the nitro group, the expected ideal geometrical requirement for such a

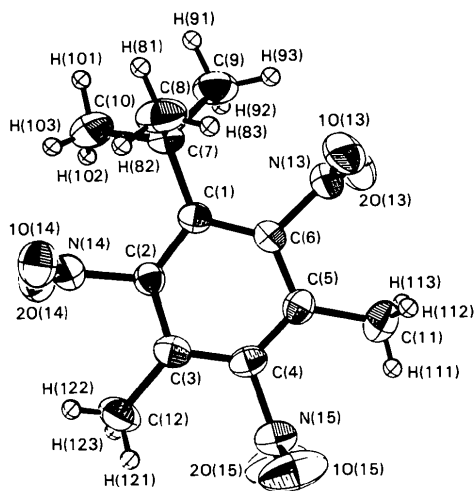


Fig. 1. ORTEP projection of compound (I) with the atom-numbering scheme and thermal ellipsoids at the 50% probability level. The H atoms are represented as spheres of arbitrary size.

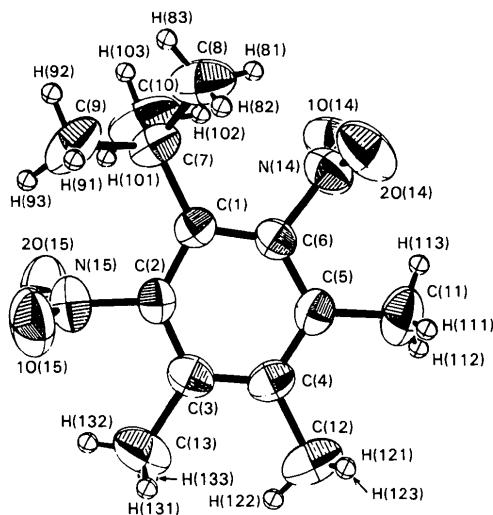


Fig. 2. ORTEP projection of compound (II) with the atom-numbering scheme and thermal ellipsoids at the 50% probability level. The H atoms are represented as spheres of arbitrary size.

reaction would correspond to 180° and 90° for the C—H...O and N—O...H angles respectively. Consideration of this criterion reduces the above eight possibilities to two, namely H(83) could be abstracted by 1O(13) or H(82) by 1O(14) (Table 3). The next step in the reaction is the C and N radical combination. However, it is observed that the distances C(8)...N(13) and C(8)...N(14) are too large for such a combination (Table 3). In order for the radical centres to combine, the *tert*-butyl group has to experience a rotation about the C(1)—C(7) bond. Therefore, it is necessary to know whether such a rotation is feasible in the crystals of (I). It is relevant to mention at this stage that there is a non-rigid librational motion about the vectors C(1)—C(7), C(2)—N(14) and C(6)—N(13) with amplitudes 6.2 (5), 6.7 (11) and 6.8 (11)° respectively. The thermal motion analysis program *THMB* developed by Trueblood (1982) was used for this analysis. Rotation in the positive direction would bring C(8) into the proximity of N(13) and rotation in the negative direction would bring C(8) nearer to N(14). The H atoms that would be abstracted in these two cases are H(83) by 1O(13) and H(82) by 1O(14) respectively. Intermolecular short contacts were calculated for the rotation of the *tert*-butyl group in both positive and negative directions. Table 5 presents the results of this analysis in terms of the quantity $D = \sum (d_o - d_c)^2$, where d_o is the standard value of the sum of the van der Waals radii for different atom pairs, and d_c the corresponding intermolecular short contact on rotation of the *tert*-butyl group. This criterion was employed by Williams (1969) for the solution of crystal structures with known molecular structures and lattice dimensions. The greater value of D for rotation in the negative direction suggests that the rotation in the positive direction is more favourable. It seems, therefore, reasonable to conclude that in the crystals of (I), the most probable reaction is abstraction of H(83) by 1O(13) followed by combination of C(8) and N(13) radicals.

Applying similar considerations, it was inferred that in the case of (II), the most probable reaction in the solid state involves abstraction of H(102) by 1O(14), followed by bond formation between C(10) and N(14) radicals leading to the product. The intramolecular geometrical parameters are given in Table 4 and the

values of D for rotation of the *tert*-butyl group are recorded in Table 5. The non-rigid libration amplitudes about the vectors C(1)—C(7), C(2)—N(15) and C(6)—N(14) in (II) are 7.0 (5), 8.8 (9), 8.0 (10)° respectively.

Table 3. *Intramolecular geometrical parameters for compound (I) with e.s.d.'s in parentheses*

O...H contacts (Å)			
1O(13)...H(83)	2.58 (3)	2O(13)...H(93)	2.45 (3)
1O(14)...H(82)	2.74 (4)	1O(14)...H(103)	2.42 (3)
1O(13)...H(93)	2.41 (3)	2O(14)...H(102)	2.57 (4)
2O(13)...H(92)	2.90 (3)	2O(14)...H(103)	2.68 (3)
C...N contacts (Å)			
C(8)...N(13)	3.550 (5)	C(9)...N(13)	2.781 (4)
C(8)...N(14)	3.640 (5)	C(10)...N(14)	2.773 (6)
C—H...O angles (°)			
C(8)—H(83)...1O(13)	136 (2)	C(9)—H(93)...2O(13)	113 (2)
C(8)—H(82)...1O(14)	130 (2)	C(10)—H(103)...1O(14)	130 (2)
C(9)—H(93)...1O(13)	124 (2)	C(10)—H(102)...2O(14)	106 (2)
C(9)—H(92)...2O(13)	87 (2)	C(10)—H(103)...2O(14)	100 (2)
N—O...H angles (°)			
N(13)—1O(13)...H(83)	100.4 (7)	N(13)—2O(13)...H(93)	65.9 (8)
N(14)—1O(14)...H(82)	101.4 (7)	N(14)—1O(14)...H(103)	71.5 (8)
N(13)—1O(13)...H(93)	67.5 (8)	N(14)—2O(14)...H(102)	83.1 (7)
N(13)—2O(13)...H(92)	82.9 (6)	N(14)—2O(14)...H(103)	60.7 (7)
Ideal value of C—H...O = 180°			
Ideal value of N—O...H = 90°			

Table 4. *Intramolecular geometrical parameters for compound (II) with e.s.d.'s in parentheses*

O...H contacts (Å)			
1O(14)...H(102)	2.51 (1)	2O(14)...H(82)	2.67 (2)
2O(15)...H(101)	2.67 (1)	1O(15)...H(91)	2.89 (2)
1O(14)...H(81)	2.31 (2)	1O(15)...H(93)	2.49 (1)
2O(14)...H(81)	2.46 (1)	2O(15)...H(93)	2.30 (2)
C...N contacts (Å)			
C(10)...N(14)	3.576 (4)	C(8)...N(14)	2.786 (5)
C(10)...N(15)	3.641 (3)	C(9)...N(15)	2.782 (3)
C—H...O angles (°)			
C(10)—H(102)...1O(14)	140 (1)	C(8)—H(82)...2O(14)	97 (1)
C(10)—H(101)...2O(15)	134 (1)	C(9)—H(91)...1O(15)	85 (1)
C(8)—H(81)...1O(14)	137 (1)	C(9)—H(93)...1O(15)	103 (1)
C(8)—H(81)...2O(14)	106 (1)	C(9)—H(93)...2O(15)	129 (1)
N—O...H angles (°)			
N(14)—1O(14)...H(102)	99.2 (3)	N(14)—2O(14)...H(82)	83.4 (3)
N(15)—2O(15)...H(101)	100.0 (3)	N(15)—1O(15)...H(91)	86.0 (3)
N(14)—1O(14)...H(81)	67.5 (4)	N(15)—1O(15)...H(93)	62.8 (4)
N(14)—2O(14)...H(81)	61.0 (3)	N(15)—2O(15)...H(93)	70.4 (4)
Ideal value of C—H...O = 180°			
Ideal value of N—O...H = 90°			

Table 5. *Sum of $(d_o - d_c)^2$ for rotation of the *tert*-butyl group*

Compound (I)				Compound (II)			
Rotation (positive direction)		Rotation (negative direction)		Rotation (positive direction)		Rotation (negative direction)	
Interval (°)	$D = \sum (d_o - d_c)^2$	Interval (°)	$D = \sum (d_o - d_c)^2$	Interval (°)	$D = \sum (d_o - d_c)^2$	Interval (°)	$D = \sum (d_o - d_c)^2$
5	0	-5	0	5	0.0081	-5	0
10	0	-10	0.0001	10	0.0309	-10	0
15	0	-15	0.0169	15	0.0622	-15	0.0016
20	0	-20	0.0562	20	0.0835	-20	0.0102
25	0	-25	0.1356	25	0.0978	-25	0.0451
30	0.0016	-30	0.2440	30	0.0982	-30	0.0916

Table 6. Selected bond distances (Å) and angles (°) involving nonhydrogen atoms in compound (I) with *e.s.d.*'s in parentheses

C(1)–C(2)	1.403 (4)	C(6)–N(13)	1.476 (4)
C(1)–C(6)	1.405 (3)	C(7)–C(8)	1.530 (5)
C(1)–C(7)	1.556 (3)	C(7)–C(9)	1.543 (5)
C(2)–C(3)	1.397 (3)	C(7)–C(10)	1.536 (4)
C(2)–N(14)	1.479 (3)	N(13)–O(13)	1.228 (3)
C(3)–C(4)	1.391 (3)	N(13)–O(13)	1.220 (4)
C(3)–C(12)	1.501 (4)	N(14)–O(14)	1.218 (4)
C(4)–C(5)	1.371 (4)	N(14)–O(14)	1.220 (4)
C(4)–N(15)	1.472 (3)	N(15)–O(15)	1.200 (4)
C(5)–C(6)	1.402 (3)	N(15)–O(15)	1.202 (4)
C(5)–C(11)	1.518 (4)		
C(2)–C(1)–C(6)	111.9 (2)	C(5)–C(6)–N(13)	112.6 (2)
C(2)–C(1)–C(7)	124.2 (2)	C(1)–C(7)–C(8)	107.4 (2)
C(6)–C(1)–C(7)	123.8 (2)	C(1)–C(7)–C(9)	112.8 (2)
C(1)–C(2)–C(3)	126.9 (2)	C(1)–C(7)–C(10)	113.6 (3)
C(1)–C(2)–N(14)	121.0 (2)	C(8)–C(7)–C(9)	108.9 (3)
C(3)–C(2)–N(14)	112.0 (2)	C(8)–C(7)–C(10)	109.9 (3)
C(2)–C(3)–C(4)	114.6 (2)	C(9)–C(7)–C(10)	104.2 (3)
C(2)–C(3)–C(12)	123.1 (3)	C(6)–N(13)–O(13)	117.5 (2)
C(4)–C(3)–C(12)	122.3 (3)	C(6)–N(13)–O(13)	118.3 (2)
C(3)–C(4)–C(5)	124.9 (2)	IO(13)–N(13)–O(13)	124.2 (3)
C(3)–C(4)–N(15)	117.2 (2)	C(2)–N(14)–O(14)	117.1 (3)
C(5)–C(4)–N(15)	117.9 (2)	C(2)–N(14)–O(14)	117.5 (3)
C(4)–C(5)–C(6)	115.4 (2)	IO(14)–N(14)–O(14)	125.3 (3)
C(4)–C(5)–C(11)	122.6 (3)	C(4)–N(15)–O(15)	117.7 (3)
C(6)–C(5)–C(11)	122.0 (3)	C(4)–N(15)–O(15)	119.1 (3)
C(1)–C(6)–C(5)	126.3 (2)	IO(15)–N(15)–O(15)	123.2 (3)
C(1)–C(6)–N(13)	121.1 (2)		

Table 7. Selected bond distances (Å) and angles (°) involving nonhydrogen atoms in compound (II) with *e.s.d.*'s in parentheses

C(1)–C(2)	1.400 (2)	C(5)–C(11)	1.510 (4)
C(1)–C(6)	1.395 (3)	C(6)–N(14)	1.477 (2)
C(1)–C(7)	1.559 (3)	C(7)–C(8)	1.553 (4)
C(2)–C(3)	1.396 (3)	C(7)–C(9)	1.546 (4)
C(2)–N(15)	1.481 (3)	C(7)–C(10)	1.524 (4)
C(3)–C(4)	1.381 (3)	N(14)–O(14)	1.218 (3)
C(3)–C(13)	1.512 (3)	N(14)–O(14)	1.224 (3)
C(4)–C(5)	1.390 (2)	N(15)–O(15)	1.213 (3)
C(4)–C(12)	1.517 (4)	N(15)–O(15)	1.222 (3)
C(5)–C(6)	1.388 (3)		
C(2)–C(1)–C(6)	110.5 (2)	C(1)–C(6)–C(5)	126.9 (2)
C(2)–C(1)–C(7)	125.0 (2)	C(1)–C(6)–N(14)	120.4 (2)
C(6)–C(1)–C(7)	124.4 (2)	C(5)–C(6)–N(14)	112.7 (2)
C(1)–C(2)–C(3)	126.5 (2)	C(1)–C(7)–C(8)	112.6 (2)
C(1)–C(2)–N(15)	120.5 (2)	C(1)–C(7)–C(9)	113.3 (2)
C(3)–C(2)–N(15)	113.0 (2)	C(1)–C(7)–C(10)	108.8 (2)
C(2)–C(3)–C(4)	118.4 (2)	C(8)–C(7)–C(9)	103.8 (2)
C(2)–C(3)–C(13)	121.3 (2)	C(8)–C(7)–C(10)	109.8 (2)
C(4)–C(3)–C(13)	120.3 (2)	C(9)–C(7)–C(10)	108.4 (2)
C(3)–C(4)–C(5)	119.3 (2)	C(6)–N(14)–O(14)	117.2 (2)
C(3)–C(4)–C(12)	120.6 (2)	C(6)–N(14)–O(14)	118.2 (2)
C(5)–C(4)–C(12)	120.0 (2)	IO(14)–N(14)–O(14)	124.4 (2)
C(4)–C(5)–C(6)	118.3 (2)	C(2)–N(15)–O(15)	118.1 (2)
C(4)–C(5)–C(11)	120.5 (2)	C(2)–N(15)–O(15)	116.8 (2)
C(6)–C(5)–C(11)	121.1 (2)	IO(15)–N(15)–O(15)	125.0 (2)

Table 8. Selected torsional angles (°) for compounds (I) and (II) with *e.s.d.*'s in parentheses

Compound (I)	Compound (II)		
C(2)–C(1)–C(7)–C(8)	91.3 (3)	C(2)–C(1)–C(7)–C(8)	148.0 (2)
C(2)–C(1)–C(7)–C(9)	–148.7 (3)	C(2)–C(1)–C(7)–C(9)	30.5 (3)
C(2)–C(1)–C(7)–C(10)	–30.5 (4)	C(2)–C(1)–C(7)–C(10)	–90.1 (3)
C(1)–C(2)–N(14)–O(14)	–79.3 (4)	C(1)–C(2)–N(15)–O(15)	–101.6 (2)
C(1)–C(2)–N(14)–O(14)	103.5 (3)	C(1)–C(2)–N(15)–O(15)	81.2 (3)
C(1)–C(6)–N(13)–O(13)	77.6 (3)	C(1)–C(6)–N(14)–O(14)	–81.4 (3)
C(1)–C(6)–N(13)–O(13)	–105.3 (3)	C(1)–C(6)–N(14)–O(14)	102.8 (2)
C(3)–C(4)–N(15)–O(15)	–94.4 (3)		
C(3)–C(4)–N(15)–O(15)	83.8 (3)		

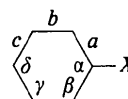
Molecular geometry and packing

The bond lengths and angles are given in Tables 6 and 7 respectively for (I) and (II) and selected torsional angles in Table 8.

The benzene ring in (I) is essentially planar, the maximum deviation of a ring atom from the least-squares plane through the ring being 0.009 (3) Å. However, the benzene ring in (II) is not as planar as in (I), the maximum deviation of a ring atom being 0.016 (2) Å. The deviation of tertiary C atom C(7) in (II) from the plane through the ring [0.016 (2) Å] is less than in (I) [0.058 (3) Å], most probably because, in (II), the ring itself underwent a distortion from planarity.

The nitro groups in both (I) and (II) are nearly perpendicular to the benzene ring (Table 8). Consequently these cannot take part in resonance with the phenyl ring which is shown by the C–N and N–O bond lengths whose values agree well with the standard values reported for an unconjugated nitro group (*International Tables for X-ray Crystallography*, 1968). The N atoms of the two nitro groups *ortho* to the *tert*-butyl group deviate markedly from the plane through the ring mainly because of steric crowding. The large deviation of the substituents *para* to the *tert*-butyl group in (I) and (II) [0.070 (3) and 0.078 (3) Å respectively] may be due to intermolecular interactions.

There is a considerable deformation of the benzene ring in both (I) and (II) (Tables 6 and 7). It may be observed that there are considerable deviations of the bond lengths and angles from the normally accepted values for a benzene ring. It is known that when there are electron-donating or -accepting substituents, the ring geometry undergoes distortion (Domenicano, Vaciago & Coulson, 1975).



The angles (α) within the ring at the C atoms carrying the nitro-group substituents are larger than the sp^2 angle. It can be noticed that these values at C(2) and C(6) in both (I) and (II) are still larger than in other nitrobenzenes (Domenicano, Vaciago & Coulson, 1975), presumably because of the adjacent bulky *tert*-butyl group.

As a whole, the asymmetry in the bond lengths and angles in the phenyl ring cannot be understood only in terms of the above substituent effects especially when the phenyl ring is fully substituted as is the case now with quite a few acceptors and bulky substituents.

The lengthening of the C_{Phe}–C_{tert} bond when compared to the C_{Phe}–C_{Me} bonds and a low value for the C(6)–C(1)–C(2) angle in both (I) and (II) arises from the overcrowding in this region of the molecule.

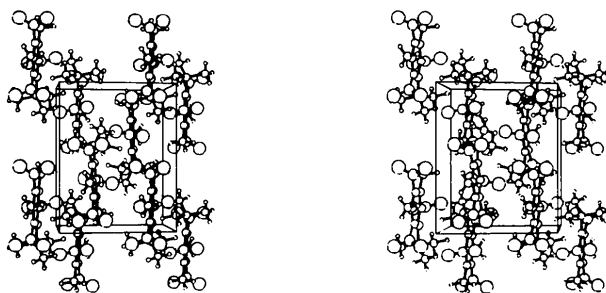


Fig. 3. Stereoscopic diagram of the packing of the molecules in the crystal structure of compound (I) viewed along the *c* axis (*a* axis horizontal, *b* axis vertical).

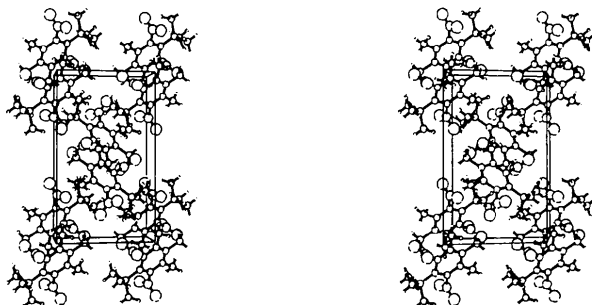


Fig. 4. Stereoscopic diagram of the packing of the molecules in the crystal structure of compound (II) viewed along the *c* axis (*a* axis horizontal, *b* axis vertical).

The packing arrangements of the molecules in compounds (I) and (II) are illustrated in Figs. 3 and 4 respectively. The crystal structures are solely stabilized by van der Waals interactions. There are only two intermolecular contacts in the range 3.30–3.33 Å for compound (II), whereas there are 13 contacts in the range 3.02–3.48 Å for compound (I). This is consistent

with the lower value of the density of the crystals of (II) (1.267 g cm⁻³) compared with that of (I) (1.384 g cm⁻³).

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The Structures of Clathrates of Bis(triphenylsilane) Oxide with Benzene and Piperidine

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Abstract. Hexaphenyldisiloxane–benzene (1/2), C₃₆H₃₀OSi₂·2C₆H₆, *M_r* = 691.0, hexagonal, *R* $\bar{3}$, *a* =

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11.196 (4), *c* = 26.515 (15) Å, *V* = 2878 (2) Å³, *Z* = 3, *D_x* = 1.20 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 1.228 cm⁻¹, *F*(000) = 1098, *T* = 150 K, *R* = 0.056 for 856 unique observed reflections. Hexaphenyldisiloxane–piperidine (1/2), C₃₆H₃₀OSi₂·2C₅H₁₁N, *M_r* = 705.1, hexagonal, *R* $\bar{3}$, *a* = 11.197 (3), *c* =

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