Crystal and Molecular Structure of 4,*N*-Dinitrobornan-2-imine (4,*N*-Dinitrocamphorimine)

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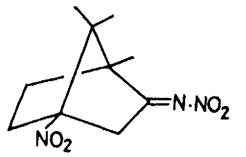
The title compound (1) is shown from a single-crystal *X*-ray diffraction study to exist in a configuration with the N(1)–N(2) and C(2)–C(3) bonds *syn*. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ and $a = 7.629(6)$, $b = 7.729(5)$, $c = 20.453(8)$: the structure was solved by direct methods and refined by full-matrix least squares to R 0.059 for 994 independent reflections. In the light of the configuration found for (1) we suggest that the previous mechanism for formation of nitro-imines be amended and propose a mechanism involving a radical pair intermediate.

In recent work we have been concerned with the structure of a nitro-olefin [1] and with the configuration of the nitro-group in *N*-nitro-imines.[2,3] While in the latter case evidence has been presented which indicates the presence of geometrical isomerism about the carbon nitrogen bond in 1,3,3-trimethyl-*N*-nitronorbornan-2-imine, the assignment of particular isomers was not possible; [3] likewise in the case of 4-substituted *N*-nitrobornan-2-imines we were unable to specify definitively the single configuration by spectroscopic means.[2] Hitherto structural information on *N*-nitro-imines has been absent and in view of their formal similarity with nitro-olefins we have determined the crystal structure of the title compound (1).



(1)

EXPERIMENTAL

Crystals of (1) were isolated according to the method of ref. 2 and recrystallised from ethyl acetate as colourless needles. Preliminary space-group data were determined from Weissenberg photographs, and accurate unit-cell dimensions were obtained by least-squares refinement of the setting angles of 12 reflections measured on an automatic diffractometer.

Crystal Data.—$C_{10}H_{15}N_3O_4$, $M = 241.2$. Orthorhombic, $a = 7.629(6)$, $b = 7.729(5)$, $c = 20.453(8)$, $U = 1\,206.0$ Å^3, $Z = 4$, $D_c = 1.3285$ g cm^{-3}, $F(000) = 512$. Space group $P2_12_12_1$ (D_2^4, No. 19), Cu-K_α radiation, $\lambda = 1.540\,51$ Å, μ(Cu-K_α) = 7.84 cm^{-1}. 994 Independent reflections were measured on a Picker FACS 1 four-circle diffractometer in the range of θ from 1 to 59°. Of these, 720 reflections had $I > 3\sigma(I)$. Lorentz and polarization, but not absorption, corrections were applied.

Structure Analysis.—The structure was solved by use of the SHELX (1976) system [4] with a multisolution application of the tangent formula.[5] All non-hydrogen atoms were located in the E map with the fifth lowest Karle [6] R factor. The structure was refined by full-matrix least-squares ($w\Delta F^2$ = min.). After three cycles with isotropic temperature factors on all atoms a difference Fourier synthesis showed that both nitro-groups in the molecule were either disordered or were librating with considerable amplitudes. The residual electron-density in the region of the nitrimino NO_2 groups was consistent with a libration of this group around the N–N bond with an amplitude of ±40° from the 'equilibrium position.' Maxima in the residual electron-density were observed at the 'equilibrium position' and the two extremes of the libration. Each oxygen atom was therefore given three positions and in the subsequent refinement the site occupancies were maintained at 1/3 for each

TABLE 1

Atomic co-ordinates ($\times 10^4$; for hydrogen $\times 10^3$), with estimated standard deviations in parentheses

	x	y	z
C(1)	3 097(9)	8 057(7)	4 083(3)
C(2)	2 898(8)	9 589(7)	4 520(3)
C(3)	2 849(10)	11 199(7)	4 110(3)
C(4)	3 076(9)	10 365(7)	3 432(3)
C(5)	4 997(9)	9 775(10)	3 375(3)
C(6)	5 026(10)	8 242(8)	3 842(3)
C(7)	2 020(9)	8 676(7)	3 478(3)
C(8)	119(9)	8 941(9)	3 614(3)
C(9)	2 231(12)	7 453(8)	2 891(3)
C(10)	2 648(12)	6 347(8)	4 374(3)
N(1)	2 826(7)	9 405(6)	5 135(2)
N(2)	2 719(10)	11 031(9)	5 493(4)
N(3)	2 583(9)	11 560(8)	2 897(3)
O(21)	1 260(20)	11 539(23)	5 591(10)
O(21′)	1 457(35)	11 086(38)	5 874(11)
O(21″)	1 620(35)	12 140(26)	5 318(11)
O(22)	4 112(22)	11 674(22)	5 677(10)
O(22′)	3 814(36)	12 175(29)	5 400(11)
O(22″)	3 804(36)	11 145(32)	5 920(10)
O(31)	2 779(23)	11 156(31)	2 332(6)
O(32)	1 653(38)	12 734(30)	3 021(23)
O(31′)	2 592(61)	10 977(46)	2 363(10)
O(32′)	2 330(47)	13 026(20)	3 024(21)
H(31)	378(5)	1 209(5)	421(3)
H(32)	169(3)	1 183(7)	415(3)
H(51)	599(6)	1 046(7)	354(2)
H(52)	525(7)	943(8)	290(2)
H(61)	590(6)	833(8)	421(2)
H(62)	534(8)	79(6)	362(2)
H(81)	−39(7)	773(4)	373(2)
H(82)	−7(8)	961(6)	405(2)
H(83)	−80(6)	942(7)	330(2)
H(91)	159(6)	633(4)	301(3)
H(92)	161(6)	791(7)	248(2)
H(93)	345(3)	714(7)	276(3)
H(101)	378(5)	654(8)	468(2)
H(102)	168(6)	581(8)	469(1)
H(103)	295(6)	532(8)	403(2)

atom. The other nitro-group in the molecule appeared to be librating about the N–C bond with a total amplitude of 30° and residual electron-density appeared only at the extremes of the libration. The oxygen atoms in this group were therefore given only two positions with a site-occupancy of each atom maintained at $\frac{1}{2}$. Refinement continued with isotropic temperature factors until R was 0.15 when those hydrogen atoms with positions defined by the molecular geometry were included; in subsequent refinement cycles non-hydrogen atoms were accorded anisotropic temperature factors. After two such cycles a difference-Fourier synthesis showed reasonable positions for the remaining hydrogen atoms, and after several more cycles the refinement converged at R 0.059. The weights were given by $w = [\sigma^2|F_o| + 0.000\,42\,F_o^2]^{-1}$ where σ is the individual estimated standard deviation for each reflection and was calculated from the diffractometer counting statistics. Final atomic co-ordinates are given in Table 1; observed structure amplitudes, calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22381 (8 pp., 1 microfiche).* Atomic scattering

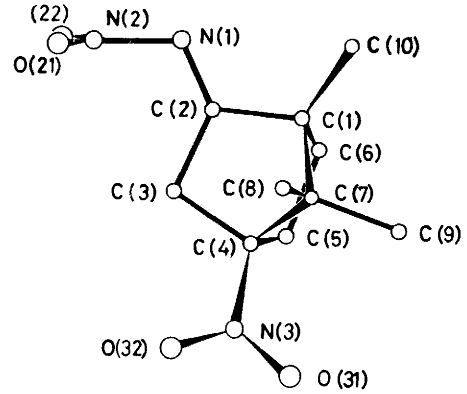


FIGURE 1 The individual molecule viewed perpendicular to the plane through N(1), C(1), and C(3), showing only the equilibrium positions of the oxygen atoms

TABLE 2

Intramolecular bond lengths (Å), corrected for libration, in (1), with estimated standard deviations in parentheses

C(1)–C(2)	1.498(8)	C(5)–C(6)	1.522(10)
C(1)–C(6)	1.567(10)	C(7)–C(8)	1.499(10)
C(1)–C(7)	1.569(9)	C(7)–C(9)	1.541(8)
C(1)–C(10)	1.497(8)	N(1)–N(2)	1.461(9)
C(2)–C(3)	1.511(8)	N(2)–O(21)	1.20(2)
C(2)–N(1)	1.273(7)	N(2)–O(22)	1.24(2)
C(3)–C(4)	1.543(9)	N(3)–O(31)	1.21(1)
C(4)–C(5)	1.547(10)	N(3)–O(32)	1.19(3)
C(4)–C(7)	1.545(8)	N(3)–O(31′)	1.19(3)
C(4)–N(3)	1.489(9)	N(3)–O(32′)	1.18(2)

TABLE 3

Intramolecular bond angld (°) in (1), with estimated standard deviation in parentheses

C(2)–C(1)–C(6)	102.3(5)	C(1)–C(7)–C(4)	91.9(5)
C(2)–C(1)–C(7)	100.3(4)	C(1)–C(7)–C(8)	114.0(5)
C(2)–C(1)–C(10)	116.2(5)	C(1)–C(7)–C(9)	112.1(5)
C(6)–C(1)–C(7)	102.6(5)	C(4)–C(7)–C(8)	113.8(5)
C(6)–C(1)–C(10)	115.1(6)	C(4)–C(7)–C(9)	114.8(5)
C(7)–C(1)–C(10)	117.9(5)	C(8)–C(7)–C(9)	109.4(6)
C(1)–C(2)–C(3)	108.9(5)	C(2)–N(1)–N(2)	113.8(5)
C(1)–C(2)–N(1)	120.7(5)	N(1)–N(2)–O(21)	115(1)
C(3)–C(2)–N(1)	130.4(5)	N(1)–N(2)–O(22)	117(1)
C(2)–C(3)–C(4)	98.9(4)	O(21)–N(2)–O(22)	128(1)
C(3)–C(4)–C(5)	107.5(6)	C(4)–N(3)–O(31)	121(1)
C(3)–C(4)–C(7)	104.0(5)	C(4)–N(3)–O(32)	118(2)
C(3)–C(4)–N(3)	112.1(5)	C(4)–N(3)–O(31′)	116(1)
C(5)–C(4)–C(7)	104.6(5)	C(4)–N(3)–O(32′)	118(2)
C(5)–C(4)–N(3)	111.7(6)	O(31)–N(3)–O(32)	119(2)
C(7)–C(4)–N(3)	116.2(5)	O(31)–N(3)–O(32′)	119(2)
C(4)–C(5)–C(6)	101.3(5)	O(32)–N(3)–O(31′)	120(3)
C(5)–C(6)–C(1)	104.8(5)	O(31′)–N(3)–O(32′)	125(2)

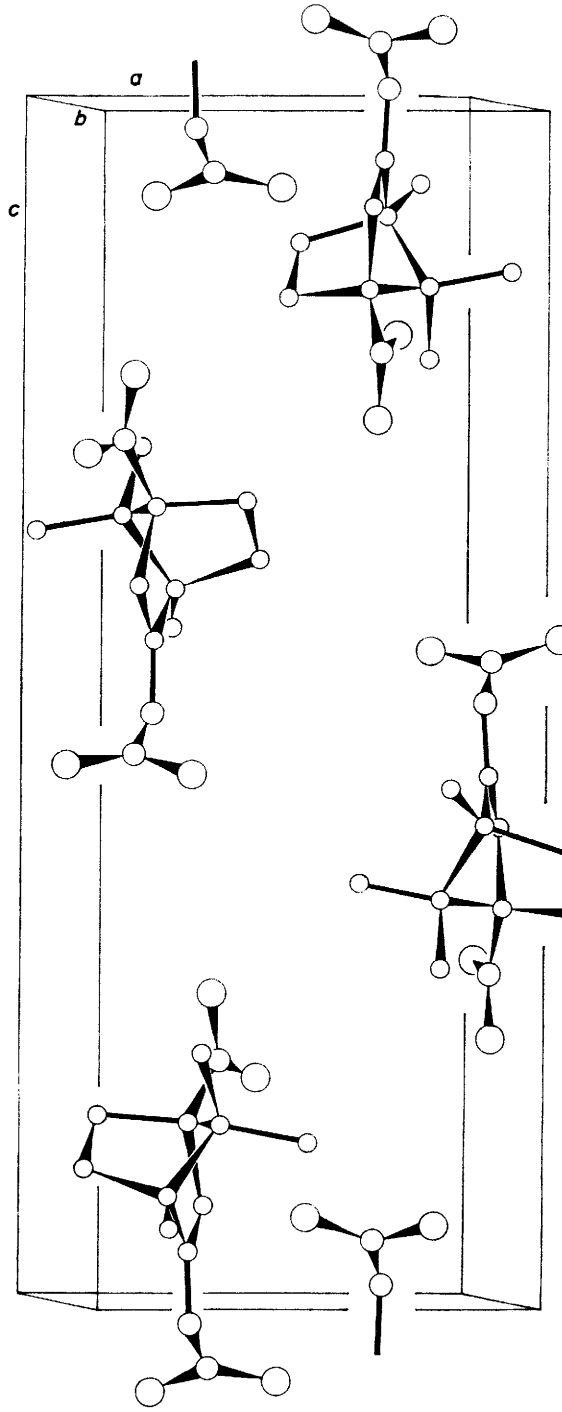


FIGURE 2 The unit cell viewed approximately along b (equilibrium positions only of oxygen atoms are shown)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

factors were taken from ref. 7 and were corrected for the real part of the anomalous dispersion effect. Interatomic distances, corrected for librations, are given in Table 2 and bond angles in Table 3. Figures 1—3 illustrate the molecule and the packing in the unit cell. Only the equilibrium positions of the oxygen atoms are shown in Figures 1 and 2.

DISCUSSION

The solid-state structure of (1) is shown in Figure 1, with the molecule viewed perpendicular to the plane through N(1), C(3), and C(1). The crystal is constructed from isolated molecules of (1) and from Figure 2 it can be seen that since neither of the nitro-groups is closely packed, it is possible that the observed uncertainty in the positions of the oxygen atoms of these groups is the result of libration rather than of specific disorder sites. The extent of the ' flapping ' is indicated in Figure 3.

Figure 1 shows clearly that the bonds N(1)–N(2) and C(2)–C(3) are *syn*; the atoms C(2), C(4), and N(2) are respectively 0.009, —0.042, —0.057 Å from the plane which contains N(1), C(3), and C(1). This plane is approximately at right angles to the equilibrium plane through the nitro-group of the nitro-imine group. This conformation effectively precludes a conjugated system between the nitro- and imino-groups and is in contrast with the result obtained for a *trans*-phenylnitroethylene in the crystal state [1] and also nitroethylene in the gas phase.[8] The reason for this difference is not apparent.

The C(2)=(N) double bond length [1.273(7) Å] agrees well with that (1.28 Å) predicted for a nonconjugated bond;[9a] recently a value of 1.278 Å was found in the semicarbazones of acetone and benzaldehyde.[10] Additionally the N–N bond length [1.461(9) Å] accords with the expected value for a single bond.[9b] By way of comparison, the N–N bond lengths in the bisnitramine 3,7-dinitro-1,3,5,7-tetrazabicyclo[3.3.1]nonane were 1.347 and 1.386 Å respectively.[11] The N–O bond lengths in the nitro- and nitrimino-groups (1.20 and 1.22 Å) are not significantly different from each other.

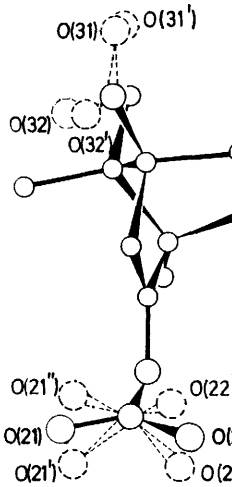
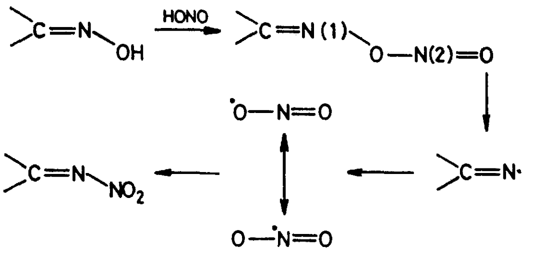


FIGURE 3 The individual molecule, showing the extent of ' disorder ' of the NO_2 groups

From the ^{13}C n.m.r. spectrum of camphor oxime [12] it has been concluded that the N–O bond is *syn* to the C(2)–C(3) bond, and with the reasonable proviso that the configurations of (1) and camphor oxime are not influenced by the substituent at C(4), the results of the present *X*-ray study permit the conclusion that conversion of oxime to nitrimine by means of nitrous acid has taken place with retention of configuration at nitrogen. This is contrary to a postulated mechanism [13] which involves rearrangement of an *N*-nitroso-nitrone obtained by *N*-nitrosation of the oxime and where overall inversion of configuration at nitrogen is required. However the observed stereochemical result is accommodated by a mechanism involving initial *O*-nitrosation and then homolytic cleavage of the weak N(1)–O bond in the resultant nitrite ester. This gives rise to a radical pair (Scheme) which recombines to yield the *N*-nitro-imine of less-hindered configuration, as found for (1). The radical-pair mechanism also accounts for formation of both geometric isomers from fenchone oxime of apparently one configuration;[3] here the fenchone system resembles a perturbed di-t-butyl ketone and there is less distinction between formation of the geometric isomers as a consequence of bond formation between the two nitrogen atoms. The dissociation–recombination mechanism (Scheme) finds precedent in the reactions of other oxime derivatives.[14]



SCHEME

We have prepared (1) several times and on no occasion have we been able to obtain evidence from ^{13}C n.m.r. spectroscopy for the alternate configuration with the N–N bond *syn* to the C(1)–C(2) bond. However, it is possible that small amounts of the less-abundant isomer are lost on recrystallisation of (1).

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