

Geometry of a *gauche* Aryltrialkylhydrazine: Structure of 2,5-Diphenyl-1,2,4,5-tetraazabicyclo[2.2.1]heptane

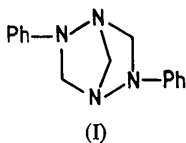
BY GEORGE A. SIM

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

(Received 15 May 1987; accepted 25 June 1987)

Abstract. $C_{15}H_{16}N_4$, $M_r = 252.34$, orthorhombic, $Pbca$, $a = 6.359$ (1), $b = 22.546$ (3), $c = 18.499$ (3) Å, $V = 2652$ (1) Å³, $Z = 8$, $D_x = 1.26$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 0.63$ mm⁻¹, $F(000) = 1072$, $T = 293$ K, $R = 0.041$ for 1783 observed reflections. The dihedral angle between the postulated lone-pair, lone-pair directions for each N–N bond is close to 90°. The N atoms are distinctly pyramidal in character, with the N–C(phenyl) bond inclined to the N–N–C(alkyl) plane at 42.8° on average. The mean N–N bond length is 1.454 Å.

Introduction. The principal product of the reaction between phenylhydrazine ($C_6H_5NHNH_2$) and excess formaldehyde (HCHO) was first isolated by Wellington & Tollens (1885) and shown to have the composition $C_{15}H_{16}N_4$. Though the reaction was explored further by Walker (1896), it was not until 1960 onwards that spectroscopic methods enabled plausible structural proposals to be put forward for the various products of the reaction (Schmitz & Ohme, 1960; Karabatos & Taller, 1968; Schmidt, 1970; Johns, Lamberton & Nelson, 1971; Hammerum, 1973). There is general agreement that the principal product (m.p. 459 K) is 2,5-diphenyl-1,2,4,5-tetraazabicyclo[2.2.1]heptane (I). Since the conformational properties of hydrazine derivatives are the subject of considerable interest (Shvo, 1975; Nelsen, 1978, 1981; Agmon, Kaftory, Nelsen & Blackstock, 1986; Nelsen, Frigo, Kim & Thompson-Colón, 1986) an X-ray diffraction characterization of compound (I) was undertaken to confirm the spectroscopic assignment of structure and to provide conformational details of this hydrazine derivative.



Experimental. The material obtained by the addition of phenylhydrazine to excess formaldehyde was recrystallized from ethanol. The m.p. (459 K) was determined on a hot-stage microscope. Crystal dimensions 0.10 ×

0.30 × 0.40 mm. Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, generator settings 43 kV, 26 mA. Cell dimensions from setting angles of 25 independent reflections with θ 15–23°; 3019 reflections surveyed in range θ 1.5–72°; $h0 \rightarrow 7$, $k0 \rightarrow 27$, $l0 \rightarrow 22$; 1783 reflections with $I > 2.5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. Corrections applied for Lorentz–polarization effects, assuming an ideally imperfect monochromator crystal, and for absorption by the empirical method of Walker & Stuart (1983). Structure determined by direct phasing using *MITHRIL* (Gilmore, 1984). H atoms located in difference Fourier syntheses. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C and N atoms and isotropic for H atoms. Convergence at $R = 0.041$, $wR = 0.057$, $S = 2.54$ for 236 parameters, $\Delta/\sigma < 0.2$, $w = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max. 0.12, min. -0.11 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on an SEL 32/37 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Discussion. Atomic coordinates are listed in Table 1 and the molecular dimensions in Table 2.* The torsion angles that define the molecular conformation are in Table 3. Fig. 1, drawn with *ORTEP* (Johnson, 1965), illustrates the molecular structure which conforms closely to C_2 symmetry.

The preferred conformation of hydrazine (N_2H_4) is *gauche*, with the lone-pair orbitals approximately perpendicular (Yamaguchi, Ichishima, Shimanouchi & Mizushima, 1959; Fink, Pan & Allen, 1967; Wolfe, 1972). Compound (I) has N(2)–phenyl *exo* and N(5)–phenyl *exo* stereochemistry, presumably for steric reasons, and as a consequence the conformation about both N–N bonds is *gauche*. If each N lone-pair orbital is assumed to bisect the C–N–C angle in a

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and additional torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44187 (16 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 and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$$

	x	y	z	U_{eq}
N(1)	0.9610 (3)	0.0923 (1)	0.8240 (1)	0.068
N(2)	0.8298 (2)	0.0996 (1)	0.8878 (1)	0.065
C(3)	0.9682 (4)	0.0845 (1)	0.9501 (1)	0.072
N(4)	1.1629 (3)	0.0639 (1)	0.9162 (1)	0.070
N(5)	1.0994 (2)	0.0091 (1)	0.8813 (1)	0.062
C(6)	0.9768 (3)	0.0279 (1)	0.8163 (1)	0.067
C(7)	1.1709 (4)	0.1048 (1)	0.8538 (1)	0.077
C(8)	0.7156 (3)	0.1529 (1)	0.8917 (1)	0.063
C(9)	0.6825 (4)	0.1891 (1)	0.8320 (1)	0.076
C(10)	0.5547 (4)	0.2385 (1)	0.8393 (2)	0.090
C(11)	0.4618 (5)	0.2525 (1)	0.9033 (2)	0.090
C(12)	0.4921 (4)	0.2165 (1)	0.9622 (1)	0.083
C(13)	0.6177 (4)	0.1671 (1)	0.9567 (1)	0.072
C(14)	1.2636 (3)	-0.0327 (1)	0.8715 (1)	0.060
C(15)	1.4578 (3)	-0.0276 (1)	0.9050 (1)	0.071
C(16)	1.6030 (4)	-0.0720 (1)	0.8976 (1)	0.085
C(17)	1.5615 (5)	-0.1219 (1)	0.8574 (1)	0.092
C(18)	1.3704 (5)	-0.1266 (1)	0.8235 (1)	0.088
C(19)	1.2216 (4)	-0.0821 (1)	0.8303 (1)	0.076

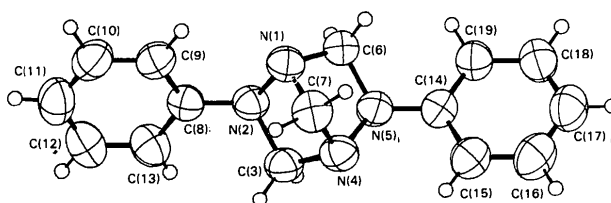


Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1 Å.

Table 2. Interatomic distances (Å) and angles (°)

N(1)–N(2)	1.455 (2)	N(1)–C(6)	1.463 (3)
N(1)–C(7)	1.472 (3)	N(2)–C(3)	1.491 (3)
N(2)–C(8)	1.406 (3)	C(3)–N(4)	1.463 (3)
N(4)–N(5)	1.452 (3)	N(4)–C(7)	1.478 (3)
N(5)–C(6)	1.495 (3)	N(5)–C(14)	1.418 (3)
C(8)–C(9)	1.390 (3)	C(8)–C(13)	1.390 (3)
C(9)–C(10)	1.385 (4)	C(10)–C(11)	1.361 (4)
C(11)–C(12)	1.370 (4)	C(12)–C(13)	1.375 (4)
C(14)–C(15)	1.387 (3)	C(14)–C(19)	1.376 (3)
C(15)–C(16)	1.369 (4)	C(16)–C(17)	1.375 (4)
C(17)–C(18)	1.371 (5)	C(18)–C(19)	1.384 (4)
N(2)–N(1)–C(6)	103.3 (2)	N(2)–N(1)–C(7)	101.2 (2)
C(6)–N(1)–C(7)	99.4 (2)	N(1)–N(2)–C(3)	105.3 (2)
N(1)–N(2)–C(8)	115.8 (2)	C(3)–N(2)–C(8)	117.4 (2)
N(2)–C(3)–N(4)	103.9 (2)	C(3)–N(4)–N(5)	103.0 (2)
C(3)–N(4)–C(7)	99.6 (2)	N(5)–N(4)–C(7)	101.1 (2)
N(4)–N(5)–C(6)	105.2 (2)	N(4)–N(5)–C(14)	114.7 (2)
C(6)–N(5)–C(14)	118.0 (2)	N(1)–C(6)–N(5)	103.8 (2)
N(1)–C(7)–N(4)	98.2 (2)	N(2)–C(8)–C(9)	122.6 (2)
N(2)–C(8)–C(13)	118.3 (2)	C(9)–C(8)–C(13)	118.9 (2)
C(8)–C(9)–C(10)	119.0 (3)	C(9)–C(10)–C(11)	121.6 (3)
C(10)–C(11)–C(12)	119.6 (3)	C(11)–C(12)–C(13)	120.1 (3)
C(8)–C(13)–C(12)	120.8 (3)	N(5)–C(14)–C(15)	122.9 (2)
N(5)–C(14)–C(19)	117.8 (2)	C(15)–C(14)–C(19)	119.2 (2)
C(14)–C(15)–C(16)	119.7 (3)	C(15)–C(16)–C(17)	121.5 (3)
C(16)–C(17)–C(18)	118.7 (3)	C(17)–C(18)–C(19)	120.6 (3)
C(14)–C(19)–C(18)	120.3 (3)		

Table 3. Important torsion angles (°)

C(6)–N(1)–N(2)–C(3)	74.4 (2)	C(3)–N(4)–N(5)–C(6)	74.9 (2)
C(6)–N(1)–N(2)–C(8)	-154.2 (2)	C(3)–N(4)–N(5)–C(14)	-153.8 (2)
C(7)–N(1)–N(2)–C(3)	-28.2 (2)	C(7)–N(4)–N(5)–C(6)	-27.8 (2)
C(7)–N(1)–N(2)–C(8)	103.2 (2)	C(7)–N(4)–N(5)–C(14)	103.4 (2)
N(2)–N(1)–C(6)–N(5)	-66.5 (2)	N(5)–N(4)–C(3)–N(2)	-67.1 (2)
C(7)–N(1)–C(6)–N(5)	37.5 (2)	C(7)–N(4)–C(3)–N(2)	36.7 (2)
N(2)–N(1)–C(7)–N(4)	51.0 (2)	N(5)–N(4)–C(7)–N(1)	51.2 (2)
C(6)–N(1)–C(7)–N(4)	-54.7 (2)	C(3)–N(4)–C(7)–N(1)	-54.2 (2)
N(1)–N(2)–C(3)–N(4)	-5.4 (2)	N(4)–N(5)–C(6)–N(1)	-6.0 (2)
C(8)–N(2)–C(3)–N(4)	-135.9 (3)	C(14)–N(5)–C(6)–N(1)	-135.4 (3)
N(1)–N(2)–C(8)–C(9)	16.8 (2)	N(4)–N(5)–C(14)–C(15)	12.7 (2)
N(1)–N(2)–C(8)–C(13)	-168.7 (3)	N(4)–N(5)–C(14)–C(19)	-171.5 (3)
C(3)–N(2)–C(8)–C(9)	142.2 (3)	C(6)–N(5)–C(14)–C(15)	137.5 (3)
C(3)–N(2)–C(8)–C(13)	-43.3 (2)	C(6)–N(5)–C(14)–C(19)	-46.8 (2)

Newman projection along the N–N bond, the lone-pair/lone-pair dihedral angle is calculated to be 88.8 (5)° for N(1)–N(2) and 89.3 (5)° for N(4)–N(5), *i.e.* close to ideal. The N atoms are distinctly pyramidal in character. The N–C(aryl) bonds are inclined at 42.5 (3)° [N(2)] and 43.1 (3)° [N(5)] to the N–N–C(alkyl) planes, intermediate between out-of-plane angles of 48–55° in *gauche* tetraalkylhydrazines (Ansell & Erickson, 1975; Nelsen, Hollinsed & Calabrese, 1977) and 37.5 (1)° in aniline (Lister, Tyler, Høg & Larsen, 1974).

The N(1)–N(2) and N(4)–N(5) bond lengths in (I), 1.455 (2) and 1.452 (3) Å, are essentially identical with the N–N bond length in hydrazine, 1.449 Å by electron diffraction (Morino, Iijima & Murata, 1960) and 1.453 Å by far infrared spectroscopy (Yamaguchi *et al.*, 1959); other *gauche* hydrazine derivatives have similar N–N bond lengths, *e.g.* 1.447 (3) Å (Ansell & Erickson, 1975) and 1.450 (3) Å (Nelsen *et al.*, 1977). Changes in hydrazine conformation affect the N–N distance and in a *trans* hydrazine, where the lone-pair/lone-pair dihedral angle is 180°, the N–N distance is increased to 1.486 (4) Å (Nelsen *et al.*, 1977). Similar results have been reported by Katritzky, Baker, Camalli, Spagna & Vaciago (1980). The N–C(alkyl) distances in (I) are 1.463 (3)–1.478 (3) Å, mean 1.469 Å, in excellent agreement with values of 1.460 (4)–1.468 (5) Å in tetraalkylhydrazines (Nelsen *et al.*, 1977; Ansell & Erickson, 1975). The N–C(aryl) distances in (I), 1.406 (3) and 1.418 (3) Å, mean 1.412 Å, are only slightly longer than the N–C distance of 1.402 (2) Å in aniline (Lister *et al.*, 1974).

The C–C(*sp*³)–C angles in (I) are substantially smaller than tetrahedral, 98.2 (2)–103.9 (2)°, and the H–C(*sp*³)–H angles are greater than tetrahedral, 112.7 (17)–116.9 (18)°.

References

AGMON, I., KAFTORY, M., NELSEN, S. F. & BLACKSTOCK, S. C. (1986). *J. Am. Chem. Soc.* **108**, 4477–4484.
 ANSELL, G. B. & ERICKSON, J. L. (1975). *J. Chem. Soc. Perkin Trans. 2*, pp. 270–271.
 FINK, W. H., PAN, D. C. & ALLEN, L. C. (1967). *J. Chem. Phys.* **47**, 895–905.
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

- HAMMERUM, S. (1973). *Acta Chem. Scand.* **27**, 779–796.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNS, S. R., LAMBERTON, J. A. & NELSON, E. R. (1971). *Aust. J. Chem.* **24**, 1859–1871.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KARABATOS, G. J. & TALLER, R. A. (1968). *Tetrahedron*, **24**, 3557–3568.
- KATRITZKY, A. R., BAKER, V. J., CAMALLI, M., SPAGNA, R. & VACIAGO, A. (1980). *J. Chem. Soc. Perkin Trans.* **2**, pp. 1733–1738.
- LISTER, D. G., TYLER, J. K., HØG, J. H. & LARSEN, N. W. (1974). *J. Mol. Struct.* **23**, 253–264.
- MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
- MORINO, Y., IJIMA, T. & MURATA, Y. (1960). *Bull. Chem. Soc. Jpn*, **33**, 46–48.
- NELSEN, S. F. (1978). *Acc. Chem. Res.* **11**, 14–20.
- NELSEN, S. F. (1981). *Acc. Chem. Res.* **14**, 131–138.
- NELSEN, S. F., FRIGO, T. B., KIM, Y. & THOMPSON-COLÓN, J. A. (1986). *J. Am. Chem. Soc.* **108**, 7926–7934.
- NELSEN, S. F., HOLLINSE, W. C. & CALABRESE, J. C. (1977). *J. Am. Chem. Soc.* **99**, 4461–4467.
- SCHMIDT, C. H. (1970). *Chem. Ber.* **103**, 986–989.
- SCHMITZ, E. & OHME, R. (1960). *Justus Liebigs Ann. Chem.* **635**, 82–91.
- SHVO, Y. (1975). *Chemistry of Hydrazo, Azo and Azoxy Groups*, edited by S. PATAI, part 2, pp. 1017–1095. New York: John Wiley.
- WALKER, J. W. (1896). *J. Chem. Soc. Trans.* **69**, 1280–1287.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- WELLINGTON, C. & TOLLENS, B. (1885). *Chem. Ber.* **18**, 3298–3311.
- WOLFE, S. (1972). *Acc. Chem. Res.* **5**, 102–111.
- YAMAGUCHI, A., ICHISHIMA, I., SHIMANOUCI, T. & MIZUSHIMA, S. (1959). *J. Chem. Phys.* **31**, 843.

Acta Cryst. (1987). **C43**, 2180–2182

The Absolute Configuration of an Iodo Derivative of Xerantholide

BY WILLIAM H. WATSON*

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

AND MAHMUT MISKI AND TOM J. MABRY

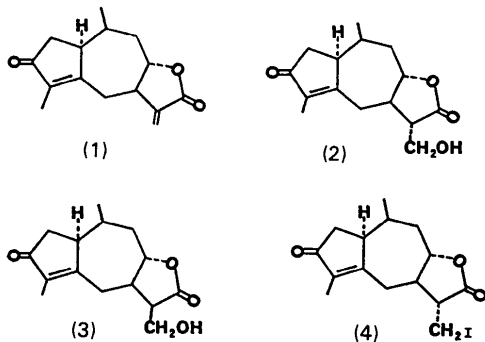
Department of Botany, The University of Texas, Austin, Texas 78713, USA

(Received 21 November 1986; accepted 9 June 1987)

Abstract. (1*R*,7*S*,8*S*,9*S*)-13-Iodoguaia-4-en-3-one-7,8 α -olide, C₁₅H₁₆IO₃, *M_r* = 374.22, monoclinic, *P*2₁, *a* = 7.403 (1), *b* = 8.820 (1), *c* = 12.054 (2) Å, β = 90.41 (2)°, *V* = 787.0 (3) Å³, *Z* = 2, *D_x* = 1.579 g cm⁻³, λ (Cu K α) = 1.54178 Å, μ = 162.12 cm⁻¹, *F*(000) = 372, *T* = 295 K, *R* = 0.056 for 1144 independent reflections. The –CH₂I moiety lies in a crystal cavity which results in a large anisotropic thermal motion. The coordinates from the iodine structure were used in a molecular-mechanics calculation to rationalize the differences in physical properties of the two hydroxymethylene derivatives of xerantholide.

Introduction. During investigations of the chemical transformation of xerantholide (1) the two C(11) hydroxymethylene derivatives (2) and (3) were prepared (Miski & Mabry, 1987). These two members of a diastereomeric pair exhibited quite different chemical and physical properties. The IR spectrum (KBr) of (2) indicates that the hydroxyl group is hydrogen-bonded intramolecularly to the lactone carbonyl while no

strong hydrogen bonding is indicated in the spectrum of (3). Compound (2) also loses water more readily than (3). Since molecular models did not provide a definitive rationalization, a structural analysis was suggested. Good single crystals of the hydroxy derivatives could not be prepared; however, a usable crystal of the iodide (4) was obtained.



Experimental. A colorless prismatic crystal of dimensions 0.25 × 0.16 × 0.09 mm was selected; Nicolet R3m/ μ update of a *P*2₁ diffractometer; data collected in the Wyckoff mode (2 θ fixed, ω varied)

* All correspondence to be addressed to this author.