

Cyclopentadecanone 2,4-dinitro-
phenylhydrazoneEric A. Noe,^a Diwakar M. Pawar^a and Frank R. Fronczek^{b*}^aDepartment of Chemistry, Jackson State University, 1400 J. R. Lynch Street, Jackson, MS 39217-0510, USA, and ^bDepartment of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

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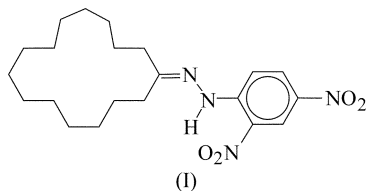
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In the title compound, $C_{21}H_{32}N_4O_4$, no disorder is present in the 15-membered hydrocarbon ring, which exists in an unsymmetrical quinquangular [12345] conformation. The 2,4-dinitrophenylhydrazone group is approximately perpendicular to the C_{15} ring, with a dihedral angle of $84.66(1)^\circ$ between their best planes.

Comment

Semiquantitative calculations for cyclopentadecane, (II), indicated that the first five lowest-energy conformations considered were all quinquangular and that the [33333] conformation was the most stable (Dale, 1973). Five triangular conformations were found among the next nine conformations in order of energy, but quadrangular conformations were absent (Dale, 1973).



MOLBUILD (Boyd, 1968; Boyd *et al.*, 1973) force-field calculations for cyclopentadecane also found five low-energy quinquangular conformations, with the [33333] conformation of lowest strain energy (Anet & Rawdah, 1978). The low-temperature 1H and ^{13}C NMR spectra of (II) showed line broadening at the lowest attainable temperatures of 123 and 127 K, respectively, but decoalescence was not observed in either case (Cheng, 1973). Pawar *et al.* (2008) later recorded the ^{13}C NMR spectra at temperatures to 100.9 K; spectra at the lowest temperatures were substantially more complicated than the two peaks in a ratio of 2:1 expected for the [33333] conformation at slow exchange. This conformation could be present but cannot be the sole conformation populated. In

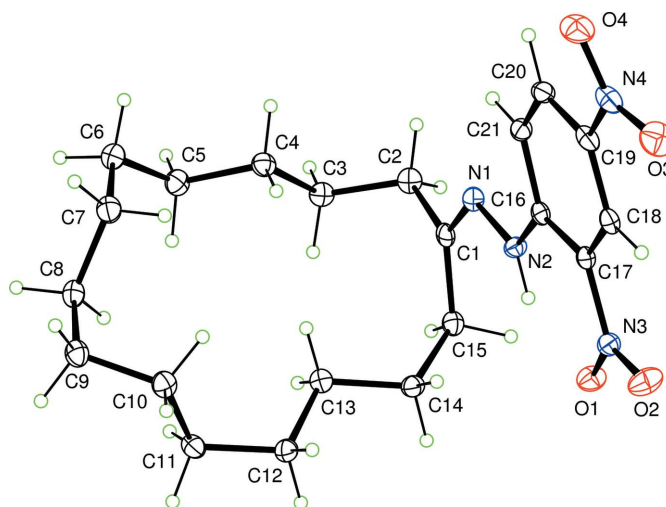
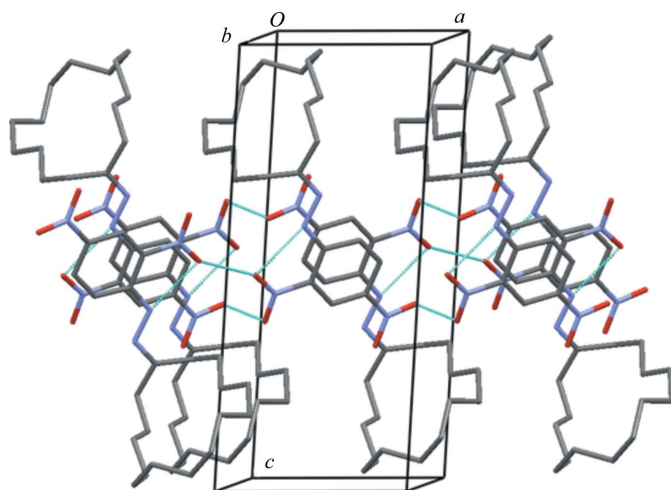


Figure 1
Displacement ellipsoid plot (50% probability) of cyclopentadecanone 2,4-dinitrophenylhydrazone, (I).

macrocyclic rings, a large number of minimum-energy structures can be populated, due to the existence of a high degree of rotational freedom. For example, 262 low-energy conformations were found within 3 kcal mol^{-1} by *MM2* for cycloheptadecane (Saunders *et al.*, 1990).

The crystal structure of cyclopentadecanone phenylsemicarbazone showed an ordered structure with hydrogen-bonded dimers (van den Hoek *et al.*, 1979), and an unexpected quadrangular conformation, *viz.* [3435], was found for the C_{15} ring. An incomplete X-ray study of cyclopentadecanone was reported (Groth, 1976), but no comment on conformation was made. We have recently reported (Noe *et al.*, 2008) the details of the structure of cyclopentadecanone, in which the C_{15} ring has the quinquangular [13353] conformation. A preliminary X-ray study of cyclopentadecanone oxime indicated that the structure is highly disordered (Groth, 1979).

Although cyclopentadecanone 2,4-dinitrophenylhydrazone, (I), was reported by Brady (1931), no structural data are available in the literature. This paper reports an X-ray analysis of the crystal structure of (I) at 90 K. Representative torsion angles defining the conformation of the 15-membered ring are listed in Table 1. The 15-membered ring is present in a quinquangular [12345] conformation with C_1 symmetry, based on the method of Dale (1973). In that system of conformational designation, corner positions are defined, and the numbers of bonds between adjacent corners are listed in brackets, in order of increasing numbers. Corners that are not on adjacent C atoms are readily recognized by having *gauche* dihedral angles of the same sign on either side. For (I), these are found at ring carbons 2, 6, and 9 in Fig. 1. Adjacent corners can be more difficult to recognize. Using the examples given for cycloundecane, cyclotridecane, and cyclopentadecane by Anet & Rawdah (1978), we also assign carbons 11 and 12 as corners. The dihedral angle centered on these two C atoms is $-78.94(18)^\circ$, and the dihedral angles on either side of it are $155.55(15)$ and $178.42(14)^\circ$, which would correspond to a

**Figure 2**

The unit cell of (I), showing intramolecular hydrogen bonding and nitro-nitro contacts as dashed lines.

gauche bond, surrounded by two that are close to *anti*. These dihedral angles are similar to the values around the one-bond segment of the [13353] conformation of cyclopentadecane, as calculated by Anet & Rawdah (1978) (166, −78, and 150°). The section of the ring between C12 and C2 is a five-bond segment between corners. Thus, beginning at corner C12 and proceeding clockwise in Fig. 1, the designation in (I) is [12345].

The C1—N1—N2—C16 torsion angle is −174.11 (15)°. The 2,4-dinitrophenylhydrazone group is nearly planar, with a mean deviation of 0.053 Å for its 14 non-H atoms, and a maximum deviation of 0.208 (1) Å for atom O4. It is nearly perpendicular to the hydrocarbon ring, forming a dihedral angle of 84.66 (1)° with the best plane of the C₁₅ ring. Those 15 C atoms exhibit a mean deviation of 0.382 Å from coplanarity, with a maximum deviation of 0.835 (1) Å for atom C1.

A projection showing intramolecular hydrogen bonding as dashed lines is shown in Fig. 2, which also illustrates close intermolecular O···O contacts between nitro groups [O1···O1(2 − *x*, −*y*, 1 − *z*) = 2.865 (2) Å and O2···O4(*x* + 1, *y*, *z*) = 3.004 (2) Å].

N—H···O hydrogen bonding (Table 2) results in a discrete six-membered ring [graph set *S*(6); Etter, 1990]. Also evident in Fig. 2 is stacking of the parallel benzene rings related by the inversion center at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The interplanar spacing is 3.295 Å, but the rings are slipped, such that the centroid-centroid distance is 3.557 Å.

Experimental

Cyclopentadecanone 2,4-dinitrophenylhydrazone, (I), was synthesized by treatment of cyclopentadecanone (0.8 g) with a 2,4-dinitrophenylhydrazine solution (12 ml) prepared from 2,4-dinitrophenylhydrazine (1 g), concentrated sulfuric acid (5 ml), water (8 ml), and ethanol (25 ml). The dinitrophenylhydrazone derivative immediately precipitated from the solution, and was isolated by filtration, washed with water, and recrystallized from ethanol [m.p. 373–375 K; literature m.p. 378 K (Brady, 1931)]. The purity of the sample was established by its ¹³C NMR spectrum.

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.288 (2)	N2—C16	1.356 (2)
N1—N2	1.3891 (19)		
C1—N1—N2	116.64 (14)	C16—N2—N1	118.84 (13)
C15—C1—C2—C3	66.69 (18)	C9—C10—C11—C12	155.55 (15)
C1—C2—C3—C4	73.82 (18)	C10—C11—C12—C13	−78.94 (18)
C2—C3—C4—C5	−178.22 (14)	C11—C12—C13—C14	178.42 (14)
C3—C4—C5—C6	178.25 (15)	C12—C13—C14—C15	176.39 (14)
C4—C5—C6—C7	−72.9 (2)	C13—C14—C15—C1	61.5 (2)
C5—C6—C7—C8	−71.38 (19)	C14—C15—C1—C2	−122.89 (16)
C6—C7—C8—C9	173.55 (14)	N1—C1—C15—C14	63.3 (2)
C7—C8—C9—C10	−72.99 (18)	C1—N1—N2—C16	−174.11 (15)
C8—C9—C10—C11	−74.00 (19)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2N···O1	0.869 (18)	1.979 (18)	2.6254 (18)	130.2 (15)

Crystal data

C ₂₁ H ₃₂ N ₄ O ₄	γ = 97.017 (13)°
<i>M_r</i> = 404.51	<i>V</i> = 1027.3 (3) Å ³
Triclinic, <i>P</i> $\bar{1}$	<i>Z</i> = 2
<i>a</i> = 7.2486 (14) Å	Mo <i>K</i> α radiation
<i>b</i> = 8.3234 (15) Å	μ = 0.09 mm ^{−1}
<i>c</i> = 17.731 (3) Å	<i>T</i> = 90 K
α = 103.419 (12)°	0.33 × 0.10 × 0.02 mm
β = 94.044 (9)°	

Data collection

Nonius KappaCCD diffractometer	4936 independent reflections
with an Oxford Cryosystems	3372 reflections with <i>I</i> > 2σ(<i>I</i>)
Cryostream cooler	<i>R</i> _{int} = 0.038
16738 measured reflections	

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.051	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.104	$\Delta\rho_{\max}$ = 0.37 e Å ^{−3}
<i>S</i> = 1.01	$\Delta\rho_{\min}$ = −0.24 e Å ^{−3}
4936 reflections	
266 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 with *U*_{iso}(H) values of 1.2*U*_{eq}(C), and thereafter treated as riding. The N—H hydrogen was refined freely.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3135). Services for accessing these data are described at the back of the journal.

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