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

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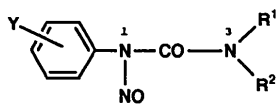
**Abstract.** 1-(4-Methoxyphenyl)-3-methyl-1-nitroso-urea (I),  $C_9H_{11}N_3O_3$ ,  $M_r = 209.21$ , tetragonal,  $P4_21c$ ,  $a = 14.232$  (1),  $c = 10.169$  (4) Å,  $V = 2060$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.349$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha_1) = 1.54050$  Å,  $\mu = 0.832$  mm<sup>-1</sup>,  $F(000) = 880$ ,  $T = 295$  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<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.179$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha_1) = 1.54050$  Å,  $\mu = 0.614$  mm<sup>-1</sup>,  $F(000) = 568$ ,  $T = 143$  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<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.190$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha_1) = 1.54050$  Å,  $\mu = 0.588$  mm<sup>-1</sup>,  $F(000) = 380$ ,  $T = 295$  K, final  $R = 0.043$  for 1493 reflections. The *Z* conformation of the *N*-nitroso-urea 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*-nitroso-ureas, known as effective antitumor agents, are chemically reactive compounds. Though many chemical modifications of *N*-nitroso-ureas 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*-nitroso-ureas. Of the *N*-nitroso-ureas, the *N*-aryl-*N*-nitroso-ureas 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*-nitroso-ureas 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*-nitroso-ureas, which will contribute to the chemistry of *N*-nitroso-ureas, 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

AFC-5 four-circle diffractometer with  $\omega$ - $2\theta$  scan method,  $\omega$ -scan width  $(1.3 + 0.14\tan\theta)^\circ$ . Intensity variation was less than 3% for the three crystals. Intensities were corrected for Lorentz and polarization factors, but an absorption correction was not applied. Structures were solved using the program package *SAP85* (Yao, Zheng, Qian, Han, Gu & Fan, 1985); a version of *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Delcercq & Woolfson, 1980). Refinement was by full-matrix least squares (on  $F^2$ ) with anisotropic temperature factors for non-H atoms. The function minimized was  $\sum w[(|F_o|)^2 - (|F_c|)^2]^2$  with  $w = 1/[\sigma^2(F_o) + 0.02(F_o)]$ ,  $\sigma(F_o)$  from counting statistics. All H atoms found on the difference map and located by calculation were refined, with initial thermal parameters set at the equivalent isotropic thermal parameter of each bonded atom. Major computations were performed on a PANAFACOM computer with the *RCRYSTAN* (Rigaku Corporation, 1985) program system. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).



- (I) Y = 4-MeO, R<sup>1</sup> = Me, R<sup>2</sup> = H  
 (II) Y = 4-Me, R<sup>1</sup> = R<sup>2</sup> = <sup>i</sup>Pr  
 (III) Y = 2-Me, R<sup>1</sup> = R<sup>2</sup> = CH<sub>2</sub>Ph

**Discussion.** Final atomic parameters are listed in Table 2.\* Selected bond lengths, angles and torsion angles are listed in Table 3. Fig. 1 shows *ORTEPII* drawings (Johnson, 1976) of (I), (II) and (III) with the atom labels.

Degradation of *N*-nitrosoureas at room temperature consists of two competitive reactions (Tanno, Sueyoshi & Kamiya, 1990); one gives triazenes *via* diazoester intermediates (diazoester rearrangement) and the other gives 4-tolyl isocyanate and the dialkylnitrosoamine *via* *O*-nitrosoisoureas (homolytic N—NO bond cleavage). <sup>13</sup>C NMR spectroscopic study of these nitrosoureas and related compounds suggested that the different reactions of those nitrosoureas were caused by the difference in the conformations of the nitrosoureas (Tanno & Sueyoshi, 1987). A coplanar form of the O=N—N—C=O moiety in the transition state prefers diazoester rearrangement, while a coplanar form of the phenyl—N—NO moiety prefers N—NO

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54816 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0547]

Table 1. *Details of data collection and structure refinement*

	(I)	(II)	(III)
Data collection			
Crystal size (mm)	0.20 × 0.10 × 0.55	0.30 × 0.35 × 0.55	0.45 × 0.30 × 0.50
Cell parameters			
No. of reflections	25	25	25
2θ range (°)	57–61	56–60	55–61
Scan speed (° min <sup>-1</sup> )	16	32	16
Maximum (sin θ)/λ (Å <sup>-1</sup> )	0.56	0.56	0.56
Range h	0–11	–15–15	–14–14
k	0–16	0–10	0–11
l	0–11	0–13	0–8
Standard reflections			
No.	3	3	3
Interval (reflections)	150	150	150
No. of reflections			
Measured	1823	2690	1750
Independent	887	2210	1589
Observed [F > 3σ(F)]	788	2010	1493
Merging R for equivalent reflections	0.03,	0.05,	0.01,
No. of unobserved reflections [σ(F) > F > 0]	827	228	129
Refinement			
R	0.052	0.045	0.043
wR	0.049	0.047	0.040
G*	1.557	3.006	2.493
No. of parameters	180	256	378
(Δ/σ) <sub>max</sub>	0.18	0.19	0.14
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.28, –0.24	0.15, –0.28	0.11, –0.22

$$*G = \sum w\{[|F_o|)^2 - (|F_c|)^2]^2 / (N_c - N_o)\}^{1/2}$$

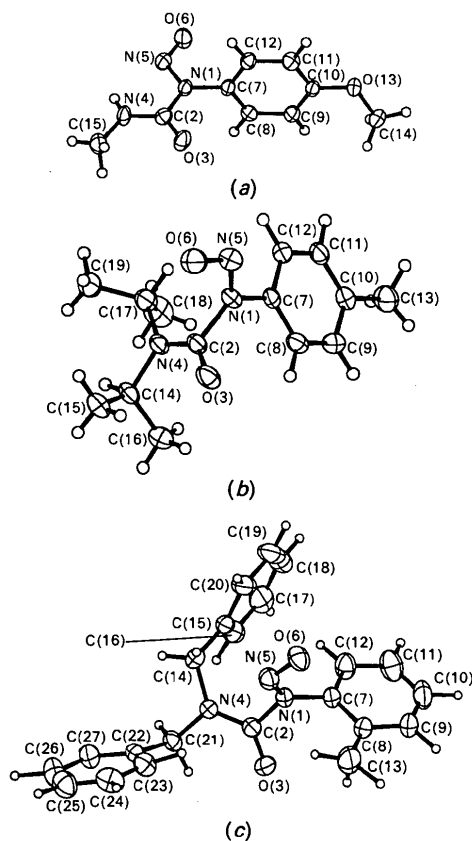


Fig. 1. *ORTEPII* drawings of (a) molecule (I), (b) molecule (II) and (c) molecule (III). Ellipsoids are drawn at the 50% probability level while isotropic H-atom thermal parameters are represented by spheres of arbitrary size.

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$B_{\text{eq}} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$				
(I)	x	y	z	$B_{\text{eq}}$
N(1)	0.8325 (3)	0.7807 (2)	-0.1467 (4)	2.24 (10)
C(2)	0.8361 (3)	0.6802 (3)	-0.1535 (5)	2.38 (13)
O(3)	0.8225 (3)	0.6353 (2)	-0.0528 (3)	3.48 (11)
N(4)	0.8568 (3)	0.6439 (3)	-0.2690 (4)	2.64 (12)
N(5)	0.8477 (3)	0.8285 (3)	-0.2602 (4)	2.71 (12)
O(6)	0.8461 (3)	0.9137 (2)	-0.2481 (3)	3.49 (11)
C(7)	0.8150 (3)	0.8278 (3)	-0.0232 (4)	2.18 (12)
C(8)	0.8880 (3)	0.8461 (3)	0.0608 (5)	2.48 (13)
C(9)	0.8709 (3)	0.8879 (3)	0.1816 (5)	2.49 (13)
C(10)	0.7800 (4)	0.9117 (3)	0.2153 (5)	2.30 (12)
C(11)	0.7066 (3)	0.8960 (3)	0.1278 (5)	2.53 (13)
C(12)	0.7236 (3)	0.8531 (3)	0.0084 (5)	2.29 (12)
O(13)	0.7545 (2)	0.9512 (2)	0.3329 (3)	2.67 (9)
C(14)	0.8239 (4)	0.9555 (4)	0.4349 (6)	3.12 (16)
C(15)	0.8635 (6)	0.5435 (5)	-0.2868 (6)	3.37 (18)
(II)				
N(1)	1.0070 (1)	0.5036 (1)	0.2937 (1)	2.24 (4)
C(2)	0.9918 (1)	0.6514 (2)	0.2418 (1)	2.31 (5)
O(3)	0.9292 (1)	0.6641 (1)	0.1683 (1)	3.25 (4)
N(4)	1.0534 (1)	0.7537 (1)	0.2799 (1)	2.36 (4)
N(5)	0.9501 (1)	0.4517 (2)	0.3723 (1)	2.79 (5)
O(6)	0.8929 (1)	0.5441 (1)	0.4086 (1)	3.58 (5)
C(7)	1.0784 (1)	0.4073 (2)	0.2501 (1)	2.09 (5)
C(8)	1.0925 (1)	0.4030 (2)	0.1353 (1)	2.63 (6)
C(9)	1.1631 (1)	0.3121 (2)	0.0936 (2)	2.82 (6)
C(10)	1.2201 (1)	0.2244 (2)	0.1662 (1)	2.53 (6)
C(11)	1.2039 (1)	0.2300 (2)	0.2809 (2)	2.61 (6)
C(12)	1.1341 (1)	0.3207 (2)	0.3245 (1)	2.53 (6)
C(13)	1.2975 (2)	0.1272 (3)	0.1212 (2)	3.59 (8)
C(14)	1.0559 (1)	0.8967 (2)	0.2174 (2)	2.98 (6)
C(15)	0.9638 (2)	0.9848 (3)	0.2284 (2)	4.00 (9)
C(16)	1.0830 (2)	0.8741 (3)	0.0955 (2)	3.73 (8)
C(17)	1.1229 (1)	0.7318 (2)	0.3769 (2)	3.02 (6)
C(18)	1.2250 (2)	0.7192 (4)	0.3376 (3)	4.67 (10)
C(19)	1.1100 (2)	0.8521 (3)	0.4658 (2)	4.65 (10)
(III)				
N(1)	0.2332 (2)	0.4962 (5)	0.9171 (4)	4.15 (9)
C(2)	0.3483 (3)	0.4965 (5)	0.9296 (5)	4.25 (11)
O(3)	0.3954 (2)	0.4002†	0.9918 (4)	5.44 (9)
N(4)	0.3932 (2)	0.6035 (4)	0.8736 (4)	4.49 (9)
N(5)	0.1813 (3)	0.5327 (5)	0.7648 (4)	5.11 (11)
O(6)	0.0843 (2)	0.5175 (5)	0.7519 (4)	5.99 (10)
C(7)	0.1809 (3)	0.4340 (5)	1.0492 (5)	4.37 (12)
C(8)	0.1458 (3)	0.3045 (6)	1.0307 (6)	5.16 (14)
C(9)	0.0959 (4)	0.2521 (7)	1.1630 (8)	6.58 (18)
C(10)	0.0824 (4)	0.3245 (8)	1.3057 (8)	7.20 (21)
C(11)	0.1169 (5)	0.4509 (9)	1.3219 (7)	7.82 (23)
C(12)	0.1657 (4)	0.5088 (7)	1.1906 (6)	6.17 (16)
C(13)	0.1582 (10)	0.2250 (8)	0.8740 (14)	8.91 (31)
C(14)	0.3400 (4)	0.7323 (5)	0.8383 (8)	5.57 (15)
C(15)	0.2892 (3)	0.7847 (5)	0.9883 (6)	4.89 (13)
C(16)	0.3449 (4)	0.7887 (6)	1.1501 (7)	5.86 (16)
C(17)	0.2954 (5)	0.8383 (7)	1.2854 (9)	7.53 (21)
C(18)	0.1915 (6)	0.8832 (7)	1.2572 (13)	8.63 (27)
C(19)	0.1378 (5)	0.8794 (7)	1.0984 (12)	8.23 (25)
C(20)	0.1862 (4)	0.8310 (6)	0.9643 (9)	6.46 (18)
C(21)	0.5086 (3)	0.6003 (6)	0.8621 (5)	4.52 (12)
C(22)	0.5336 (3)	0.6051 (5)	0.6792 (5)	4.12 (10)
C(23)	0.4763 (3)	0.5319 (6)	0.5501 (6)	5.49 (14)
C(24)	0.5076 (5)	0.5287 (8)	0.3870 (6)	6.68 (18)
C(25)	0.5951 (5)	0.5978 (8)	0.3510 (7)	7.12 (20)
C(26)	0.6515 (4)	0.6722 (8)	0.4773 (7)	7.09 (19)
C(27)	0.6201 (3)	0.6762 (6)	0.6413 (6)	5.35 (14)

†Origin-defining coordinate.

bond cleavage to generate nitric oxide. The torsion angles N(5)—N(1)—C(2)—O(3),  $-179.8 (5)^\circ$ , and O(6)—N(5)—N(1)—C(2),  $-178.3 (4)^\circ$ , in (I), indicate a coplanar form of this site suggesting the tendency to proceed to diazoester rearrangement. The torsion angles C(8)—C(7)—N(1)—N(5),

Table 3. Selected bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ )

	(I)	(II)	(III)
N(1)—N(5)	1.357 (6)	1.327 (2)	1.345 (5)
N(1)—C(2)	1.433 (6)	1.487 (2)	1.447 (5)
N(1)—C(7)	1.445 (6)	1.429 (2)	1.443 (6)
C(2)—O(3)	1.224 (6)	1.210 (2)	1.219 (5)
C(2)—N(4)	1.318 (6)	1.328 (2)	1.328 (7)
N(4)—C(14)		1.494 (2)	1.485 (7)
N(4)—C(15)	1.443 (8)		
N(4)—C(17)		1.482 (3)	
N(4)—C(21)			1.472 (5)
N(5)—O(6)	1.219 (5)	1.240 (2)	1.227 (5)
C(10)—O(13)	1.370 (6)		
C(10)—C(13)		1.500 (3)	
C(8)—C(13)			1.497 (12)
O(13)—C(14)	1.433 (7)		
N(5)—N(1)—C(2)	117.0 (4)	122.0 (1)	116.0 (3)
N(5)—N(1)—C(7)	122.3 (4)	118.2 (1)	122.9 (3)
C(2)—N(1)—C(7)	120.7 (4)	119.4 (1)	119.8 (3)
O(3)—C(2)—N(4)	125.2 (5)	127.7 (2)	125.9 (3)
O(3)—C(2)—N(1)	118.5 (4)	118.0 (1)	117.7 (4)
N(4)—C(2)—N(1)	116.3 (4)	114.3 (1)	116.5 (4)
C(2)—N(4)—C(14)		117.8 (1)	125.8 (3)
C(2)—N(4)—C(15)	121.0 (4)		
C(2)—N(4)—C(17)		123.9 (1)	
C(2)—N(4)—C(21)			117.9 (4)
C(14)—N(4)—C(17)		118.2 (1)	
C(14)—N(4)—C(21)			116.0 (4)
O(6)—N(5)—N(1)	114.3 (4)	114.0 (1)	114.5 (3)
C(8)—C(7)—N(1)	119.9 (4)	119.8 (1)	120.6 (4)
C(12)—C(7)—N(1)	118.9 (4)	119.5 (1)	117.2 (5)
O(13)—C(10)—C(9)	124.5 (4)		
O(13)—C(10)—C(11)	115.1 (4)		
C(13)—C(10)—C(9)		120.9 (2)	
C(13)—C(10)—C(11)		120.8 (2)	
C(13)—C(8)—C(7)			122.3 (6)
C(13)—C(8)—C(9)			120.7 (6)
C(10)—O(13)—C(14)	117.8 (4)		
C(8)—C(7)—N(1)—C(2)	85.2 (5)	-37.1 (2)	-94.6 (5)
C(8)—C(7)—N(1)—N(5)	-93.8 (5)	136.4 (2)	72.0 (5)
O(6)—N(5)—N(1)—C(2)	-178.3 (4)	-9.3 (2)	172.2 (4)
O(6)—N(5)—N(1)—C(7)	0.6 (4)	177.3 (2)	5.1 (4)
N(5)—N(1)—C(2)—O(3)	-179.8 (5)	-79.1 (2)	-132.4 (5)
N(1)—C(2)—N(4)—C(14)	168.5		15.1 (4)
N(1)—C(2)—N(4)—C(15)	179.1 (5)		
N(1)—C(2)—N(4)—C(17)		8.3 (2)	
N(1)—C(2)—C(4)—C(21)			-171.7 (5)

$136.4 (4)^\circ$ , and O(6)—N(5)—N(1)—C(7),  $177.3 (2)^\circ$ , in (II), suggest the occurrence of N—NO bond cleavage. These findings are consistent with the results of thermolysis of compounds (I) and (II) at room temperature. However, the *N*-nitrosoarea having *E* conformation does not suggest the occurrence of diazoester rearrangement in (I) [O(6)—N(5)—N(1)—C(2)  $-178.3 (4)^\circ$ ], and the *Z* form in (II) [O(6)—N(5)—N(1)—C(2)  $-9.3 (2)^\circ$ ] prefers this rearrangement because the nitroso O(6) atom points toward the carbonyl C(2) atom with which the O(6) atom reacts in the rearrangement. These differences are probably caused by the difference between the solution and crystalline states. In (III) the nitroso group takes an *E* conformation [O(6)—N(5)—N(1)—C(2)  $172.2 (4)^\circ$ ] which is ascribed to the bulky substituents at the N(4) position.

The nitroso N—O bond lengths in (I) and (III), 1.219 (5) and 1.227 (5)  $\text{\AA}$  respectively, are consistent with those found in 1-(2-chloroethyl)-3-(*trans*-4-methylcyclohexyl)-1-nitrosoarea (1.218  $\text{\AA}$ ) (Smith

& Camerman, 1978) and *N*-methyl-*N*-nitroso-urea [1.231 (2) Å], *N,N'*-dimethyl-*N*-nitroso-urea [1.227 (2) Å], 2-nitroso-2-azabicyclo[2.2.2]octan-3-one [1.227 (5) Å] and *N*-methyl-*N*-nitroso-*p*-nitrobenzamide [1.218 (4) Å] (Prout, Fail, Hernandez-Cassou & Ming Miao, 1982). However, a comparatively long nitroso N—O bond [1.240 (2) Å] and a short N(1)—N(5) bond [1.327 (2) Å] were observed in (II). These results and the N(1)—C(7) bond length [1.429 (2) Å] as well as the prolonged urea C—N bond length [C(2)—N(1) 1.487 (2) Å] suggest conjugation through the phenyl—N—N=O moiety instead of the urea moiety in (II). Intermolecular hydrogen bonds and unusual short non-bonded contacts are not observed.

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## Structure of the Low-Melting Phase of Petroselinic Acid

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**Abstract.** *cis*-6-Octadecenoic acid, C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>, *M<sub>r</sub>* = 282.47, orthorhombic, *Pbca*, *a* = 7.311 (1), *b* = 5.565 (1), *c* = 88.01 (1) Å, *V* = 3581.1 (8) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.05 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 4.74 cm<sup>-1</sup>, *F*(000) = 1264, *T* = 263 K, *R*(*F*) = 0.054 for 1633 unique observed reflections with *F* > 3σ(*F*). Two bimolecular layers forming a double-layered polytype structure exist within a repeating unit along the *c* axis. The *cis* olefin group [C(5)—C(6)=C(7)—C(8)] has a 157, 0, -160° conformation, deviating significantly from the standard skew, *cis*, skew' conformation. The hydrocarbon chains on either side of

the olefin group adopt all-*trans* conformations and form an orthorhombic polyethylene-type subcell.

**Introduction.** Petroselinic acid (*cis*-6-octadecenoic acid) is a naturally occurring *cis*-monounsaturated fatty acid with a rather unusual crystal structure. It contains an even-numbered hydrocarbon chain on the methyl-terminal side of the C=C bond, and its polymorphism differs from that of other *cis*-monounsaturated fatty acids (Sato, Yoshimoto, Suzuki, Kobayashi & Kaneko, 1990). There are two polymorphic phases: a low-melting (LM) and a high-