mutually connected by asymmetric intermolecular hydrogen bonds giving rise to a network of chains parallel to the [111] direction.

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Structure of *N*-Nitroso-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one

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Abstract. $C_{17}H_{17}N_3O_2$, $M_r = 295.34$, orthorhombic, $P2_12_12_1$, $a = 7.659\,(1)$, $b = 12.741\,(1)$, $c = 15.095\,(1)$ Å, $V = 1473.19\,(2)$ Å^3, $Z = 4$, $D_m = 1.33$, $D_x = 1.32$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.68$ mm^{-1}, $F(000) = 624$, $T = 295$ K, $R = 0.031$ for 1549 unique observed reflections with $I > 2.5\sigma(I)$. The seven-membered heterocyclic ring adopts a boat conformation flattened at the nitroso end of the ring. The substituent phenyl rings occupy pseudo-axial positions and the nitroso group is coplanar with the C(2), N(1), C(7) plane of the central ring. The crystal structure is stabilized by intermolecular N—H···O and weak C—H···O hydrogen bonds.

Introduction. Ever since the first demonstration of carcinogenicity in *N*-nitroso compounds (Magee & Barnes, 1956), there have been extensive biochemical and physicochemical studies on their structure–activity relationships (Lijinsky, 1984; Druckrey, Preussmann, Ivankovic & Schmahl, 1967; Magee, Montesano & Preussman, 1976; Preussman, 1984). There is, however, little information on the detailed geometries of *N*-nitroso compounds although several solution NMR spectroscopic investigations have been carried out (Fraser & Grindley, 1975; Forrest, Hooper & Ray, 1974; Ellis, Jones & Papadopoulos, 1974). We have undertaken the synthesis (Senthilkumar, Jeyaraman, Murray & Singh, 1992) and structure analysis of a series of cyclic nitrosamines. The crystal structure analysis of *N*-nitroso-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one (I) is reported here.

Experimental. Colourless parallelopiped crystals obtained by slow evaporation from ethanol solution. Density measured by flotation in a chlorobenzene–bromobenzene mixture. Cell dimensions were obtained from 20 reflections ($6.5 < \theta < 34.2°$), on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected up to $(\sin\theta)/\lambda = 0.626$ Å^{-1}, with ω–2θ

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Table 1. *Final fractional coordinates and equivalent temperature factors for non-*H *atoms, with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$ (Å^2)
N(1)	−0.0576 (2)	0.2385 (1)	0.2735 (1)	0.0283 (4)
C(2)	0.1221 (3)	0.2137 (2)	0.2450 (1)	0.0303 (6)
C(3)	0.2181 (3)	0.1481 (2)	0.3141 (1)	0.0352 (6)
N(4)	0.2056 (3)	0.1940 (2)	0.4023 (1)	0.0353 (5)
C(5)	0.0577 (3)	0.1918 (2)	0.4493 (1)	0.0314 (5)
O(1)	0.0418 (2)	0.2388 (1)	0.5204 (1)	0.0425 (5)
C(6)	−0.0879 (4)	0.1267 (3)	0.4112 (2)	0.0350 (6)
C(7)	−0.1766 (3)	0.1764 (2)	0.3301 (1)	0.0289 (5)
C(8)	0.1345 (3)	0.1657 (2)	0.1527 (1)	0.0341 (6)
C(9)	0.2172 (4)	0.2218 (2)	0.0863 (2)	0.0498 (8)
C(10)	0.2436 (5)	0.1777 (3)	0.0036 (2)	0.0663 (11)
C(11)	0.1819 (5)	0.0780 (3)	−0.0135 (2)	0.0674 (11)
C(12)	0.0987 (4)	0.0221 (3)	0.0515 (2)	0.0598 (9)
C(13)	0.0753 (4)	0.0654 (2)	0.1351 (2)	0.0429 (7)
C(14)	−0.2844 (3)	0.0975 (2)	0.2763 (1)	0.0319 (6)
C(15)	−0.3499 (3)	0.0071 (2)	0.3148 (2)	0.0400 (6)
C(16)	−0.4525 (4)	−0.0620 (2)	0.2663 (2)	0.0516 (8)
C(17)	−0.4905 (4)	−0.0416 (2)	0.1788 (2)	0.0535 (9)
C(18)	−0.4299 (4)	0.0491 (3)	0.1409 (2)	0.0558 (9)
C(19)	−0.3276 (4)	0.1179 (2)	0.1888 (2)	0.0467 (7)
N(20)	−0.1305 (3)	0.3284 (1)	0.2480 (1)	0.0394 (5)
O(2)	−0.0431 (3)	0.3816 (1)	0.1963 (1)	0.0505 (5)

Table 2. *Bond lengths* (Å), *selected bond angles* (°) *and torsion angles* (°), *with e.s.d.'s in parentheses*

C(2)—N(1)	1.476 (3)	C(12)—C(13)	1.389 (4)
C(2)—C(3)	1.525 (3)	C(8)—C(13)	1.382 (4)
N(4)—C(3)	1.457 (2)	C(14)—C(7)	1.534 (3)
N(4)—C(5)	1.337 (3)	C(14)—C(15)	1.384 (4)
O(1)—C(5)	1.235 (2)	C(15)—C(16)	1.389 (4)
C(5)—C(6)	1.507 (3)	C(16)—C(17)	1.377 (4)
C(7)—C(6)	1.538 (3)	C(18)—C(17)	1.370 (5)
N(1)—C(7)	1.478 (3)	C(19)—C(18)	1.380 (4)
C(8)—C(2)	1.524 (2)	C(14)—C(19)	1.386 (3)
C(8)—C(9)	1.384 (4)	N(20)—O(2)	1.231 (2)
C(9)—C(10)	1.383 (4)	C(10)—C(11)	1.379 (5)
C(12)—C(11)	1.369 (4)	N(1)—N(20)	1.331 (2)

N(1)—C(2)—C(3)	111.6 (2)	C(6)—C(7)—N(1)	114.1 (2)
C(2)—C(3)—N(4)	111.9 (2)	C(7)—N(1)—C(2)	128.9 (2)
C(3)—N(4)—C(5)	122.1 (2)	N(1)—C(2)—C(8)	114.2 (2)
N(4)—C(5)—C(6)	115.8 (2)	N(1)—C(7)—C(14)	112.2 (2)
C(5)—C(6)—C(7)	113.6 (2)	N(1)—N(20)—O(2)	115.4 (2)
N(20)—N(1)—C(2)	119.4 (2)	N(20)—N(1)—C(7)	111.7 (1)
C(3)—C(2)—C(8)	112.0 (2)	N(4)—C(5)—O(1)	122.3 (2)
C(14)—C(7)—C(6)	112.7 (2)	C(6)—C(5)—O(1)	121.9 (2)

N(1)—C(2)—C(3)—N(4)	−50.4 (2)	C(14)—C(7)—N(1)—C(2)	−87.7 (2)
C(2)—C(3)—N(4)—C(5)	72.8 (3)	C(3)—N(4)—C(5)—O(1)	−173.2 (2)
C(3)—N(4)—C(5)—C(6)	8.1 (3)	C(7)—C(6)—C(5)—O(1)	107.5 (2)
N(4)—C(5)—C(6)—C(7)	−73.9 (3)	C(2)—N(1)—N(20)—O(2)	4.8 (2)
C(5)—C(6)—C(7)—N(1)	33.8 (2)	C(7)—N(1)—N(20)—O(2)	−175.9 (2)
C(6)—C(7)—N(1)—C(2)	42.1 (3)	C(14)—C(7)—N(1)—N(20)	93.0 (2)
C(7)—N(1)—C(2)—C(3)	−30.7 (3)	C(8)—C(2)—N(1)—N(20)	−83.2 (2)
C(8)—C(2)—N(1)—C(7)	97.6 (2)		

scans using Ni-filtered Cu $K\alpha$ radiation, from a crystal of size 0.25 × 0.13 × 0.4 mm; index range $0 \le h \le 9$, $0 \le k \le 15$, $0 \le l \le 18$; two reflections (231, $21\bar{2}$) monitored periodically showed no evidence of crystal decay; Lorentz and polarization corrections were applied, but the data were not corrected for absorption. Of the 2120 independent reflections measured, 1549 were considered observed [$I > 2.5\sigma(I)$]. Structure solution by direct methods using *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987).

Refinement by full-matrix least squares using *SHELX*400 (enhanced version of *SHELX*76; Sheldrick, 1976). Non-H atoms were refined anisotropically and H atoms located from difference electron density maps were refined isotropically. The number of parameters refined was 267. The final discrepancy indices were $R = 0.031$, $wR = 0.035$ and $S = 1.156$ with individual weights, $w \propto 1/[\sigma^2(F) + 0.001(F^2)]$; $(\Delta/\rho)_{\rm max} = 0.005$ and the heights in the final $\Delta\rho$ map were within +0.15 and −0.19 e Å^{-3}. The atomic scattering factors were as supplied in *SHELX*76. All calculations were performed on a VAX 11/785 computer.

Discussion. The final fractional coordinates and equivalent temperature factors are listed in Table 1. The bond lengths, selected bond angles and torsion angles of the non-H atoms of the molecule are listed in Table 2.* Fig. 1 shows the atomic numbering scheme.

The functional group of *N*-nitroso compounds is the N—N=O moiety. The N—N and N—O bond lengths are 1.331 (2) and 1.231 (2) Å respectively; the N—N—O angle is 115.3 (1)°. The displacement of N(1) from the plane defined by the atoms C(2), N(20) and C(7) is 0.002 (1) Å showing essentially planar geometry at the N(1) atom. The N—N—O geometry of the present compound conforms to that

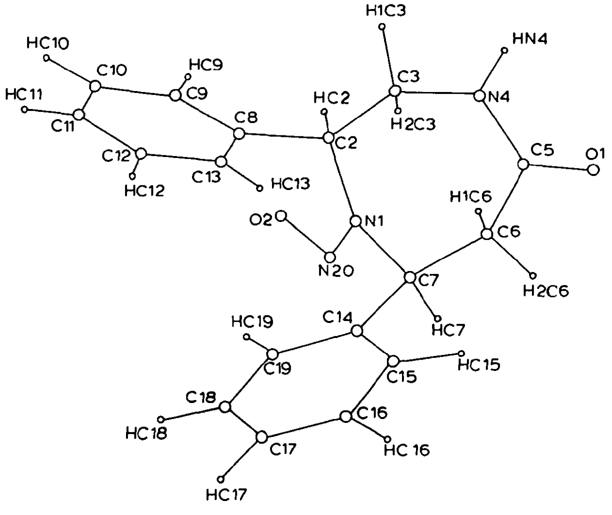

Fig. 1. View down the y axis showing the atomic numbering scheme.

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* 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 54808 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0105]

determined for gaseous nitrosodimethylamine (Rademacher & Stolevik, 1969) from electron diffraction studies. The N—N bond exhibits partial double-bond character which leads to restricted rotation about the bond as also found from solution NMR studies (Cooney & Brownstein, 1974).

The nitroso group has a coplanar orientation with respect to atoms C(2) and C(7), as is evident from the torsion angles C(2)—N(1)—N(20)—O(2) = 4.8 (2) and C(7)—N(1)—N(20)—O(2) = −175.9 (2)°.

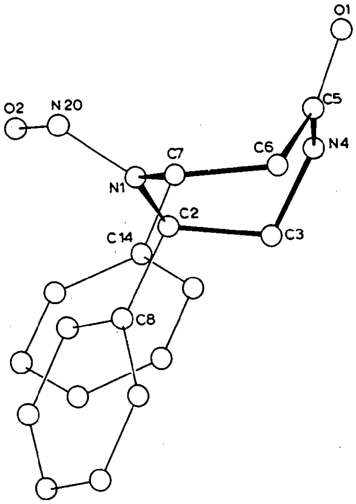

Fig. 2. View illustrating the boat conformation of the central ring.

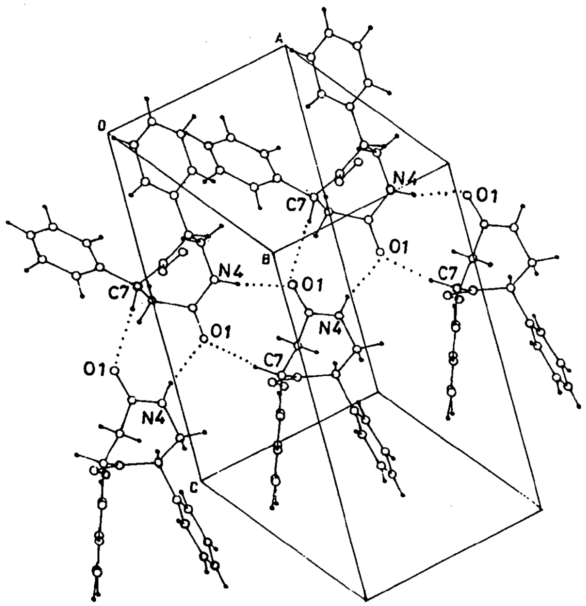

Fig. 3. Crystal packing showing the hydrogen-bonding pattern: N(4)—H···O(1^{i}) 2.954 (3) Å, 159.9 (2)°; O(1)···H—C(7^{ii}) 3.303 (3) Å, 139.1 (2)° [(i) $x + 0.5$, $-y + 0.5$, $-z + 1$; (ii) $-x + 0.5$, $-y + 0.5$, $-z + 1$].

The dihedral angle between the phenyl rings is 145.3°.

The C(2)—N(1)—C(7) bond angle is 128.9 (1)° which is in close agreement with the 130.2 (5)° found in 2,2,7,7-tetramethyl-5-oxo-homopiperazin-1-oxyl (Grand & Rey, 1979) where the phenyl rings are replaced by methyl and N—N=O by the N—O groups. The geometry around the N(4)—C(5) bond agrees with the dimensions of the standard *cis* peptide unit (Ramachandran & Sasisekaran, 1968). In the title compound, the amide group adopts the *cis* form with a torsion angle of 8.1 (3)° about the N(4)—C(5) bond which is greater than that determined by Winkler & Dunitz (1975) for caprolactam (−4.1°) where N(1) of (I) is replaced by C. The presence of the *cis* form in the present structure is in line with the observation that only nine- and larger membered rings can accommodate torsions of 180° about one of the bonds required for the *transoid* form (Dunitz, 1979).

Comparison of the torsion angles for the seven-membered ring with those predicted for the boat form of cycloheptane from theoretical calculations (Bocian & Strauss, 1977) clearly shows that the title compound adopts a flattened boat conformation as illustrated in Fig. 2. The ring conformation seen here is unlike the solid-state structure of ε-caprolactam which is close to that of chair cycloheptene calculated by force-field methods (Alder & White, 1988). The asymmetry parameter (Duax & Norton, 1975) for the best mirror passing through N(1) and bisecting the N(4)—C(5) bond is ΔC_s[N(1)] = 12.1°.

A view of the crystal packing showing the hydrogen-bonding pattern is given in Fig. 3.

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Structure of *N*-Aryl-*N*-nitrosoureas

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Abstract. 1-(4-Methoxyphenyl)-3-methyl-1-nitrosourea (I), $C_9H_{11}N_3O_3$, $M_r = 209.21$, tetragonal, $P\bar{4}2_1c$, $a = 14.232\,(1)$, $c = 10.169\,(4)$ Å, $V = 2060\,(1)$ Å^3, $Z = 8$, $D_x = 1.349$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1.54050$ Å, $\mu = 0.832$ mm^{-1}, $F(000) = 880$, $T = 295$ K, final $R = 0.052$ for 788 reflections. 3,3-Diisopropyl-1-nitroso-1-(4-tolyl)urea (II), $C_{14}H_{21}N_3O_2$, $M_r = 263.34$, monoclinic, $P2_1/a$, $a = 13.854\,(1)$, $b = 9.071\,(1)$, $c = 11.808\,(1)$ Å, $\beta = 92.14\,(1)°$, $V = 1482.9\,(3)$ Å^3, $Z = 4$, $D_x = 1.179$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1.54050$ Å, $\mu = 0.614$ mm^{-1}, $F(000) = 568$, $T = 143$ K, final $R = 0.045$ for 2010 reflections. 3,3-Dibenzyl-1-nitroso-1-(2-tolyl)urea (III), $C_{22}H_{21}N_3O_2$, $M_r = 359.43$, monoclinic, $P2_1$, $a = 12.639\,(1)$, $b = 10.185\,(1)$, $c = 7.851\,(1)$ Å, $\beta = 96.92\,(1)°$, $V = 1003.3\,(1)$ Å^3, $Z = 2$, $D_x = 1.190$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1.54050$ Å, $\mu = 0.588$ mm^{-1}, $F(000) = 380$, $T = 295$ K, final $R = 0.043$ for 1493 reflections. The *Z* conformation of the *N*-nitrosourea in (II) was observed, while (I) and (II) take *E* form [C(2)—N(1)—N(5)—O(6) −178.3 (4)° in (I), −9.3 (2)° in (II) and 172.2 (4)° in (III)].

Introduction. The *N*-nitrosoureas, known as effective antitumor agents, are chemically reactive compounds. Though many chemical modifications of *N*-nitrosoureas have been carried out in order to obtain more potent antitumor compounds (Tsujihara, Ozaki, Morikawa & Arai, 1981), they are limited to the species of *N*-alkyl-*N*-nitrosoureas. Of the *N*-nitrosoureas, the *N*-aryl-*N*-nitrosoureas are a potent group of compounds whose chemical properties appear not to have been reported because of their instability. We recently prepared novel *N*-aryl-*N*-nitrosoureas to shed light on their chemical properties (Sueyoshi & Tanno, 1985; Tanno & Sueyoshi, 1987; Tanno, Sueyoshi & Kamiya, 1990). The present paper describes an X-ray crystallographic analysis of three *N*-aryl-*N*-nitrosoureas, which will contribute to the chemistry of *N*-nitrosoureas, including the chemical reactivity which gives rise to the instability.

Experimental. Compounds (I) and (II) were prepared according to our previous reports (Sueyoshi & Tanno, 1985; Tanno & Sueyoshi, 1987; Tanno, Sueyoshi & Kamiya, 1990). (III) was obtained in a similar way as (II). As these three compounds are unstable at room temperature they were recrystallized from *n*-hexane/ether in a refrigerator. Compound (II) is highly unstable at room temperature and so the experiment was undertaken at 143 K. Details of data collection and refinement are listed in Table 1. Intensity data were collected with a Rigaku

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