N-n-Butyl-2,3-dimethyl-1,4-*endo*-(3',4'-pyrrolidino)-1,4-dihydronaphthalene Hydrochloride, C20H27N.HCl

By Patrick Argos and Rex Clayton

Pomona College, Departments of Physics and Chemistry, Claremont, California 91711, *U.S.A.*

Abstract. Triclinic, $P\bar{1}$, $a = 7\cdot36(2)$, $b = 11\cdot05(2)$, $c = 11\cdot76(2)$ Å, $\alpha = 108\cdot9(2)°$, $\beta = 85\cdot4(2)°$, $\gamma = 96\cdot6(2)°$, $Z = 2$ $\varrho_x = 1\cdot17(7)$, $\varrho_c = 1\cdot168$ g cm^{-3}. Direct methods utilizing diffractometer data were used to solve the structure. Final R index 0·066. The positions of all atoms were determined except nine hydrogen atoms at the three terminal carbon positions. Toroids of electron density on a final difference Fourier map indicated their near free rotation. Deviations from theoretical values in bond angles and distances were not in general significant.

Introduction. Crystals of $C_{20}H_{27}N$ HCl were grown from an aqueous solution of ethanol. The crystal system and approximate cell parameters were determined from precession photographs taken with Cu $K\alpha$ radiation ($\lambda = 1\cdot5405$ Å) and from single-crystal diffractometry employing Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). The lack of observed systematic absences indicated space groups $P1$ or $P\bar{1}$. However, since density measurements (by

flotation, $\varrho = 1\cdot17(7)$ g cm^{-3}) indicated $Z = 2$ (calculated density $1\cdot168$ g cm^{-3} and Wilson and E-value statistical distribution showed the structure to be centrosymmetric, $P\bar{1}$ was selected as the space group.

4352 independent reflections were measured within $2\theta = 56\cdot0°$ by a Picker FACS I single-crystal diffractometer. 1249 reflections were excluded from the refinement, their intensity values being less than 3σ. The intensities were measured by a Wyckoff *et al.*, (1967) step-scan procedure and background corrections were

Table 1. *Starting phases and assigned symbols*

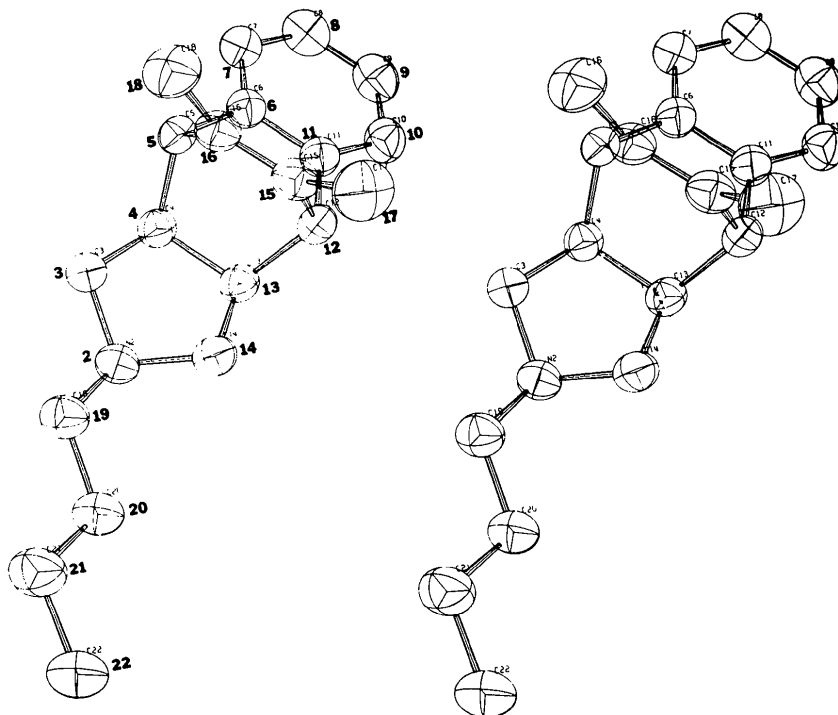| H	K	L	E	Phases Start	Phases Final
2	−2	1	4·874	+	+
5	−4	5	3·918	+	+
8	−1	−4	2·340	−	−
7	5	2	3·314	A	+
1	−2	3	3·059	B	−
1	4	1	2·988	C	−

Fig. 1. Stereoscopic view (H atoms not shown). Orientations of ellipsoids are scaled to include 50% probability (Johnson, 1965).

made as a function of 2θ from a background curve measured at 2° intervals in 2θ. Linear interpolation was used between background points. No absorption or extinction corrections were made.

The Patterson map did not yield a unique chlorine position and the structure was solved by direct methods. Sign relationships were determined for 232 of the largest
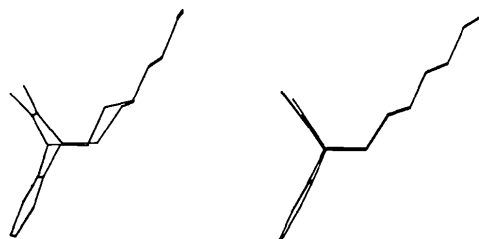

Fig. 2. Stereoscopic stick diagram of $C_{20}H_{27}N$ (H atoms not shown). The principal planes are clearly indicated.

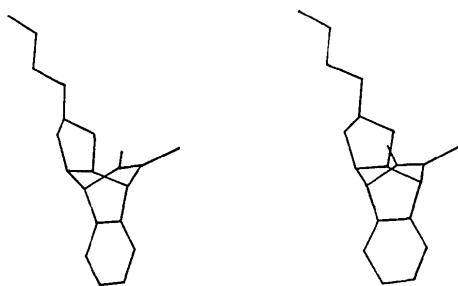Fig. 3. Stereoscopic stick diagram of $C_{20}H_{27}N$ (H atoms not shown). The ring composition is clearly shown.

E's using the symbolic addition procedure described by Karle & Karle (1966) in terms of three initially assigned phases and three symbolic phases (Table 1). The correct structure was recognized on one of the eight resulting E maps. Chlorine, nitrogen and seventeen of the twenty carbon atom positions were unambiguously located. The remaining three carbon atom positions were located from a Fourier synthesis map using 700 of the largest structure factors. 18 of 27 hydrogen positions were found by use of a weighted difference map (Meyers, 1971).

The structure was refined by block-diagonal least-squares analysis employing convergence-acceleration factors. The final R index based on all measured reflections was 0·078. However, R was 0·066 for those reflections used in the refinement. Unit weights for all reflections were adopted. A final difference Fourier map confirmed the structure and indicated toroids of electron density at three terminal carbons [C(17), C(18), C(22)] where the remaining nine hydrogen atoms were expected. They are nearly freely rotating. The scattering factors used in the refinement for the carbon, chlorine, nitrogen, and hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962).

Atomic coordinates and thermal parameters are given in Table 2. The estimated standard deviations were obtained in the usual way from the variance-covariance matrix. The final shifts were no larger than 0·1 of the estimated standard deviations.

Discussion. Zuzak (1967) has studied the biological activity (toxicity, analgesia, spasmodicity, and so forth) of several N-substituted-2,3-dimethyl-1,4-*endo*-(3′,4′-

Table 2. *The final positional and thermal parameters*

The parameters and standard deviations (in parentheses) for the least significant digit of the nonhydrogen atoms are $\times 10^4$.

The expression for the temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)]$.

	$X/a(\sigma)$	$Y/b(\sigma)$	$Z/c(\sigma)$	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{23}(\sigma)$	$B_{13}(\sigma)$	$B_{12}(\sigma)$
Cl(1)	7021 (2)	1984 (1)	365 (1)	164 (2)	168 (2)	196 (2)	176 (3)	−101 (3)	28 (3)
N(2)	3020 (4)	1817 (3)	−91 (3)	142 (6)	91 (3)	65 (3)	52 (5)	−16 (6)	34 (7)
C(3)	2541 (5)	885 (4)	−1306 (3)	196 (8)	77 (4)	65 (3)	42 (6)	−24 (8)	8 (9)
C(4)	3611 (5)	1468 (3)	−2199 (3)	151 (7)	69 (3)	66 (3)	40 (5)	−15 (7)	30 (8)
C(5)	2550 (5)	1330 (3)	−3334 (3)	143 (7)	65 (3)	62 (3)	31 (5)	−21 (7)	3 (7)
C(6)	3835 (5)	1984 (3)	−4071 (3)	134 (6)	77 (4)	70 (3)	51 (7)	−17 (7)	22 (8)
C(7)	4535 (5)	1421 (4)	−5232 (3)	162 (7)	90 (4)	73 (3)	48 (6)	7 (8)	53 (9)
C(8)	5698 (6)	2184 (4)	−5787 (4)	168 (8)	128 (5)	90 (4)	86 (8)	37 (9)	77 (1)
C(9)	6166 (6)	3472 (4)	−5172 (4)	164 (8)	128 (5)	111 (5)	128 (8)	12 (10)	5 (10)
C(10)	5466 (5)	4035 (4)	−3999 (4)	175 (8)	89 (4)	101 (4)	83 (7)	−42 (9)	−24 (9)
C(11)	4293 (5)	3289 (3)	−3455 (3)	144 (7)	77 (4)	73 (3)	53 (6)	−28 (8)	11 (8)
C(12)	3341 (5)	3733 (3)	−2222 (3)	180 (8)	63 (3)	69 (3)	30 (5)	−38 (8)	11 (8)
C(13)	4033 (5)	2931 (3)	−1496 (3)	146 (7)	74 (3)	66 (3)	36 (5)	−36 (7)	6 (8)
C(14)	3065 (6)	3116 (4)	−257 (3)	201 (8)	80 (4)	66 (3)	29 (6)	−30 (8)	28 (9)
C(15)	1310 (5)	3350 (4)	−2380 (3)	151 (7)	94 (4)	65 (3)	50 (6)	−13 (8)	61 (9)
C(16)	891 (5)	2100 (4)	−2946 (3)	128 (6)	93 (4)	64 (3)	55 (6)	−19 (7)	22 (8)
C(17)	−18 (6)	4377 (5)	−1908 (5)	235 (11)	121 (5)	120 (5)	36 (9)	−6 (12)	183 (13)
C(18)	−1001 (5)	1423 (5)	−3249 (4)	135 (7)	132 (5)	112 (5)	74 (8)	−55 (10)	−29 (10)
C(19)	1728 (5)	1576 (4)	881 (3)	163 (8)	107 (4)	70 (3)	52 (6)	−3 (8)	7 (9)
C(20)	2119 (5)	2541 (4)	2108 (4)	174 (8)	110 (5)	67 (3)	47 (6)	−6 (8)	27 (10)
C(21)	757 (6)	2241 (5)	3057 (4)	219 (10)	139 (6)	77 (4)	57 (8)	24 (10)	−19 (12)
C(22)	954 (6)	3285 (5)	4287 (4)	227 (10)	135 (6)	68 (4)	39 (7)	1 (10)	49 (12)

Table 2 (cont.)

The positional parameters of the hydrogen atoms are × 10³

	$X/a(\sigma)$	$Y/b(\sigma)$	$Z/b(\sigma)$	$B_{iso}(\sigma)$
H(23)	434 (5)	173 (3)	9 (3)	3·8 (0·8)
H(24)	291 (5)	−1 (4)	−136 (4)	5·0 (1·0)
H(25)	110 (5)	83 (4)	−135 (3)	4·1 (0·9)
H(26)	488 (5)	105 (3)	−244 (3)	3·5 (0·8)
H(27)	214 (4)	40 (3)	−379 (3)	2·8 (0·7)
H(28)	404 (5)	46 (4)	−570 (3)	4·8 (1·0)
H(29)	653 (8)	172 (6)	−665 (5)	10·1 (1·8)
H(30)	712 (6)	408 (4)	−556 (4)	5·8 (1·1)
H(31)	578 (6)	497 (4)	−353 (4)	5·4 (1·1)
H(32)	366 (5)	465 (4)	−184 (3)	4·4 (0·9)
H(33)	547 (5)	317 (3)	−138 (3)	3·1 (0·8)
H(34)	391 (5)	379 (4)	42 (3)	4·4 (0·9)
H(35)	161 (5)	337 (4)	−23 (3)	4·4 (0·9)
H(36)	36 (6)	162 (4)	60 (4)	5·2 (1·0)
H(37)	192 (6)	57 (4)	92 (4)	6·2 (1·1)
H(38)	203 (8)	356 (5)	207 (5)	9·3 (1·6)
H(39)	350 (5)	247 (4)	230 (4)	4·8 (1·0)
H(40)	−55 (7)	211 (5)	279 (4)	7·8 (1·4)
H(41)	142 (10)	121 (7)	313 (7)	15·0 (2·5)

pyrrolidino)-1,4-dihydronaphthalene hydrochlorides in an attempt to relate their stereospecific arrangement with biological function. Details of the structure-function relationship of $C_{20}H_{27}N.HCl$ can be found in the discussion by Zuzak (1967). The present crystal structure of the n-butyl form is a conformation of the atomic arrangement proposed by Zuzak.

Table 3. Bond distances and their standard deviations (in parentheses) for the least significant figures

1–23	1·999 (38) Å	10–11	1·387 (6) Å
2–23	1·036 (37)	11—6	1·402 (6)
2–19	1·499 (5)	11–12	1·513 (6)
2–14	1·505 (5)	12–32	0·976 (46)
2—3	1·507 (6)	12–15	1·516 (6)
3–24	1·032 (45)	12–13	1·561 (4)
3–25	1·062 (38)	13–33	1·067 (36)
3—4	1·525 (5)	13–14	1·532 (6)
4–26	1·068 (37)	14–34	1·080 (41)
4—5	1·557 (6)	14–35	1·136 (39)
4–13	1·565 (6)	15–16	1·335 (7)
5–27	1·014 (40)	15–17	1·521 (7)
5—6	1·511 (5)	16–18	1·515 (6)
5–16	1·524 (5)	19–36	1·096 (43)
6—7	1·388 (6)	19–37	1·152 (50)
6–11	1·402 (6)	19–20	1·516 (5)
7–28	1·058 (48)	20–39	1·075 (41)
7—8	1·404 (6)	20–38	1·152 (63)
8–29	1·139 (70)	20–21	1·532 (7)
8—9	1·388 (8)	21–40	1·018 (52)
9–30	1·097 (45)	21–41	1·315 (83)
9–10	1·400 (8)	21–22	1·535 (7)
10–31	1·011 (52)		

Bond distances are given in Table 3, and bond angles in Table 4. Cl(1) is hydrogen-bonded to N(2) through H(23). Deviations from theoretical values in bond angles and distances were not in general significant. The molecule with ellipsoids of vibration is shown in Fig. 1; Figs 2 and 3 are stick diagrams showing angular

Table 4. Bond angles and their standard deviations (in parentheses) for the least significant figures

23—2–19	108·8 (3·9)°	32–12–15	114·3 (3·2)°
23—2–14	106·2 (3·9)	32–12–13	111·2 (3·2)
23—2—3	109·9 (3·9)	11–12–15	107·4 (0·4)
19—2–14	116·6 (0·5)	11–12–13	105·7 (0·5)
19—2—3	111·1 (0·5)	15–12–13	107·7 (0·6)
14—2—3	104·0 (0·5)	33–13–14	108·6 (3·1)
24—3—5	109·1 (4·2)	33–13–12	109·4 (3·2)
24—3—4	108·3 (4·1)	33–13—4	110·9 (3·1)
24—3—4	113·8 (4·2)	14–13–12	114·4 (0·5)
25—3—2	106·9 (3·7)	14–13—4	104·7 (0·4)
25—3—4	113·9 (3·7)	12–13—4	108·7 (0·6)
2—3—4	104·2 (0·4)	34–14–35	114·3 (4·5)
26—4—3	108·9 (3·4)	34–14—2	108·1 (4·0)
26—4—5	110·9 (3·3)	34–14–13	108·7 (3·9)
26—4–13	108·0 (3·3)	35–14—2	109·3 (3·7)
3—4—5	114·0 (0·5)	35–14–13	112·1 (3·7)
3—4–13	105·9 (0·5)	2–14–13	103·7 (0·4)
5—4–13	108·8 (0·5)	16–15–12	114·1 (0·5)
27—5—6	113·2 (2·5)	16–15–17	126·8 (0·5)
27—5–16	109·7 (2·5)	12–15–17	119·1 (0·5)
27—5—4	112·8 (2·5)	15–16–18	126·9 (0·5)
6—5–16	107·1 (0·5)	15–16—5	113·9 (0·5)
6—5—4	105·0 (0·5)	18–16—5	119·2 (0·5)
16—5—4	108·8 (0·4)	36–19–37	111·5 (4·8)
7—6–11	120·7 (0·5)	36–19—2	105·4 (4·0)
7—6—5	126·7 (0·5)	36–19–20	112·0 (4·0)
11—6—5	112·6 (0·4)	37–19—2	107·6 (4·2)
28—7—6	118·1 (3·0)	37–19–20	108·0 (4·2)
28—7—8	122·6 (3·0)	2–19–20	112·3 (0·5)
6—7—8	118·9 (0·5)	39–20–38	108·3 (5·3)
29—8—9	117·8 (4·4)	39–20–19	107·6 (4·0)
29—8—7	120·4 (4·4)	39–20–21	110·8 (4·0)
9—8—7	120·3 (0·6)	38–20–19	109·2 (5·1)
30—9—7	122·3 (4·2)	38–20–21	111·2 (5·1)
30—9–10	117·0 (4·2)	19–20–21	109·6 (0·5)
8—9–10	120·7 (0·6)	40–21–41	115·9 (6·6)
31–10–11	118·8 (3·3)	40–21–20	111·5 (5·0)
31–10—9	122·1 (3·3)	40–21–22	110·8 (5·0)
11–10—9	119·1 (0·6)	41–21–20	99·4 (6·4)
10–11—6	120·3 (0·6)	41–21–22	107·3 (6·4)
10–11–12	126·9 (0·6)	20–21–22	111·5 (0·6)
6–11–12	112·8 (0·4)	2–23—1	165·2 (5·6)
32–12–11	110·1 (3·2)		

perspectives. A list of structure factors is obtainable*.

All computer calculations were performed using the NCR Crystallographic Programs for the IBM/360 System (Ahmed, Hall, Pippy & Saunderson, 1967). *ORTEP* (Johnson, 1965) was used to draw Fig. 1.

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(Ethylene)platinum Dichloride–Di-t-butyl Sulphurdiimine

By RINA T. KOPS, EVELINE VAN AKEN AND H. SCHENK

Laboratory for Crystallography, University of Amsterdam, Nieuwe Prinsengracht 126, Amsterdam, The Netherlands

Abstract. Monoclinic, $P2_1/c$, $a=6\cdot212$ (1), $b=17\cdot307$ (1), $c=15\cdot156$ (4) Å, $\beta=98\cdot29$ (4)°, $C_{10}H_{22}Cl_2N_2PtS$, $Z=4$. The title complex was synthesized by Kuyper, Vrieze & Oskam (1972) by treating ethylene-platinum-chloride with di-t-butyl-sulphurdiimine.

The two S–N double bonds of the sulphurdiimine ligand have lengths of 1·57 (2) and 1·53 (2) Å.

Introduction. Approximately 2500 independent reflexions were collected by means of a Nonius automatic three-circle diffractometer (Cu $K\alpha$, θ–2θ-scan) of which 1511 were above the significance level of $2\cdot5\sigma$. The platinum atom was located from a Patterson synthesis. A superposition map based on all symmetry-related platinum atoms revealed the other non-hydrogen atoms. The refinement was carried out by means of a block-diagonal least-squares procedure to a final R value of 8·8%. Platinum, sulphur and chlorine were refined anisotropically and carbon and nitrogen isotropically. Atomic scattering factors, including $\Delta f'$ and $\Delta f''$ for Pt, S and Cl, were taken from *International Tables for X-ray Crystallography* (1962). No attempt was made to locate the hydrogen atoms. The final parameters are given in Table 1, bond lengths in Fig. 1, and bond angles in Table 2.

Results and discussion. The X-ray analysis was carried out in order to determine the bonding between the sulphurdiimine and the platinum atom.

Pt(1), N(1), C(1) and C(2) and the middle of O(9)–C(10) are coplanar within the limits of accuracy. The ligands are bonded to the platinum atom in an approximately square configuration (Fig. 1). The
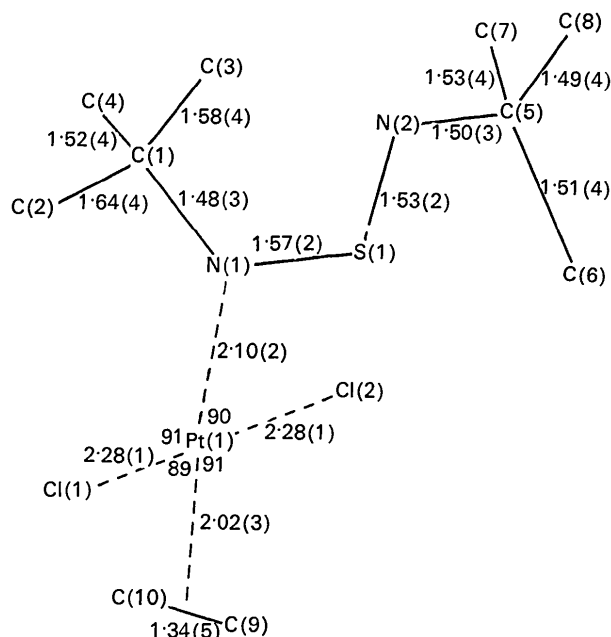

Fig. 1. Bond lengths (Å) with e.s.d.'s. The angles between the ligands of the platinum atom are indicated.

Table 1. *Fractional atomic parameters* ($\times 10^4$)

The thermal parameters are given as U_{ij} or U_{iso} ($\times 10^3$). E.s.d.'s are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	419 (2)	3840 (1)	3924 (1)	58 (1)	52 (1)	35 (1)	11 (1)	6 (1)	10 (1)
Cl(1)	−2085 (14)	2973 (4)	4288 (5)	82 (6)	73 (4)	72 (4)	2 (4)	21 (4)	22 (4)
Cl(2)	2896 (14)	4714 (5)	3569 (5)	77 (6)	99 (6)	69 (4)	−19 (5)	2 (4)	23 (4)
S(1)	−2357 (11)	4805 (3)	2593 (3)	66 (4)	39 (3)	36 (3)	11 (3)	−1 (3)	1 (2)