Table 4. *Torsional angles in the tricyclic nucleus* (°) (*e.s.d.*=0·4°)

| C(8)–N(1)–C(1)–C(2) | 66·2 | C(7')–N(2)–C(2)–C(1) | −67·2 |
| C(7') | C(2) | −66·7 | C(9) | C(1) | 65·7 |

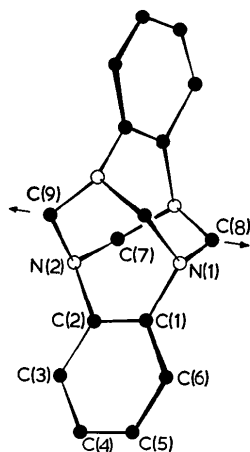| C(8)–N(1)–C(1)–C(2)	66·2		C(7')–N(2)–C(2)–C(1)	−67·2
C(7') C(2)	−66·7		C(9) C(1)	65·7
C(1)–N(1)–C(8)–N(1')	−78·7		C(2)–N(2)–C(7')–N(1')	78·3
C(7') N(1')	53·2		C(9) N(1')	−53·9
C(1)–N(1)–C(7')–N(2')	79·2		C(2)–N(2)–C(9)–N(2')	−78·3
C(8) N(2')	−52·4		C(7) N(2')	53·7
N(1)–C(1)–C(2)–N(2)	0·3			

Fig. 1. The geometry and numbering of the molecule. Primed atoms are generated by the action of the crystallographic diad shown.

non-hydrogen atoms) is less than 3·50 Å. Although the molecule lies on a crystallographic diad axis, its real symmetry is almost the expected D_{2d}. The bond lengths are all as expected [C–C(aromatic)=1·39 Å (av.); C(sp^2)–N=1·437, C(sp^3)–N=1·475 Å, the latter in good agreement with the corresponding value in (I) of 1·470

Å]. The bond angles in the tricyclic nucleus show the same sort of increases from the tetrahedral value as found in (I); the angles to be discussed have been averaged on the basis of D_{2d} symmetry and those for (I) are given in parentheses. The methylene bridges have an N–C–N angle of 118·6 (116·9°) but the other angle in the cyclooctane ring (114·8°) is considerably smaller than in (I) (119·3°). The geometry of the two-carbon bridges is very similar in the two molecules and the small differences can be explained by the different lengths of the C–C bonds. The torsional angles in the tricyclic system are also essentially the same in both molecules. We conclude therefore that the geometry found for (I) is not inconsistent with that required for a D_{2d} conformation, but naturally cannot dismiss the other possibilities put forward (Murray-Rust, 1974).

References

Bischoff, C. A. (1898). *Ber. dtsch. chem. Ges.* **31**, 3248–3260.

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

Main, P. (1971). LSAM programs, Univ. of York.

Murray-Rust, P. (1974). *J. Chem. Soc. Perkin* II, 1136–1141.

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

5,8-Di-t-butyl-3,3-dimethyl-9-isopropylidene-5,8-diaza-4,7-dioxabicyclo[4,2,1]nonan-2-one

By Judith Murray-Rust and Peter Murray-Rust

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

Abstract. $C_{18}H_{32}N_2O_3$, $M=324·46$, orthorhombic, $Pna2_1$ (No. 33), $a=18·13$ (2), $b=11·56$ (2), $c=9·45$ (2) Å, from precession photographs, refined by diffractometer (Mo $K\alpha$ radiation). D_m (flotation)$=1·09$ g cm^{-3}; for $Z=4$, $D_c=1·09$ g cm^{-3}. The structure was solved by direct methods, and refinement converged at $R=$ 0·051; the molecule contains bridged five- and seven-membered rings, each of which contains a hydroxylamine group.

Introduction. Systematic absences $0kl$ $k+l=2n+1$, $h0l$ $h=2n+1$, indicated space groups $Pnam$ (No. 62)

or $Pna2_1$ (No. 33). The infrared and n.m.r. spectra (Craig, Murray-Rust, Murray-Rust & Roberts, 1973) suggested that the compound did not possess hydroxyl, acetylenic or allenic groups, but probably contained two different t-butyl groups, four methyl groups (two of which are similar and possibly belong to an isopropylidene group) and two non-identical protons. This indicates that the molecule does not have a centre of symmetry, and is very unlikely to have a mirror plane or twofold axis. There are eight asymmetric units in the unit cell of $Pnam$, so that if the molecule is in this space group it must lie on a special position (either m or $\bar{1}$): as this is not likely $Pna2_1$ was selected. Since the structure was solved and refined satisfactorily in this space group, no calculations were made in $Pnam$.

Data were collected for layers $hk0$–8 (967 reflexions) and $h0$–8l (761 reflexions) on a Hilger–Watts linear diffractometer with Mo $K\alpha$ radiation ($\lambda=0.71071$ Å); reflexions were considered observed if $I>3\sigma(I)$. After application of Lorentz and polarization corrections (but no extinction or absorption correction) the data

Table 1. *The order in which atom peaks were identified during phase recycling (at that stage all were assumed to be carbon)*

	Number of peaks	Atom identifiers (see Fig. 1)
Initial peaks from E map	6	C(1), C(2), C(3), C(8), C(9), N(1)
1st recycle; $\|E\| \geq 1.68$, $\|F_c\| \geq 0.33 \times \|F_o\|$	4	C(10), C(18), N(2), O(1)
2nd recycle; $\|E\| \geq 1.69$, $\|F_c\| \geq 0.50 \times \|F_o\|$	8	C(6), C(7), C(11), C(12), C(13), C(14), O(2), O(3)
3rd recycle; $\|E\| \geq 1.74$, $\|F_c\| \geq 0.60 \times \|F_o\|$	5	C(4), C(5), C(15), C(16), C(17)

Table 2. *Positional and thermal parameters*

(a) Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters of non-hydrogen atoms. β_{11} etc. are the coefficients in the expression for the anisotropic temperature factor: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$, multiplied by 10^4.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2186 (3)	273 (5)	109 (0)	24 (2)	77 (6)	112 (9)	−4 (3)	9 (4)	−12 (6)
C(2)	2198 (3)	496 (5)	1684 (8)	24 (2)	72 (5)	113 (9)	−5 (3)	5 (3)	−12 (6)
C(3)	2666 (3)	−474 (5)	2287 (9)	31 (2)	82 (6)	101 (9)	−2 (3)	−4 (4)	−4 (6)
C(4)	2190 (4)	−1501 (6)	2679 (9)	44 (3)	96 (6)	101 (9)	18 (3)	18 (4)	24 (7)
C(5)	1577 (3)	−1924 (5)	1699 (10)	26 (2)	76 (6)	152 (11)	5 (3)	10 (4)	4 (7)
C(6)	1572 (4)	−3272 (6)	1696 (11)	49 (3)	69 (5)	202 (13)	−6 (4)	7 (5)	−6 (8)
C(7)	819 (3)	−1470 (6)	2194 (10)	30 (2)	114 (8)	185 (13)	4 (3)	28 (5)	23 (8)
C(8)	1850 (3)	1310 (5)	2390 (10)	33 (2)	87 (6)	119 (11)	18 (3)	8 (4)	−12 (7)
C(9)	1852 (4)	1386 (7)	3982 (11)	43 (3)	120 (8)	157 (12)	3 (4)	7 (5)	−39 (8)
C(10)	1401 (4)	2219 (6)	1639 (10)	36 (3)	91 (7)	170 (11)	−1 (3)	1 (5)	−3 (8)
C(11)	3941 (3)	−415 (5)	1271 (11)	25 (2)	78 (6)	227 (16)	−1 (3)	−2 (5)	−15 (9)
C(12)	4269 (4)	−1069 (6)	2566 (12)	29 (2)	115 (9)	276 (17)	6 (3)	−36 (5)	12 (10)
C(13)	4352 (4)	−811 (6)	−71 (11)	34 (3)	130 (8)	196 (12)	3 (4)	29 (5)	−6 (10)
C(14)	4002 (4)	929 (6)	1490 (12)	38 (3)	79 (6)	302 (19)	−19 (3)	0 (6)	−7 (10)
C(15)	1307 (3)	−552 (6)	−1660 (10)	36 (3)	82 (7)	140 (11)	6 (3)	−18 (4)	−15 (7)
C(16)	1891 (4)	−1101 (6)	−2657 (9)	48 (3)	98 (6)	126 (11)	18 (4)	−12 (5)	−21 (7)
C(17)	597 (4)	−1283 (7)	−1655 (12)	32 (2)	120 (8)	246 (11)	−3 (4)	−26 (5)	−26 (9)
C(18)	1107 (4)	688 (6)	−2152 (11)	50 (3)	104 (7)	150 (12)	22 (4)	−36 (5)	7 (7)
N(1)	3161 (2)	−844 (4)	1106 (9)	25 (2)	85 (5)	145 (8)	−6 (2)	1 (4)	−6 (6)
N(2)	1542 (2)	−471 (4)	−172 (8)	28 (2)	64 (5)	146 (9)	2 (2)	5 (3)	−0 (5)
O(1)	2874 (2)	−268 (4)	−182 (8)	27 (1)	108 (5)	128 (7)	5 (2)	6 (3)	−0 (5)
O(2)	1745 (2)	−1634 (3)	253 (8)	29 (1)	71 (4)	120 (6)	3 (2)	−3 (3)	−3 (4)
O(3)	2270 (3)	−1949 (5)	3822 (8)	66 (3)	145 (6)	150 (9)	−12 (3)	−3 (4)	46 (6)

(b) Coordinates ($\times 10^4$) of hydrogen atoms (all having $B_{iso}=7.0$ Å²)

	x/a	y/b	z/c		x/a	y/b	z/c
H(1)	2194 (43)	1078 (68)	−348 (98)	H(17)	4161 (44)	−2044 (62)	2214 (93)
H(2)	2865 (40)	−199 (66)	3107 (94)	H(18)	4925 (45)	−545 (61)	32 (93)
H(3)	1197 (43)	−3649 (63)	1210 (97)	H(19)	4217 (40)	−297 (67)	−835 (90)
H(4)	2138 (43)	−3511 (61)	1279 (100)	H(20)	4362 (41)	−1749 (66)	13 (110)
H(5)	1602 (43)	−3388 (64)	2678 (94)	H(21)	3750 (42)	1341 (63)	683 (85)
H(6)	671 (41)	−1759 (66)	3194 (103)	H(22)	4598 (44)	1166 (63)	1366 (92)
H(7)	818 (41)	−495 (65)	2259 (90)	H(23)	3747 (42)	1178 (66)	2502 (100)
H(8)	406 (42)	−1686 (75)	1571 (93)	H(24)	2091 (40)	−2000 (63)	−2310 (90)
H(9)	1371 (44)	1353 (69)	4392 (89)	H(25)	1754 (41)	−1129 (64)	−3631 (99)
H(10)	2103 (41)	2189 (71)	4350 (88)	H(26)	2427 (42)	−403 (66)	−2427 (90)
H(11)	2213 (44)	748 (69)	4213 (86)	H(27)	711 (43)	−2143 (64)	−1408 (91)
H(12)	1611 (45)	3025 (68)	1933 (94)	H(28)	125 (40)	−667 (63)	−987 (101)
H(13)	920 (48)	2022 (66)	1639 (94)	H(29)	334 (44)	−1259 (66)	−2576 (101)
H(14)	1638 (42)	2270 (68)	475 (90)	H(30)	1555 (44)	1037 (69)	−2295 (90)
H(15)	4127 (43)	−649 (68)	3637 (100)	H(31)	722 (42)	1189 (68)	−1564 (103)
H(16)	4847 (41)	−685 (65)	2695 (94)	H(32)	779 (43)	584 (64)	−3077 (95)

were scaled by a Wilson plot, merged to produce a unique set of 1049 reflexions [residual on merging, $R_m = \sum \|F_1\| - |F_2\|/\sum \frac{1}{2}(|F_1| + |F_2|) = 0.054$], and $|E|$ values calculated.

An unsuccessful attempt was made to solve the structure automatically with *MULTAN* (Main, Woolfson & Germain, 1971). Manual phase determination was then tried, with three reflexions to fix the origin, but initially taking no account of the enantiomorph. Indications were found for four other reflexions by the symbolic addition procedure, and when these were introduced into *MULTAN* two almost identical phase sets were output, giving two very similar E maps, from which six coplanar peaks at distances of about 1·5 Å from each other were isolated. Assuming these (and subsequently located peaks) to be carbon atoms, the rounds of phase recycling (Karle, 1970) gave all 23 atomic positions (Table 1). The assignment of correct scattering factors was largely based on chemical considerations: the t-butyl groups were easily identified, as were carbonyl and isopropylidene, and the remaining atoms were identified from the geometry around them. The structure thus obtained was confirmed by one cycle of full-matrix least-squares refinement of positional and isotropic thermal parameters, when no abnormal temperature factors were observed.

Full-matrix refinement was carried out with our modification of the *PORFLS* program (Powell & Griffiths, 1969). Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Five cycles of refinement of the overall scale factor, positional and isotropic thermal parameters gave $R = 0.120$ $(R = \sum \|F_o| - |F_c\|/\sum |F_o|)$, and a further three cycles including anisotropic temperature factors gave $R = 0.089$; unit weights were used throughout. A difference map calculated at this stage gave reasonable positions for all 32 hydrogen atoms. They were assigned an isotropic temperature factor $B = 7.0$ Å^2 which was not refined. Four cycles of refinement including refinement of the hydrogen atom positions converged at $R = 0.051$, when all the shifts in parameters were less than the standard deviations. Atomic coordinates and thermal parame-

ters are given in Table 2.* The numbering of the atoms is shown in Fig. 1, and bond lengths and angles are given in Table 3.

Table 3. *Bond lengths and angles*

(a) Bond lengths (Å). Average e.s.d.'s for heavy-atom bonds 0·01 Å; for bonds to hydrogen 0·08 Å.

C(1)—C(2)	1·51	C(15)-C(17)	1·54	C(12)-H(15)	1·15
C(1)—N(2)	1·47	C(15)-C(18)	1·55	C(12)-H(16)	1·14
C(1)—O(1)	1·42	C(15)-N(2)	1·47	C(12)-H(17)	1·19
C(2)—C(3)	1·52	N(1)—O(1)	1·48	C(13)-H(18)	1·09
C(2)—C(8)	1·31	N(2)—O(2)	1·45	C(13)-H(19)	0·97
C(3)—C(4)	1·51	C(1)—H(1)	1·03	C(13)-H(20)	1·09
C(3)—N(1)	1·49	C(3)—H(2)	0·91	C(14)-H(21)	1·01
C(4)—C(5)	1·53	C(6)—H(3)	0·93	C(14)-H(22)	1·12
C(4)—O(3)	1·21	C(6)—H(4)	1·13	C(14)-H(23)	1·10
C(5)—C(6)	1·56	C(6)—H(5)	0·94	C(16)-H(24)	1·14
C(5)—C(7)	1·54	C(7)—H(6)	1·04	C(16)-H(25)	0·95
C(5)—O(2)	1·44	C(7)—H(7)	1·13	C(16)-H(26)	1·28
C(8)—C(9)	1·51	C(7)—H(8)	0·99	C(17)-H(27)	1·04
C(8)—C(10)	1 51	C(9)—H(9)	0·95	C(17)-H(28)	1·28
C(11)-C(12)	1·56	C(9)—H(10)	1·09	C(17)-H(29)	0·99
C(11)-C(13)	1·54	C(9)—H(11)	1·01	C(18)-H(30)	0·92
C(11)-C(14)	1·57	C(10)-H(12)	1·04	C(18)-H(31)	1·06
C(11)-N(1)	1·51	C(10)-H(13)	0·90	C(18)-H(32)	1·06
C(15) C(16)	1·55	C(10)—H(14)	1·18		

(b) Bond angles (°); e.s.d. (average) = 0·6°.

C(1)-C(2)-C(3)	104·6	C(6)—C(5)—C(7)	109·6
C(1)-C(2)-C(8)	128·0	C(6)—C(5)—O(2)	103·4
C(1)-N(2)-O(2)	106·8	C(7)—C(5)—O(2)	113·3
C(1)-O(1)-N(1)	110·3	C(9)—C(8)—C(10)	115·5
C(2)-C(1)-N(2)	106·7	C(11)-N(1)—O(1)	105·5
C(2)-C(1)-O(1)	104·7	C(12)-C(11)-C(13)	108·6
C(2)-C(3)-C(4)	110·7	C(4)—C(3)—N(1)	107·5
C(2)-C(3)-N(1)	105·5	C(12)-C(11)-C(14)	110·5
C(2)-C(8)-C(9)	123·1	C(12)-C(11)-N(1)	106·3
C(2)-C(8)-C(10)	121·3	C(13)-C(11)-N(1)	105·7
C(3)-C(2)-C(8)	127·3	C(14)-C(11)-N(1)	113·9
C(3)-C(4)-C(5)	121·1	C(15)-N(2)—O(2)	106·2
C(3)-C(4)-O(3)	119·3	C(16)-C(15)-C(17)	110·3
C(1)-N(2)-C(15)	116·0	C(16)-C(15)-C(18)	110·8
C(3)-N(1)-C(11)	113·1	C(16)-C(15)-N(2)	114·1
C(3)-N(1)-O(1)	105·9	C(17)-C(15)-C(18)	108·2
C(4)-C(5)-C(6)	109·0	C(17)-C(15)-N(2)	105·9
C(4)-C(5)-C(7)	110·9	C(18)-C(15)-N(2)	107·2
C(4)-C(5)-O(2)	110·3	N(2)—C(1)—O(1)	113·9
C(5)-C(4)-O(3)	119·5	C(13)-C(11)-C(14)	111·6
C(5)-O(2)-N(2)	115·2		

Discussion. The title compound was obtained as the major thermal decomposition of (I), *i.e.* the reaction

$$2C_9H_{16}NO + O \rightarrow C_{18}H_{32}N_2O_3$$
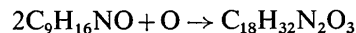
took place (either in presence or absence of oxygen), corresponding to dimerization with incorporation of an additional oxygen atom. This was unexpectedly different from the thermal decomposition of the similar

Fig. 1. The configuration and atom numbering of the molecule.

nitroxide radical (II) (Craig & Roberts, 1972), and the structure of the product could not be deduced by comparison with this reaction.

(I)   (II)

(III)
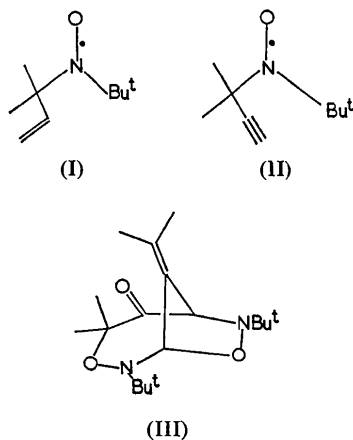
The X-ray analysis was undertaken to find the molecular structure of the unexpected product, and has shown it to be (III). A speculation has been made as to the mechanism of its formation and the origin of the additional oxygen atom (Craig et al., 1973), but confirmation of this requires more experimental work with isotopically substituted molecules. The bicyclic ring system was hitherto unknown, but its detailed geometry does not appear to be remarkable. The five-membered ring and isopropylidene group should all be planar, and the least-squares plane is given in Table 4. The N–O bond lengths are consistent with other determinations of this distance (Murray-Rust, Murray-Rust & Riddell, 1974) in cyclic molecules, and the other lengths and angles are within typical ranges for organic compounds. There are no molecular

contacts less than 3·5 Å, so packing forces are unlikely to affect the geometry.

Table 4. *Least-squares best plane through the five-membered ring and isopropylidene group*

Equation of plane: $13·63x + 7·61y - 0·04z = 3·48$

Atom	Distance from plane (Å)
C(1)	−0·30
C(2)	−0·12
C(3)	−0·22
N(1)	0·18
O(1)	0·23
C(8)	0·03
C(9)	0·08
C(10)	0·11

We thank R. L. Craig for supplying the crystals.

References

CRAIG, R. L., MURRAY-RUST, J., MURRAY-RUST, P. & ROBERTS, J. S. (1973). *Chem. Commun.* pp. 751–752.
CRAIG, R. L. & ROBERTS, J. S. (1972). *Chem. Commun.* pp. 1142–1143.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
KARLE, J. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, pp. 37–40. Copenhagen: Munksgaard.
MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *The MULTAN Computer Program for the Automatic Solution of Crystal Structures*, Univs. of York and Louvain.
MURRAY-RUST, J., MURRAY-RUST, P. & RIDDELL, F. G. R. (1974). *Tetrahedron*, **30**, 1087–1096.
POWELL, M. T. G. & GRIFFITHS, A. (1969). CRYSTAL 69 system of crystallographic programs, Portsmouth Polytechnic.

The Crystal and Molecular Structure of 1,5-Cyclooctadieneacetylacetonatorhodium(I)

By P. A. TUCKER, W. SCUTCHER AND D. R. RUSSELL

Department of Chemistry, University of Leicester, Leicester LE1 7RH, England

Abstract. $C_{13}H_{19}O_2Rh$, monoclinic, space group Cc, with $a = 6·854$ (5), $b = 18·645$ (10), $c = 9·864$ (7) Å, $\beta = 93·1$ (2)°, $U = 1258·7$ Å³, $Z = 4$, $D_c = 1·64$ g cm⁻³. R is 0·040 for 1884 counter reflexions. Mean Rh–O and Rh–C bond lengths are 2·060 and 2·103 Å respectively.

Introduction. The yellow transparent crystals commonly have the forms {100}, {021} and {0$\bar{2}$1}. The cell dimensions were determined from precession photographs. The intensities of reflexions with $\theta < 30°$ were measured on a Stoe Weissenberg diffractometer in ten layers, $0kl$ through $9kl$, with monochromatic Mo $K\alpha$ radiation and an ω-scan technique. A crystal of approximate dimensions $0·081 \times 0·031 \times 0·017$ cm was used. The 1884 reflexions with significant intensity $[I < 3\sigma(I)]$ and with $\sin \theta/\lambda > 0·1$ Å⁻¹ were corrected for Lorentz and