

Cyclotridecanone 2,4-dinitrophenylhydrazone

Edward J. Valente,^a Diwaker M. Pawar,^b Frank R. Fronczek^c and Eric A. Noe^{b*}^aDepartment of Chemistry and Biochemistry, Mississippi College, Clinton, MS 39058, USA, ^bDepartment of Chemistry, Jackson State University, 1400 J. R. Lynch Street, Jackson, MS 39217, USA, and ^cDepartment of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA
Correspondence e-mail: ean12001@yahoo.com

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In cyclotridecanone 2,4-dinitrophenylhydrazone, C₁₉H₂₈N₄O₄, the 13-membered carbocycle exists in the triangular [337] conformation. The 2,4-dinitrophenylhydrazone group is almost perpendicular to the 13-membered ring, with a dihedral angle of 82.66 (2)° between the mean planes. The dinitrophenylhydrazone rings are packed parallel to each other and separated by 3.28 (1) Å. The NH group forms an intramolecular hydrogen bond to a nitro O atom, and there is a weaker C—H···O interaction between a cyclotridecane CH group and a symmetry-related 4-nitro O atom, with a C···O distance of 3.436 (2) Å and a 150° angle about the H atom. The structure, in combination with additional evidence, indicates that [337] is the preferred conformation of cyclotridecane and other simple 13-membered rings.

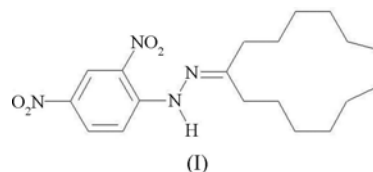
Comment

The conformations of larger odd-numbered carbocycles, such as cyclotridecane, are less well characterized than those with an even number of ring atoms. Semiquantitative calculations for eight conformations of cyclotridecane predicted a lowest-energy quinquangular [12433] conformation (Dale, 1973). Subsequently, *MOLBUILD* force-field calculations on five likely conformations and on 1,1-dimethylcyclotridecane suggested a [13333] conformational minimum (Anet & Rawdah, 1978). A communication by Gotō & Ōsawa (1989) reported a conformational search for cyclotridecane and other cycloalkanes by a corner flapping method and using Allinger's MM2 force field. The number of hours required and the number of conformations generated were reported, but the description of the conformations was limited to a list of coordinates for carbon and steric energies (see supplementary material). From the coordinates, we have generated the lowest energy conformation and found that the dihedral angles correspond to the [337] conformation. From experimental studies, low-temperature ¹H (127 K) and ¹³C (123 K) NMR

spectra for cyclotridecane show some broadening of resonances, and no information on likely conformers could be extracted (Cheng, 1973). The linewidth for the ¹H signal at 127 K was 10 Hz. Several broadened resonances were found in the ¹³C NMR spectrum at 88 K (Gill *et al.*, 2008).

The X-ray structure of α,ω -bis(methyldodeca-1,12-diylammonio)hexane dibromide showed a quinquangular [13333] conformation for an ordered model and a similar [13333] and a [346] conformation for a disordered model (Rubin *et al.*, 1984). An X-ray study of dimethyl 1-hydroxycyclotridecylphosphonate revealed two conformations, one of which was the [13333] conformation (Samuel & Weiss, 1969). Two other solid derivatives studied by X-ray crystallography include cyclotridecanone oxime, (II), at 113 K (Groth, 1979) and cyclotridecanone phenylsemicarbazone, (III), at 123 K (Groth, 1980). Both of these crystal structures showed the triangular [337] conformation.

The present study reports an X-ray analysis of the crystal structure of the title compound, (I), at 90 K.



As found in (II) and (III), the 13-membered ring is present in a [337] conformation (Fig. 1). In Dale's (1973) system of nomenclature, corner positions are defined as those ring atoms having *gauche* torsion angles of the same sign on either side. The numbers of bonds between the corners are given in sequence within brackets. The torsion angles for the C₁₃ ring in (I) are summarized in Table 1, where C3, C6 and C9 are corners. In (I) and (II), the ring substituent is located on atom C1 (Fig. 1); in (III), the substituent is at an adjacent position (C13). The angle between the mean plane of the 13-membered ring and the benzene ring in (I) is 82.66 (2)°. The dinitro-

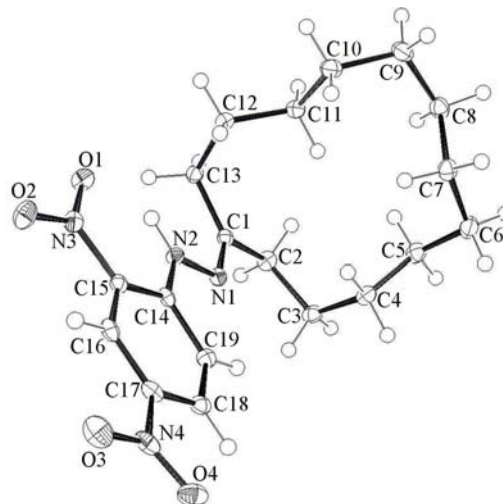


Figure 1
A displacement ellipsoid plot (at the 50% probability level) of (I).

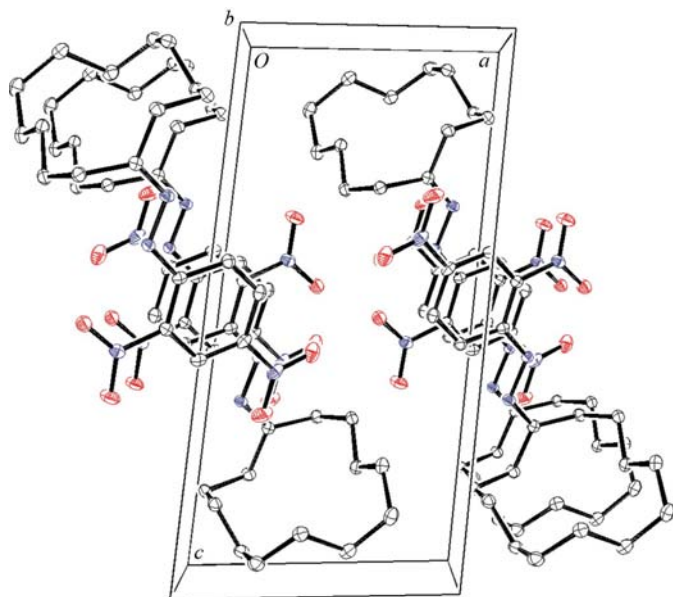


Figure 2
The unit cell of (I).

phenylhydrazone rings pack parallel to each other around centers at $(1, 1, \frac{1}{2})$ and are separated by 3.28 (1) Å (Fig. 2). The NH group forms an intramolecular hydrogen bond with nitro atom O1, forming a six-membered ring of graph set $S(6)$ (Etter, 1990). Additionally, there is a weaker $C-H \cdots O$ interaction between atoms C7 and $O3^i$, with a $C \cdots O$ distance of 3.436 (2) Å [symmetry code: (i) $-x + 2, -y + 2, -z + 1$].

The similar macrocyclic ring conformations found for (I), (II) and (III) suggests that the [337] conformation may be preferred. This agrees with the MM2 study of Gotō & Ōsawa (1989) and the results (Gill *et al.*, 2008) of a stochastic search of cyclotridecane conformational space by Allinger's MM4 program. Geminal disubstitution in the dibromide salt and hydroxy phosphonate derivatives described previously may influence their adopted conformations.

Experimental

Compound (I) was synthesized by treatment of cyclotridecanone (0.2 g) with 2,4-dinitrophenylhydrazine solution (3 ml) prepared from 2,4-dinitrophenylhydrazine (1 g), concentrated sulfuric acid (5 ml), water (8 ml) and ethanol (25 ml). The dinitrophenylhydrazone derivative precipitated immediately from the solution and was isolated by filtration, washed with water and recrystallized from ethanol [m.p. 377–378 K; literature m.p. 386.7–387.7 K (Zakharkin *et al.*, 1962)]. Yellow blade-shaped crystals were grown by slow evaporation from ethanol.

Crystal data

$C_{19}H_{28}N_4O_4$	$\gamma = 80.234 (8)^\circ$
$M_r = 376.45$	$V = 948.7 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.7859 (10) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.8937 (10) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 16.130 (2) \text{ \AA}$	$T = 90 \text{ K}$
$\alpha = 81.979 (7)^\circ$	$0.40 \times 0.08 \times 0.03 \text{ mm}$
$\beta = 77.608 (8)^\circ$	

Table 1
Selected torsion angles ($^\circ$).

C1–N1–N2–C14	–177.27 (11)	C5–C6–C7–C8	–73.64 (15)
N2–N1–C1–C13	1.98 (17)	C6–C7–C8–C9	165.98 (11)
C13–C1–C2–C3	161.03 (11)	C7–C8–C9–C10	–59.54 (15)
C2–C1–C13–C12	–106.70 (12)	C8–C9–C10–C11	–42.72 (16)
C1–C2–C3–C4	–67.14 (15)	C9–C10–C11–C12	–176.67 (11)
C2–C3–C4–C5	–74.04 (14)	C10–C11–C12–C13	–164.47 (10)
C3–C4–C5–C6	174.27 (11)	C11–C12–C13–C1	61.91 (14)
C4–C5–C6–C7	–76.56 (15)		

Table 2
Hydrogen-bond geometry (Å, $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2–H2N \cdots O1	0.899 (15)	1.961 (15)	2.6302 (14)	129.9 (12)
C7–H7A \cdots O3 ⁱ	0.99	2.54	3.4363 (18)	150

Symmetry code: (i) $-x + 2, -y + 2, -z + 1$.

Data collection

Nonius KappaCCD diffractometer	5518 independent reflections
(with an Oxford Cryosystems Cryostream cooler)	3974 reflections with $I > 2\sigma(I)$
26226 measured reflections	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.099$	$\Delta\rho_{max} = 0.34 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{min} = -0.26 \text{ e \AA}^{-3}$
5518 reflections	
248 parameters	

H atoms on C atoms were placed in calculated positions, guided by difference maps, with C–H bond distances in the range 0.95–0.99 Å and thereafter treated as riding atoms using the *SHELXL97* (Sheldrick, 2008) defaults. The N-bound H-atom coordinates were refined. All H-atom displacement parameters were assigned as $1.2U_{eq}(C,N)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; structure solution: *SIR97* (Altomare *et al.*, 1999); structure refinement: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); preparation of publication material: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3158). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Anet, F. A. L. & Rawdah, T. N. (1978). *J. Am. Chem. Soc.* **100**, 7810–7814.
- Cheng, A. K.-T. (1973). Doctoral thesis, University of California, Los Angeles, USA.

- Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gill, G., Pawar, D. M., Brown, J. III & Noe, E. A. (2008). Manuscript in preparation.
- Gotō, H. & Ōsawa, E. (1989). *J. Am. Chem. Soc.* **111**, 8950–8951.
- Groth, P. (1979). *Acta Chem. Scand. Ser. A*, **33**, 503–513.
- Groth, P. (1980). *Acta Chem. Scand. Ser. A*, **34**, 609–620.
- Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, A. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Rubin, B. H., Williamson, M., Takeshita, M., Menger, F. M., Anet, F. A. L., Bacon, B. & Allinger, N. L. (1984). *J. Am. Chem. Soc.* **106**, 2088–2092.
- Samuel, G. & Weiss, R. (1969). *Tetrahedron Lett.* **40**, 3529–3532.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Zakharkin, L. I., Vinogradova, L. P., Korneva, V. V. & Zav'valov, S. I. (1962). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 1309–1311.