

gemeinsamen isotropen Temperaturfaktor verfeinert. $R = 0,031$, $wR = 0,028$. Restelektronendichte $\rho_{\min} = -0,3$, $\rho_{\max} = 0,2 \text{ e } \text{Å}^{-3}$. Keine Extinktionskorrektur. Atomformfaktoren: Cromer & Mann (1968). f' , f'' : Cromer & Liberman (1970). Rechenprogramme: Müller (1971), Sheldrick (1976, 1986), Johnson (1965).

Die Atomparameter sind in Tabelle 1, Die Bindungsabstände und -winkel in Tabelle 2 aufgeführt.* Fig. 1 und 2 zeigen das Molekül und die Kristallpackung.

Verwandte Literatur. Frühere Strukturbestimmung: Larsson (1960a). Andere Verbindungen mit verschiedenen Alkylgruppen bei gleichem Molekülgerüst: Larsson (1960b); Podberezkaya, Magarill, Baidina, Borisov, Gorsh, Kanev & Martynova (1982); Martynova, Korchkov & Semyannikov (1983).

* Die H-Atomkoordinaten, die Parameter für den anisotropen Temperaturfaktor und die Liste der beobachteten und berechneten Strukturparameter sind beim British Library Document Supply Centre (Supplementary Publication No. SUP 51735: 5 pp.) hinterlegt. Kopien sind erhältlich durch: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Wir danken dem Fonds der Chemischen Industrie für die Unterstützung dieser Arbeit.

Literatur

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1897.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 JOHNSON, C. K. (1965). *ORTEP*. Bericht ORNL-3794. Oak Ridge National Laboratory, Tennessee, VStA.
 LARSSON, K. (1960a). *Ark. Kemi*, **16**, 203–208.
 LARSSON, K. (1960b). *Ark. Kemi*, **16**, 209–214, 215–219.
 MARTYNOVA, T. N., KORCHKOV, V. P. & SEMYANNIKOV, P. P. (1983). *J. Organomet. Chem.* **258**, 277–282.
 MÜLLER, U. (1971). *CADLP*. Programm zur Auswertung und Lp-Korrektur von Diffraktometerdaten. Univ. Marburg, Bundesrepublik Deutschland.
 PODBEREZSKAYA, N. V., MAGARILL, S. A., BAIDINA, I. A., BORISOV, S. V., GORSH, L. E., KANEV, A. N. & MARTYNOVA, T. N. (1982). *J. Strukt. Khim.* **23**(3), 120–130; *J. Struct. Chem.* **23**, 422–431.
 SHELDRIK, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. Göttingen, Bundesrepublik Deutschland.

Acta Cryst. (1989). **C45**, 1107–1109

Structure of 2,4,6-Trinitrophenylhydrazine

BY JUDITH L. FLIPPEN-ANDERSON

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington DC 20375, USA

AND DOUGLAS S. DUDIS

Chemistry Department, US Naval Academy, Annapolis, MD 21402, USA

(Received 17 August 1988; accepted 4 January 1989)

Abstract. $\text{C}_6\text{H}_5\text{N}_5\text{O}_6$, $M_r = 243.13$, monoclinic, $P2_1/n$, $a = 13.472$ (3), $b = 9.806$ (2), $c = 14.002$ (5) Å, $\beta = 100.36$ (2)°, $V = 1819.8$ (9) Å³, $Z = 8$, $D_x = 1.775 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.5 \text{ cm}^{-1}$, $F(000) = 992$, $T = 225 \text{ K}$, final $R = 0.0356$, $wR = 0.0401$ for 1972 independent reflections. There are two independent molecules in the asymmetric unit, statistically identical to one another in terms of bond lengths and angles. They differ in the torsion angles of the groups pendant to the phenyl rings (but by no more than 10°). The C–C distances in the phenyl rings are substantially (25σ) longer for the bonds adjacent to the hydrazine moiety [1.428 (5) Å av.] relative to those adjacent to the nitro group *para* to the hydrazine moiety [1.376 (10) Å av.] The molecules have both inter- and intramolecular hydrogen bonding.

Experimental. Clear orange $0.36 \times 0.72 \times 0.08 \text{ mm}$ data crystal recrystallized from ethyl acetate from material provided by Dr Paul Bolduc of Eglin Air Force Base. Automated Nicolet *R3m/v* diffractometer with incident beam monochromator. 25 centered reflections within $25 \leq 2\theta \leq 30^\circ$ used for determining lattice parameters. $[(\sin \theta)/\lambda]_{\max} = 0.54 \text{ Å}^{-1}$, range of hkl : $-14 \leq h \leq 14$, $0 \leq k \leq 10$, $-14 \leq l \leq 0$. Standards (814, 020, 006) monitored every 60 reflections with random variation of 2.5% over data collection, $\theta/2\theta$ mode, scan width 1.4° , scan rate a function of count rate ($14.0^\circ \text{ min}^{-1}$ minimum, $60.0^\circ \text{ min}^{-1}$ maximum), 2769 reflections measured, 2389 unique, $R_{\text{int}} = 0.0170$, 1972 observed with $F_o > 3\sigma(|F_o|)$. Data corrected for Lorentz, polarization but not absorption effects. Structure solved by direct methods. The

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	6450 (2)	3637 (3)	3038 (2)	20 (1)
N(1a)	7201 (2)	3865 (2)	3779 (2)	25 (1)
N(1b)	8123 (2)	4389 (3)	3594 (2)	29 (1)
C(2)	5633 (2)	2713 (3)	3071 (2)	22 (1)
N(2)	5539 (2)	2010 (3)	3963 (2)	29 (1)
O(2a)	6050 (1)	2404 (2)	4734 (1)	35 (1)
O(2b)	4948 (2)	1052 (2)	3921 (2)	51 (1)
C(3)	4920 (2)	2405 (3)	2269 (2)	24 (1)
C(4)	4974 (2)	3007 (3)	1398 (2)	24 (1)
N(4)	4210 (2)	2701 (2)	557 (2)	28 (1)
O(4a)	4343 (2)	3138 (2)	-240 (1)	38 (1)
O(4b)	3477 (1)	2020 (2)	666 (1)	37 (1)
C(5)	5724 (2)	3948 (3)	1316 (2)	25 (1)
C(6)	6416 (2)	4275 (3)	2121 (2)	21 (1)
N(6)	7058 (2)	5459 (2)	2012 (2)	25 (1)
O(6a)	7031 (1)	6422 (2)	2558 (1)	34 (1)
O(6b)	7530 (2)	5451 (2)	1344 (1)	37 (1)
C(11)	6523 (2)	3578 (3)	8287 (2)	20 (1)
N(11a)	7200 (2)	3893 (3)	9075 (2)	27 (1)
N(11b)	7709 (2)	5158 (3)	9139 (2)	35 (1)
C(12)	5843 (2)	2452 (3)	8235 (2)	21 (1)
N(12)	5906 (2)	1481 (2)	9024 (2)	27 (1)
O(12a)	6561 (2)	1653 (2)	9754 (1)	43 (1)
O(12b)	5303 (1)	538 (2)	8951 (1)	33 (1)
C(13)	5091 (2)	2223 (3)	7440 (2)	22 (1)
C(14)	4981 (2)	3100 (3)	6668 (2)	22 (1)
N(14)	4165 (2)	2893 (3)	5845 (2)	27 (1)
O(14a)	4040 (2)	3761 (2)	5208 (1)	43 (1)
O(14b)	3644 (2)	1867 (2)	5838 (1)	41 (1)
C(15)	5637 (2)	4173 (3)	6645 (2)	23 (1)
C(16)	6396 (2)	4372 (3)	7419 (2)	20 (1)
N(16)	7174 (2)	5344 (2)	7244 (2)	26 (1)
O(16a)	8028 (1)	4897 (2)	7290 (2)	40 (1)
O(16b)	6913 (1)	6499 (2)	6995 (2)	38 (1)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

C(1)—N(1a)	1.331 (3)	C(1)—C(2)	1.434 (4)
C(1)—C(6)	1.421 (3)	N(1a)—N(1b)	1.412 (3)
C(2)—N(2)	1.452 (3)	C(2)—C(3)	1.374 (4)
N(2)—O(2a)	1.234 (3)	N(2)—O(2b)	1.226 (3)
C(3)—C(4)	1.368 (4)	C(4)—N(4)	1.450 (3)
C(4)—C(5)	1.388 (4)	N(4)—O(4a)	1.237 (3)
N(4)—O(4b)	1.224 (3)	C(5)—C(6)	1.366 (4)
C(6)—N(6)	1.472 (3)	N(6)—O(6a)	1.221 (3)
N(6)—O(6b)	1.222 (3)	C(11)—N(11a)	1.336 (3)
C(11)—C(12)	1.429 (4)	C(11)—C(16)	1.427 (3)
N(11a)—N(11b)	1.413 (3)	C(12)—N(12)	1.448 (3)
C(12)—C(13)	1.382 (4)	N(12)—O(12a)	1.236 (3)
N(12)—O(12b)	1.223 (3)	C(13)—C(14)	1.368 (4)
C(14)—N(14)	1.457 (3)	C(14)—C(15)	1.379 (4)
N(14)—O(14a)	1.223 (3)	N(14)—O(14b)	1.225 (3)
C(15)—C(16)	1.364 (4)	C(16)—N(16)	1.469 (3)
N(16)—O(16a)	1.223 (3)	N(16)—O(16b)	1.217 (3)
C(2)—C(1)—N(1a)	124.2 (2)	C(6)—C(1)—N(1a)	121.8 (2)
C(6)—C(1)—C(2)	114.0 (2)	N(1b)—N(1a)—C(1)	119.3 (2)
N(2)—C(2)—C(1)	120.9 (2)	C(3)—C(2)—C(1)	122.8 (2)
C(3)—C(2)—N(2)	116.3 (2)	O(2a)—N(2)—C(2)	118.9 (2)
O(2b)—N(2)—C(2)	118.6 (2)	O(2b)—N(2)—O(2a)	122.5 (2)
C(4)—C(3)—C(2)	119.5 (3)	N(4)—C(4)—C(3)	119.3 (3)
C(5)—C(4)—C(3)	121.1 (3)	C(5)—C(4)—N(4)	119.5 (2)
O(4a)—N(4)—C(4)	117.6 (2)	O(4b)—N(4)—C(4)	118.9 (2)
O(4b)—N(4)—O(4a)	123.5 (2)	C(6)—C(5)—C(4)	119.2 (3)
C(5)—C(6)—C(1)	123.2 (2)	N(6)—C(6)—C(1)	121.1 (2)
N(6)—C(6)—C(5)	115.3 (2)	O(6a)—N(6)—C(6)	117.5 (2)
O(6b)—N(6)—C(6)	118.1 (2)	O(6b)—N(6)—O(6a)	124.3 (2)
C(12)—C(11)—N(11a)	124.0 (2)	C(16)—C(11)—N(11a)	122.4 (2)
C(16)—C(11)—C(12)	113.6 (2)	N(11b)—N(11a)—C(11)	120.5 (2)
N(12)—C(12)—C(11)	121.3 (2)	C(13)—C(12)—C(11)	122.6 (2)
C(13)—C(12)—N(12)	116.2 (2)	O(12a)—N(12)—C(12)	118.4 (2)
O(12b)—N(12)—C(12)	119.1 (2)	O(12b)—N(12)—O(12a)	122.5 (2)
C(14)—C(13)—C(12)	119.6 (3)	N(14)—C(14)—C(13)	119.7 (2)
C(15)—C(14)—C(13)	121.2 (2)	C(15)—C(14)—N(14)	119.1 (2)
O(14a)—N(14)—C(14)	117.7 (2)	O(14b)—N(14)—C(14)	118.1 (2)
O(14b)—N(14)—O(14a)	124.2 (2)	C(16)—C(15)—C(14)	119.0 (3)
C(15)—C(16)—C(11)	123.7 (2)	N(16)—C(16)—C(11)	121.1 (2)
N(16)—C(16)—C(15)	114.6 (2)	O(16a)—N(16)—C(16)	116.8 (2)
O(16b)—N(16)—C(16)	118.3 (2)	O(16b)—N(16)—O(16a)	124.6 (2)

least-squares refinement used program *SHELXTL* (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, $g = 0.00023$. Secondary-extinction parameter $p = 0.0006$ (1) in $F_c^* = F_o/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$. There were 348 parameters refined: atom coordinates, anisotropic thermal parameters for all non-H atoms, H atoms refined isotropically. $(\Delta/\sigma)_{max} = 0.01$, $R = 0.0356$, $wR = 0.0401$, $S = 1.39$. Final difference Fourier excursions 0.18 and -0.19 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).† Atom numbering for Table 1, atom coordinates, and Table 2, bond distances and angles, follows that shown in Fig. 1.

Related literature. The structure of the free radical 2,2-diphenyl-1-picrylhydrazyl (Kiers, de Boer, Oltof & Spek, 1976) also shows a substantial elongation of the

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51739 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

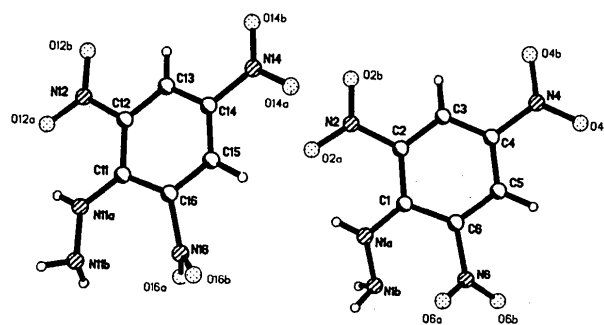


Fig. 1. Perspective drawings of the two independent molecules of 2,4,6-trinitrophenylhydrazine.

phenyl C—C distances adjacent to the hydrazine moiety [1.424 (2) \AA av.] relative to those adjacent to the nitro group *para* to the hydrazine moiety [1.386 (2) \AA av.]. The one-electron reduced species 2,2-diphenyl-1-picrylhydrazine (Gopal, Robertson & Weil, 1983) shows similar differences [1.461 (3) av. *vs.* 1.393 (4) \AA]. These appear to be the only structures reported for compounds having a 2,4,6-trinitrophenyl substituent on a hydrazine.

This work was supported in part by the Air Force Armament Laboratory, Energetic Materials Branch.

References

GOPAL, R., ROBERTSON, B. & WEIL, J. (1983). *Can. J. Chem.* **61**, 2735–2739.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KIERS, J., DE BOER, L., OLTOF, R. & SPEK, A. L. (1976). *Acta Cryst.* **B32**, 2297–2305.

SHELDRICK, G. M. (1980). *SHELXTL80. An Integrated System for Solving, Refining and Displaying Crystal Structures for Diffraction Data*. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1989). **C45**, 1109–1110

3-endo-(1-Naphthylamino)camphor

BY EMIKO YAGI, YUJI OHASHI, MASAYOSHI ISHIGE AND KOKO MAEDA*

Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan

(Received 8 December 1988; accepted 6 February 1989)

Abstract. $C_{20}H_{23}NO$, $M_r = 293.41$, monoclinic, $C2/c$, $a = 25.515$ (3), $b = 7.0774$ (6), $c = 19.149$ (2) Å, $\beta = 108.12$ (1)°, $V = 3286.5$ (7) Å³, $Z = 8$, $D_x = 1.190$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 0.485$ mm⁻¹, $F(000) = 1264$, $T = 293$ K, final $R = 0.050$, $wR = 0.068$ for 2434 independent observed reflections. The geometry around the central N atom bridging the naphthyl and camphor moieties is: N(1)–C(1') = 1.397 (3), N(1)–C(3) = 1.448 (3) Å and C(3)–N(1)–C(1') = 120.8 (2)°. There are no unusually short contacts between the molecules.

Experimental. The title compound was synthesized by the method of Forster and Spinner (Yagi, Ishige, Nagasawa & Maeda, 1989). Recrystallization from chloroform–ethanol (1:3 v/v) gave colorless needles; crystal size 0.4 × 0.4 × 0.2 mm. Rigaku AFC-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, ω – 2θ scan technique; cell parameters refined by least squares on the basis of 15 independent 2θ values in the range of 43–59°; 2862 reflections measured,

* To whom correspondence should be addressed.

Table 1. Final atomic coordinates ($\times 10^3$) with their e.s.d.'s and equivalent isotropic thermal parameters (Å^2) for non-H atoms

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
C(1)	8200 (1)	3834 (2)	1326 (1)	3.9
C(2)	8473 (1)	3124 (2)	783 (1)	3.7
C(3)	8889 (1)	1602 (2)	1169 (1)	3.7
C(4)	8844 (1)	1707 (3)	1951 (1)	4.2
C(5)	9097 (1)	3599 (3)	2283 (1)	5.4
C(6)	8672 (1)	5054 (3)	1848 (1)	5.4
C(7)	8218 (1)	2032 (3)	1797 (1)	4.4
C(8)	7850 (1)	449 (3)	1366 (2)	5.8
C(9)	8060 (1)	2388 (4)	2491 (1)	6.8
C(10)	7660 (1)	4851 (3)	984 (1)	5.2
C(1')	9818 (1)	614 (2)	1161 (1)	3.8
C(2')	9786 (1)	–1088 (3)	1497 (1)	4.7
C(3')	10191 (1)	–2470 (3)	1569 (1)	5.6
C(4')	10628 (1)	–2177 (3)	1326 (1)	5.3
C(5')	11145 (1)	–65 (3)	747 (1)	5.3
C(6')	11207 (1)	1638 (4)	452 (1)	5.7
C(7')	10814 (1)	3064 (3)	392 (1)	5.4
C(8')	10364 (1)	2749 (3)	615 (1)	4.3
C(9')	10284 (1)	999 (2)	920 (1)	3.7
C(10')	10688 (1)	–442 (3)	996 (1)	4.3
O(1)	8413 (1)	3718 (2)	172 (1)	5.3
N(1)	9417 (1)	2018 (2)	1067 (1)	4.5

Table 2. Selected bond distances (Å) and angles (°)

C(1)–C(2)	1.505 (2)	C(1)–C(6)	1.565 (3)
C(1)–C(7)	1.554 (3)	C(1)–C(10)	1.511 (3)
C(2)–C(3)	1.533 (2)	C(2)–O(1)	1.209 (2)
C(3)–C(4)	1.539 (3)	C(3)–N(1)	1.448 (3)
C(4)–C(5)	1.536 (3)	C(4)–C(7)	1.550 (3)
C(5)–C(6)	1.540 (3)	C(7)–C(8)	1.528 (3)
C(7)–C(9)	1.525 (4)	C(1')–C(2')	1.379 (3)
C(1')–C(9')	1.430 (2)	C(1')–N(1)	1.397 (3)
C(2')–C(3')	1.398 (3)	C(3')–C(4')	1.353 (3)
C(4')–C(10')	1.410 (3)	C(5')–C(6')	1.362 (4)
C(5')–C(10')	1.415 (3)	C(6')–C(7')	1.403 (4)
C(7')–C(8')	1.361 (3)	C(8')–C(9')	1.411 (3)
C(9')–C(10')	1.426 (2)		
C(2)–C(1)–C(6)	101.3 (1)	C(2)–C(1)–C(7)	101.0 (1)
C(2)–C(1)–C(10)	114.6 (2)	C(6)–C(1)–C(7)	101.8 (1)
C(6)–C(1)–C(10)	115.5 (2)	C(7)–C(1)–C(10)	120.0 (2)
C(1)–C(2)–C(3)	107.6 (1)	C(1)–C(2)–O(1)	127.3 (2)
C(3)–C(2)–O(1)	124.9 (2)	C(2)–C(3)–C(4)	100.6 (1)
C(2)–C(3)–N(1)	109.1 (1)	C(4)–C(3)–N(1)	118.4 (2)
C(3)–C(4)–C(5)	107.2 (2)	C(3)–C(4)–C(7)	101.9 (1)
C(5)–C(4)–C(7)	103.0 (2)	C(4)–C(5)–C(6)	103.0 (2)
C(1)–C(6)–C(5)	104.5 (2)	C(1)–C(7)–C(4)	94.3 (1)
C(1)–C(7)–C(8)	112.7 (2)	C(1)–C(7)–C(9)	113.7 (2)
C(4)–C(7)–C(8)	114.7 (2)	C(4)–C(7)–C(9)	113.2 (2)
C(8)–C(7)–C(9)	107.9 (2)	C(2')–C(1')–C(9')	119.5 (2)
C(2')–C(1')–N(1)	122.3 (2)	C(9')–C(1')–N(1)	118.2 (2)
C(1')–C(2')–C(3')	120.6 (2)	C(2')–C(3')–C(4')	121.5 (2)
C(3')–C(4')–C(10')	120.2 (2)	C(6')–C(5')–C(10')	121.4 (2)
C(5')–C(6')–C(7')	119.9 (2)	C(6')–C(7')–C(8')	120.5 (2)
C(7')–C(8')–C(9')	121.3 (2)	C(1')–C(9')–C(8')	122.9 (2)
C(1')–C(9')–C(10')	118.6 (2)	C(8')–C(9')–C(10')	118.4 (2)
C(4')–C(10')–C(5')	122.0 (2)	C(4')–C(10')–C(9')	119.5 (2)
C(5')–C(10')–C(9')	118.5 (2)	C(3)–N(1)–C(1')	120.8 (2)