$+0.013|F_o|^2)^{-1}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

Final values of atomic positions and temperature parameters are listed in Table 1. The conformations of the two independent molecules are illustrated in Fig. 1. The programs used in the refinement were the X-RAY System (Stewart, Kundell & Baldwin, 1970) and the figures were drawn with the program *ORTEP* (Johnson, 1965).

Discussion. 1,3-Dichloroacetone has an unusually high melting point of 45° C compared with other chlorinated acetones, ranging from monochloroacetone (m.p. $-44{\cdot}4$°C) to hexachloroacetone (m.p. -2°C). This could be due to a favourable packing of the molecules and/or the presence of O···Cl charge-transfer bonds.

Bond lengths and angles for the two independent molecules are listed in Table 1. Due to the synperiplanar conformation of the Cl–C–C=O groups short intramolecular O···Cl distances of 2·93–2·95 Å are found.

Least-squares planes through the non-hydrogen atoms are listed in Table 1 with distances of the atoms from the planes.

The packing of the molecules is shown in Fig. 2. No intermolecular contacts significantly shorter than the expected van der Waals contacts are found in the structure. A packing coefficient was calculated (Kitaigorodskii, 1961) and found to be 0·664, indicating a favourable packing of the molecules.

References

Dewar, R. K. B. (1968). *Use of Computers in the X-ray Phase Problem.* Dissertation, Univ. of Chicago.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP.* ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*, p. 106. New York: Consultants Bureau.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The X-RAY System. Univ. of Maryland, College Park, Maryland.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30339 (26 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The Nitroxide Radical *exo*-2-Iodomethyl-2,4,4-*exo*-6-tetramethyl-3-azabicyclo[3,3,1]nonan-7-on-3-oxyl

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Abstract. $C_{12}H_{21}INO_2$, $M = 350{\cdot}32$. Orthorhombic, $P2_12_12_1$, $a = 16{\cdot}16$ (2), $b = 14{\cdot}46$ (2), $c = 6{\cdot}20$ (1) Å, from precession photographs, refined by diffractometer. $Z = 4$, D_m(flotation) = 1·60 g cm^{-3}, $D_c = 1{\cdot}605$ g cm^{-3}. The compound, whose structure could not be established spectroscopically, was crystallized from chloroform as thin red needles. The structure, refined to $R = 0{\cdot}049$, shows the compound to be the 2-*exo* isomer in the chair-chair conformation. The nitroxide group shows a distortion from planarity of 17°.

Introduction. Systematic absences $h00$, h odd, $0k0$, k odd and $00l$, l odd gave the space group as $P2_12_12_1$. Data were collected for layers $h0l$ to $h5l$ and $hk0$ to $hk5$ with a Hilger–Watts linear diffractometer (Mo $K\alpha$ radiation). 1978 reflexions were collected of which 1474 had intensities greater than 3σ. The agreement between the two sets of data is shown in a merging R of 0·048 $[R = \sum|(F_1 - F_2)|/\frac{1}{2}\sum(F_1 + F_2)]$. Lorentz and polarization corrections were applied (but none for absorption) and layer scales were obtained through common reflexions. The iodine atom was located from a sharpened Patterson function and the remaining non-hydrogen atoms from a Fourier synthesis. Refinement was by full-matrix least-squares calculations with our adaptation of the *PORFLS* program in the CRYSTAL 69 system of Powell & Griffiths (1968). Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Five cycles of refinement of positional and isotropic thermal parameters gave $R = 0{\cdot}100$ ($R = ||F_o| - |F_c||/\sum|F_o|$), and a further six cycles including anisotropic thermal parameters with the weighting scheme $w = 1$ if $F_o < 40$, $w = 1/[1 + (F_o - 40)^2/2500]$ otherwise, converged with $R = 0{\cdot}049$.* No attempt was made

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Table 1. *Atomic positions and anisotropic temperature factors* ($\times 10^4$)

The expression used for the anisotropic temperature factor was

$$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+\beta_{23}kl)\}.$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	5295 (6)	1048 (7)	−492 (19)	37 (4)	43 (4)	284 (32)	−11 (3)	−37 (10)	8 (10)
C(2)	5759 (7)	267 (6)	744 (18)	53 (5)	36 (5)	238 (32)	−5 (3)	18 (10)	5 (9)
C(3)	6495 (7)	628 (7)	1899 (22)	48 (4)	41 (4)	346 (35)	16 (3)	15 (11)	−14 (13)
C(4)	7051 (6)	1291 (7)	693 (21)	39 (4)	45 (4)	362 (43)	1 (3)	0 (10)	1 (11)
C(5)	6580 (6)	2048 (6)	−585 (16)	36 (4)	42 (4)	174 (26)	1 (3)	−10 (8)	−12 (8)
C(6)	6176 (6)	2769 (6)	985 (14)	31 (3)	37 (4)	162 (27)	−1 (3)	5 (7)	−1 (8)
C(8)	4839 (6)	1709 (8)	969 (19)	22 (3)	56 (5)	371 (39)	−7 (3)	0 (9)	45 (11)
C(9)	5902 (7)	1590 (7)	−1999 (16)	51 (5)	51 (5)	153 (27)	−9 (4)	2 (9)	8 (10)
C(10)	6764 (7)	3079 (8)	2786 (17)	38 (4)	64 (6)	229 (29)	9 (4)	−17 (10)	−15 (10)
C(11)	5333 (6)	3617 (7)	−294 (22)	34 (3)	39 (4)	406 (29)	8 (3)	17 (11)	40 (11)
C(12)	4369 (8)	1199 (9)	2370 (26)	48 (5)	65 (6)	510 (51)	−13 (5)	67 (13)	44 (16)
C(13)	4162 (7)	2276 (12)	−364 (29)	34 (4)	107 (9)	575 (56)	4 (6)	−69 (12)	94 (19)
C(14)	6023 (9)	−503 (9)	−885 (25)	68 (7)	49 (5)	507 (46)	−4 (6)	40 (14)	−55 (14)
N	5417 (4)	2337 (5)	2053 (13)	26 (3)	45 (4)	201 (22)	0 (3)	20 (6)	2 (8)
O(1)	6670 (6)	376 (6)	3725 (13)	66 (4)	78 (5)	257 (23)	21 (3)	−3 (8)	33 (9)
O(2)	5131 (5)	2332 (6)	3671 (13)	50 (3)	73 (5)	234 (24)	8 (3)	51 (7)	−14 (9)
I	6315 (0)	4477 (0)	−1678 (1)	46 (0)	42 (0)	330 (2)	−10 (0)	16 (1)	0 (1)

to locate the hydrogen atoms or to determine the absolute configuration. Atomic parameters are given in Table 1, the conformation of the molecule and bond lengths in Fig. 1, bond and torsional angles in Tables 2 and 3, and intermolecular contact distances in Table 4.

Table 2. *Bond angles* (*e.s.d.* = 0·4°)

C(1)-C(2)-C(3)	111·6°	C(5)—C(6)—C(10)	112·8°
C(1)-C(2)-C(14)	109·4	C(5)—C(6)—C(11)	110·7
C(1)-C(8)-C(12)	112·8	C(5)—C(6)—N	111·6
C(1)-C(8)-C(13)	110·4	C(6)—C(5)—C(9)	109·9
C(1)-C(8)-N	112·1	C(6)—C(11)-I	112·8
C(1)-C(9)-C(5)	108·5	C(6)—N——C(8)	123·2
C(2)-C(1)-C(8)	113·4	C(6)—N——O(2)	117·1
C(2)-C(1)-C(9)	110·8	C(8)—C(1)—C(9)	110·2
C(2)-C(3)-C(4)	117·5	C(8)—N——O(2)	116·9
C(2)-C(3)-O(1)	121·8	C(10)—C(6)—C(11)	111·1
C(3)-C(2)-C(14)	110·1	C(10)-C(6)—N	107·0
C(3)-C(4)-C(5)	114·1	C(11)-C(6)—N	102·9
C(4)-C(3)-O(1)	120·5	C(12)—C(8)—C(13)	106·7
C(4)-C(5)-C(6)	110·7	C(12)—C(8)—N	105·8
C(4)-C(5)-C(9)	109·5	C(13)—C(8)—N	108·6

Table 3. *Torsional angles in the two rings of the bicyclo*[3,3,1] *system*

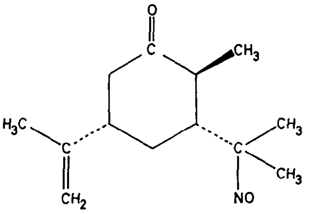
(e.s.d. = 0,5°)

(*a*) Nitroxide ring		(*b*) Carbonyl ring	
C(6)-C(5)	−46°	C(4)-C(5)	+50°
C(5)-C(9)	+63	C(5)-C(9)	−59
C(9)-C(1)	−65	C(9)-C(1)	+61
C(1)-C(8)	+48	C(1)-C(2)	−53
C(8)-N	−35	C(2)-C(3)	+44
N——C(6)	+33	C(3)-C(4)	−44

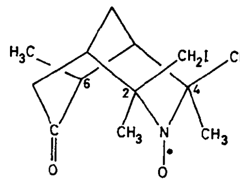
Table 4. *Intermolecular contact distances less than* 3·70 Å (*e.s.d.* = 0·01 Å)

C(14)···O(2)	$\bar{x}, \frac{1}{2}+y, 1\frac{1}{2}-z$	3·34 Å
O(1) ···C(9)	$x, y, 1+z$	3·41
C(4)····O(1)	$\bar{x}-\frac{1}{2}, \bar{y}, z-\frac{1}{2}$	3·41
O(2) ···C(9)	$x, y, 1+z$	3·46

Discussion. In the course of an investigation of the synthesis (Motherwell & Roberts, 1972*a*) and chiroptical properties (Roberts & Thomson, 1972) the nitroso-olefin (I) derived from (+)-carvone was cyclized with iodine in chloroform solution. Two isomeric products were obtained and whilst the spectral data of one were completely consistent with the 2-*endo* epimer of the title compound, the other had anomalous spectral data, particularly the electron spin resonance and circular dichroism (Motherwell & Roberts, 1972*b*). Both compounds could be reduced to the same 2,2-dimethyl derivative but conclusive proof that the second compound was (II) was only provided by the crystal structure. (The absolute configuration has been assumed to be directly related to the known configuration of (+)-carvone.)



(I)



(II)

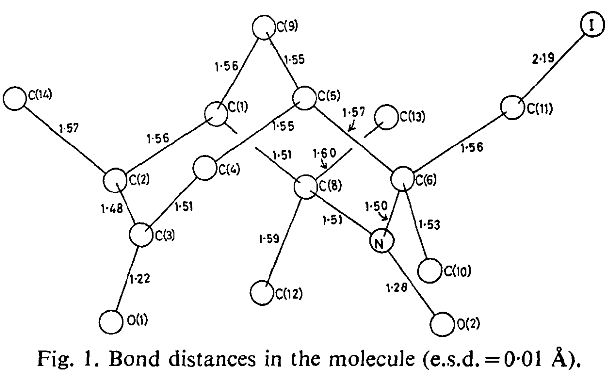


Fig. 1. Bond distances in the molecule (e.s.d. = 0·01 Å).

The crystal structure analysis shows the molecule to be (II) and that it adopts the expected chair-chair conformation. The bond lengths are all within the accepted ranges and the N–O length of 1·28 Å in the nitroxide group agrees with previous crystal structure analyses of these radicals [N–O (av.) = 1·28 Å] (Rassat & Rey, 1973).

The geometry of the nitroxide group is of interest as this group has not been extensively studied. A summary of the results obtained so far (Rassat & Rey, 1973) suggests that in non-planar rings the nitroxide group is pyramidal, with the N–O bond at 19(2)° to the C–N–C plane. The present structure shows an angle of 17·0 (5)°. The distortion from planarity is outwards from the body of the molecule as this does most to relieve steric interactions with the carbonyl group. By comparison, the carbonyl group is planar within experimental error.

The conformation of the molecule, although the expected twin-chair, shows some distortion from ideal geometry even when the effects of the sp^2 hybridized C(3) and N are considered. The bond angles at C(2), C(4), C(6), and C(8) are all opened by 3–4° and the torsional angles in the rings suggest considerable flattening of the rings, particularly round the nitroxide group, where they are some 10° smaller than near the carbonyl group. This might be due to a greater flexibility in the C–N–C system of nitroxide radicals. Additional evidence for the distortion of the ring system is shown by the interplanar angle C(2)C(3)C(4)/C(6)NC(8) of 41·3 (7)° which for an ideal 3,7-dione system would be less than 10°.

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References

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

MOTHERWELL, W. B. & ROBERTS, J. S. (1972*a*). *Chem. Commun.* pp. 328–329.

MOTHERWELL, W. B. & ROBERTS, J. S. (1972*b*). *Tetrahedron Lett.* pp. 4287–4289.

POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69 system of crystallographic programs, Portsmouth Polytechnic.

RASSAT, A. & REY, P. (1973). *Tetrahedron*, **29**, 1599–1603.

ROBERTS, J. S. & THOMSON, C. (1972). *J. Chem. Soc. Perkin* II, 2129–2140.

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Tetraamminepalladium(II) Pyrazine-2,5-dicarboxylate

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Abstract. $[Pd(NH_3)_4]C_4N_2H_2(CO_2)_2$, $C_6H_{14}O_4N_6Pd$, M.W. 340·6, triclinic, $P\bar{1}$, $a = 7·145$ (1), $b = 10·685$ (1), $c = 3·771$ (1) Å, $\alpha = 99·10$ (1), $\beta = 98·78$ (1), $\gamma = 97·90$ (1)°, 23°C, $Z = 1$, $D_x = 2·041$, $D_m = 2·040$ g cm^{-3}, $V = 277·07$ Å^3. Full-matrix least-squares refinement of 1268 observed reflections collected with θ–2θ scans on a Syntex $P2_1$ yielded a final agreement index, R, of 0·038. Multiple hydrogen bonds are formed between the square-planar tetraamminepalladium(II) cations and the pyrazine-2,5-dicarboxylate anions.

Introduction. The unit-cell dimensions were determined by a least-squares refinement of 29 high-angle reflections (Cu $K\alpha_1 = 1·54050$, Cu $K\alpha_2 = 1·54433$ Å). The

Table 1. *Atomic coordinates and thermal parameters with e.s.d.'s*

Positional parameters are × 10^4; β_{11}, β_{22} and β_{12} are × 10^4; β_{33}, β_{13} and β_{23} are × 10^3.

The thermal parameters are of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0	0	0	63 (1)	42 (1)	44 (1)	20 (1)	4 (0)	0 (0)
O(1)	4918 (6)	1699 (4)	5808 (12)	200 (11)	48 (4)	82 (4)	25 (5)	6 (2)	−2 (1)
O(2)	7884 (6)	2781 (4)	6438 (13)	162 (11)	84 (5)	99 (5)	58 (6)	16 (2)	−1 (1)
N(1)	2731 (7)	−146 (5)	−762 (14)	103 (10)	83 (6)	71 (5)	42 (6)	10 (2)	−1 (1)
N(2)	842 (7)	1904 (5)	1974 (14)	134 (11)	64 (5)	63 (5)	22 (6)	6 (2)	2 (1)
N(3)	3676 (7)	3863 (4)	8759 (14)	102 (10)	51 (5)	85 (5)	13 (6)	8 (2)	−3 (1)
C(1)	6155 (9)	2682 (5)	6752 (15)	156 (14)	56 (6)	45 (5)	44 (7)	5 (2)	2 (1)
C(2)	5530 (8)	3913 (5)	8482 (15)	108 (12)	48 (5)	43 (4)	25 (6)	6 (2)	1 (1)
C(3)	6812 (8)	5039 (6)	9732 (18)	96 (12)	57 (6)	84 (6)	20 (7)	11 (2)	−1 (2)