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Crystal Structure of *N*-Benzyl-α-methoxycarbonylmethanimine *N*-Oxide

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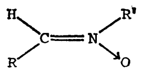
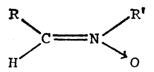
The geometry of *N*-benzyl-α-methoxycarbonylmethanimine *N*-oxide in the crystalline state was established to be *Z* by X-ray crystal analysis. The crystal was monoclinic, space group Pc, $a=11.069(1)$, $b=5.2335(7)$, $c=8.620(1)$ Å, $\beta=105.37(1)°$, $Z=2$. The final R value was 0.037 for 1760 reflections.

During the last decade, many approaches have been developed by using a nitrone as a constructive unit to provide various kinds of natural products.[1–4] Most of these nitrones have been cyclic, while acyclic ones have been limited to special cases.[4]

Acyclic nitrones, in contrast to cyclic ones, have the possibility of geometrical isomerism around a C=N bond. However, aldonitrones have generally been shown to exist only in a stable *Z*-configuration (**1a**), both in crystals[5] and in solution.[6]



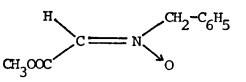
1a



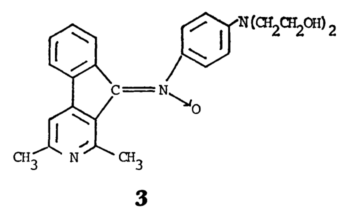
1b

In 1974, Bjørgo and his co-workers[7] isolated *E*-aldonitrone (**1b**, R:pentamethylphenyl, R′:methyl) by the oxidation of a corresponding imine with *m*-chloroperbenzoic acid and found that the *E*-isomer isomerized to the more stable *Z*-isomer when heated at 35 °C in the presence of benzoic acid. The final *E*/*Z* ratio was found to be 0.20 in $CDCl_3$.

Recently, we found that *N*-benzyl-α-methoxycarbonylmethanimine *N*-oxide (**2**) and its analogues exist in one configuration in the ctystalline state, but in solution exhibit a facile isomerization to give a mixture of *E*- and *Z*-isomers——the *E*/*Z* ratio being 1.6 in $CDCl_3$ (Fig. 1).[8] The assignment of the configuration was deduced from the difference in the chemical shifts of the benzylic protons in the two isomers.



2



3

Soon after, a similar time-dependent isomerization of a ketonitrone, **3**, was reported.[9] In both nitrones, **2** and **3**, an *E*-isomer, which is generally thought to be thermodynamically unstable, is predominant in solution.

In this investigation, a single-crystal X-ray analysis of **2** was performed in order to clarify the configuration in the crystalline state.

Experimental

Data Collection. *N*-Benzyl-α-methoxycarbonylmethanimine *N*-oxide (**2**)[4b)] was slowly crystallized from benzene. Preliminary oscillation and Weissenberg photographs showed the space group to be either Pc or P2/c. The density was measured by the flotation method in a heptane–carbon tetrachloride mixture. The unit-cell dimensions were refined on a Rigaku automatic four circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (40 kV, 100 mA). The crystal data are shown in Table 1.

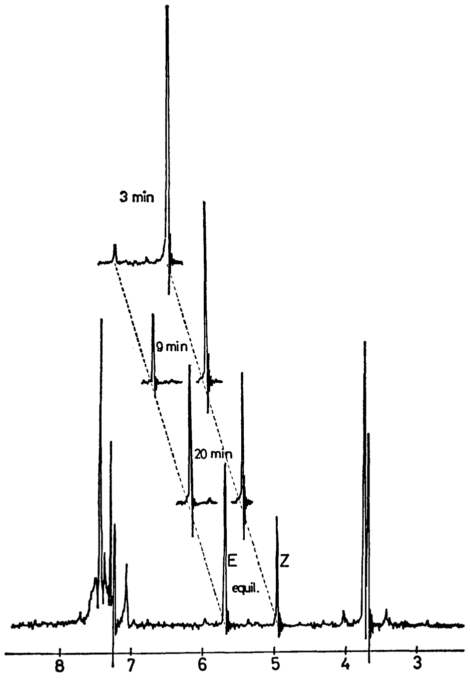


Fig. 1. Time-dependence of the intensities of the benzylic protons in the NMR spectra of **2** in $CDCl_3$.

TABLE 1. CRYSTAL DATA

$C_{10}H_{11}NO_3$	M.W. = 193.2
Monoclinic	Pc
$a=11.069(1)$ Å	
$b=\ 5.2335(7)$ Å	
$c=\ 8.620(1)$ Å	
$\beta=105.37(1)°$	
$D_m=1.32$ g cm^{-3}	
$D_x=1.33$ g cm^{-3}	
$Z=2$	

The intensity data were collected, using a single crystal with dimensions of $0.45\times0.50\times0.53$ mm^3, on a diffractometer by the $\omega/2\theta$ scanning technique within $67°>2\theta$ at room temperature. The intensities of three standard reflections, measured every 50 reflections, were stable within a 2% fluctuation during the course of the data collection.

Of the 1981 unique observed reflections, 1760 reflections with $|F_o|\geq3\sigma(F)$ were used for the structure determinations. The intensities were corrected for Lorentz and polarization effects, but not for absorption. All the computations

Table 2. The final atomic parameters and estimated standard deviations

(1) The non-hydrogen atoms ($\times 10^4$) with the equivalent isotropic temperature factors.[13]

Atom	x	y	z	B_{eq}/Å^2
C(1)	−749(3)	3193(6)	−2040(4)	5.26
O(2)	162(3)	3812(3)	−559(4)	4.64
C(3)	660(3)	1839(3)	388(4)	3.53
O(4)	388(3)	−358(3)	76(4)	4.90
C(5)	1546(3)	2870(3)	1830(4)	3.52
N(6)	2261(3)	1471(2)	2952(3)	3.36
O(7)	2352(3)	−956(2)	2943(4)	4.42
C(8)	3080(3)	2783(3)	4393(4)	3.75
C(9)	4431(3)	2599(3)	4375(4)	3.37
C(10)	4917(3)	4386(4)	3510(4)	4.00
C(11)	6161(3)	4243(4)	3462(4)	4.75
C(12)	6926(3)	2348(5)	4288(4)	4.79
C(13)	6449(3)	567(5)	5150(4)	5.07
C(14)	5213(3)	685(3)	5198(4)	4.39

(2) The hydrogen atoms ($\times 10^3$).

Atom	x	y	z	B/Å^2
H(1)	−99(3)	486(7)	−253(5)	4.6(7)
H(2)	−139(3)	236(6)	−183(4)	4.3(7)
H(3)	−40(3)	212(7)	−261(4)	4.5(7)
H(4)	160(2)	457(5)	196(3)	1.9(4)
H(5)	283(2)	457(5)	440(3)	2.3(4)
H(6)	295(3)	178(5)	535(3)	3.1(5)
H(7)	442(3)	580(4)	297(3)	2.7(5)
H(8)	653(3)	549(5)	292(3)	3.0(5)
H(9)	769(3)	224(6)	426(4)	3.5(6)
H(10)	691(3)	−65(6)	570(4)	3.7(6)
H(11)	487(3)	−55(7)	580(5)	5.0(8)

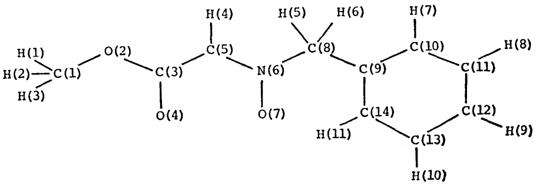
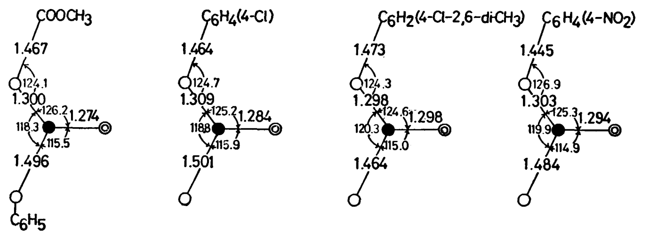


Fig. 2. Numbering diagram for **2**.



(a) **2** (b) **4**[5a)] (c) **5**[5b] (d) **6**[5c)]

Fig. 3. Geometries around the nitrone chromophore. ●: Nitrogen, ◎: Oxygen, ○: Carbon

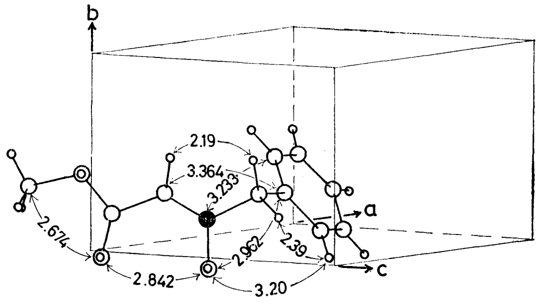


Fig. 4. The conformation of **2** projected on the ester plane.
Small circles show hydrogen atoms.

were carried out on a FACOM M-200 computer in the Science Information Processing Center of the University of Tsukuba.

Structure Determination. Since the number of molecules in the unit cell was 2, the space goup P2/c was certainly excluded. The structure was solved by using Patterson and Fourier methods and was refined by the full-matrix least-squares method with the *RFINE*-2 program.[10)] The atomic scattering factors, given by Cromer and Mann[11)] for C, N, or O, and listed on the table[12)] for H were used.

From the analysis of a three-dimensional Patterson map, the coordinates of a benzene ring were placed on the plane which includes the Y axis and declines 62° from the X-Y plane. The repeated removal-addition of atoms on difference Fourier syntheses revealed the positions of all the non-hydrogen atoms. A nitrone chromophore, instead of a benzene ring, was finally found to be placed on that plane. The R value at this stage was 0.258 and was reduced to 0.062 when refined with anisotropic temperature factors. Then, the positions of the hydrogens were obtained from a difference Fourier synthesis and were also refined. The final refinement with anisotropic temperature factors for all non-hydrogen atoms and with an isotropic one for hydrogens reduced the R value to 0.037. The residuals in the difference map were within the range of ± 0.17 e/Å^3. The final atomic parameters are listed in Table 2 (for the numbering diagram, see Fig. 2). The $F_o - F_c$ table is kept as Document No. 8305 at the Chemical Society of Japan.

Results and Discussion

The configuration around the C=N bond was clearly established to be Z as was previously assumed.[8)]

The bond distances and bond angles are listed in Table 3. The geometry around the nitrone chromophor is in good agreement with those of N-methyl-α-(4-chlorophenyl)methanimine N-oxide (**4**),[5a)] N-methyl-α-(4-chloro-2,6-dimethylphenyl)methanimine N-oxide (**5**),[5b)] and N-methyl-α-(4-nitrophenyl)methanimine N-oxide (**6**),[5c)] as is shown in Fig. 3, and no unusual bond distances or angles were observed.

The conformation of the molecule projected on the ester plane [O(2)–C(3)–O(4)] is illustrated in Fig. 4. The figures show some short interatomic distances within a molecule. The ester and the nitrone chromophores exist essentially on the same plane (Table 4). This is due to the conjugation effect of both chromophores. Similar effects had also been observed in **4** and **6** as the coplanarity of the benzene ring with the nitrone chromophore. On the other hand, the benzene ring in **2** is twisted toward the direction of minimizing the van der Waals interaction between O(7)–C(9) and N(6)–C(10).

The crystal structure projected on the (100) plane

Table 3. The bond distances and angles with their standard deviations

Bond distance	l/Å	Bond distance	l/Å
C(1)-O(2)	1.438(4)	C(1)-H(1)	0.97(4)
O(2)-C(3)	1.341(3)	C(1)-H(2)	0.89(4)
C(3)-O(4)	1.201(2)	C(1)-H(3)	0.92(4)
C(3)-C(5)	1.467(4)	C(5)-H(4)	0.90(2)
C(5)-N(6)	1.300(3)	C(8)-H(3)	0.97(3)
N(6)-O(7)	1.274(2)	C(8)-H(6)	1.02(3)
N(6)-C(8)	1.496(3)	C(10)-H(7)	0.97(2)
C(8)-C(9)	1.503(5)	C(11)-H(8)	0.95(3)
C(9)-C(10)	1.390(4)	C(12)-H(9)	0.85(3)
C(9)-C(14)	1.389(3)	C(13)-H(10)	0.87(3)
C(10)-C(11)	1.390(5)	C(14)-H(11)	0.97(4)
C(11)-C(12)	1.374(4)		
C(12)-C(13)	1.381(5)		
C(13)-C(14)	1.381(5)		
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
C(1)-O(2)-C(3)	116.4(2)	C(8)-C(9)-C(10)	119.3(2)
O(2)-C(3)-O(4)	124.3(3)	C(8)-C(9)-C(14)	121.9(3)
O(2)-C(3)-C(5)	107.9(2)	C(10)-C(9)-C(14)	118.8(3)
O(4)-C(3)-C(5)	127.8(2)	C(9)-C(10)-C(11)	120.4(2)
C(3)-C(5)-N(6)	124.1(2)	C(10)-C(11)-C(12)	120.2(3)
C(5)-N(6)-O(7)	126.2(2)	C(11)-C(12)-C(13)	119.6(3)
C(5)-N(6)-C(8)	118.3(1)	C(12)-C(13)-C(14)	120.6(3)
O(7)-N(6)-C(8)	115.5(2)	C(13)-C(14)-C(9)	120.4(3)
N(6)-C(8)-C(9)	110.3(3)		

Table 4. Least-squares planes and dihedral angles
$X=ax+cz\cos\beta,\ Y=by,\ Z=cz\sin\beta$

(1) Equation

I: the ester group [O(2)-C(3)-O(4)]
$-0.8808X+0.0707Y+0.4681Z+0.347=0.0$

II: the nitrone chromophore [C(5)-N(6)-O(7)]
$-0.8889X-0.0744Y+0.4521Z+0.573=0.0$

III: the benzene ring [C(9)-C(10)-C(11)-C(12)-C(13)-C(14)]
$-0.0499X-0.5860Y-0.8088Z+3.933=0.0$

(2) Dihedral angle

between I and II planes (ϕ/°)	8.4
between II and III planes	106.1

is shown in Fig. 5. All the intermolecular atomic contacts are usual van der Waals distances, the shortest ones are O(2) (x, y, z)—O(4) (x, $y+1$, z) (3.10 Å) between non-hydrogen atoms and H(6) (x, y, z)—O(7) (x, $-y$, $z+0.5$) (2.53 Å) involving hydrogen atoms. The value of 2.53 Å is just the sum of the Kitaigorodskii intermolecular radii, R;[14] the C–H··· O attraction, initially found in 2-methyl-3-(4-chloro-2,6-dimethylphenyl)oxazolidine (2.30 Å)[15] and followed in **4** (2.15 Å)[5b] and **5** (2.14 Å),[5b] was not recognized in the present nitrone **2**.

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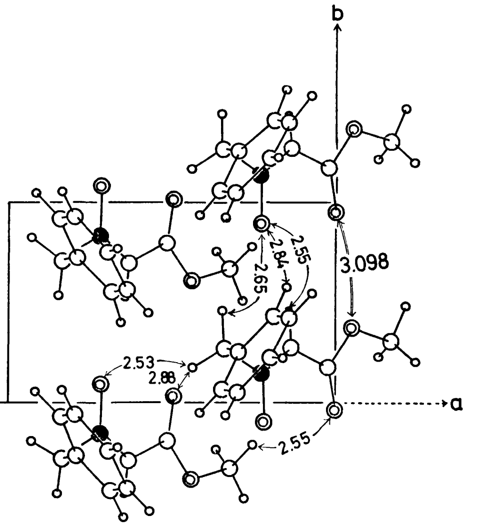

Fig. 5. The crystal structure of **2** projected on (100) plane.

References

1) For a recent review, see J. J. Tufariello, *Acc. Chem. Res.*, **12**, 396 (1979).

2) M. Wovkulich and M. R. Uskoković, *J. Am. Chem. Soc.*, **103**, 3956 (1981).

3) T. Iwashita, T. Kusumi, and H. Kakisawa, *J. Org. Chem.*, **47**, 230 (1982).

4) a) Y. Inouye, Y. Watanabe, S. Takahashi, and H. Kakisawa, *Bull. Chem. Soc. Jpn.*, **52**, 3763 (1979); b) J. Hara, Y. Inouye, and H. Kakisawa, *ibid.*, **54**, 3871 (1981).

5) a) K. Folting, W. N. Lipscomb, and B. Jerslev, *Acta Chem. Scand.*, **17**, 2138 (1963); b) K. G. Jensen and B. Jerslev,

Acta Crystallogr., *Sect. B*, **25**, 916 (1969); c) F. Bachechi and L. Zambonelli, *ibid.*, **31**, 2499 (1975).

6) a) J. Thesing and W. Sirrenberg, *Chem. Ber.*, **91**, 1978 (1958); b) D. R. Boyd, W. B. Jennings, and R. Spratt, *J. Chem. Soc.*, *D*, **1970**, 745.

7) J. Bjørgo, D. R. Boyd, and D. C. Neill, *J. Chem. Soc., Chem. Commun.*, **1974**, 478.

8) Y. Inouye, J. Hara, and H. Kakisawa, *Chem. Lett.*, **1980**, 1407.

9) D. Tresselt and W. Schulze, *Pharmazie*, **36**, 405 (1981).

10) L. W. Finger and E. Prince, U. S. Nat. Bur. Stand. Tech. Note, 854 (1975).

11) D. T. Cromer and J. Mann, *Acta Crystallogr.*, *Sect. A*, **24**, 321 (1968).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

13) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

14) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York (1961).

15) B. Jerslev, *Acta Crystallogr.*, **23**, 645 (1967).