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# Structures of 5-[3-(4-Carbamoyl-4-piperidinopiperidino)propyl]-3-chloro-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (*A*),* $C_{28}H_{37}ClN_4O$, 3-Chloro-5-[3-(2-oxo-1,2,3,5,6,7,8,8a-octahydroimidazo[1,2-*a*]pyridine-3-spiro-4′-piperidino)propyl]-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (*B*), $C_{28}H_{35}ClN_4O$, and 5-[3-(2-Oxo-1,2,3,5,6,7,8,8a-octahydroimidazo[1,2-*a*]pyridine-3-spiro-4′-piperidino)propyl]-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine (*C*), $C_{28}H_{36}N_4O$

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(*Received* 22 *August* 1983; *accepted* 12 *October* 1983)

**Abstract.** (*A*): $M_r = 481\cdot09$, monoclinic, $C2/c$, $a = 27\cdot81\ (1)$, $b = 8\cdot589\ (2)$, $c = 22\cdot14\ (1)$ Å, $\beta = 102\cdot82\ (4)^\circ$, $U = 5164\ (4)$ Å$^3$, $Z = 8$, $D_m = 1\cdot23$, $D_x = 1\cdot24$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot179$ mm$^{-1}$, $T = 298$ K, $F(000) = 2064$, $R = 0\cdot0639$ for 2566 observed reflexions. (*B*): $M_r = 479\cdot07$, triclinic, $P\bar{1}$, $a = 11\cdot515\ (5)$, $b = 11\cdot837\ (5)$, $c = 10\cdot744\ (3)$ Å, $\alpha = 92\cdot71\ (3)$, $\beta = 112\cdot73\ (3)$, $\gamma = 68\cdot76\ (3)^\circ$, $U = 1255\ (1)$ Å$^3$, $Z = 2$, $D_m = 1\cdot26$, $D_x = 1\cdot28$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) $= 0\cdot184$ mm$^{-1}$, $T = 298$ K, $F(000) = 512$, $R = 0\cdot0658$ for 3114 observed reflexions. (*C*): $M_r = 444\cdot63$, monoclinic, $A2/a$, $a = 27\cdot29\ (1)$, $b = 10\cdot254\ (5)$, $c = 18\cdot108\ (5)$ Å, $\beta = 97\cdot20\ (2)^\circ$, $U = 5027\ (3)$ Å$^3$, $Z = 8$, $D_m = 1\cdot17$, $D_x = 1\cdot18$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) $= 0\cdot078$ mm$^{-1}$, $T = 298$ K, $F(000) = 1920$, $R = 0\cdot0620$ for 2851 observed reflexions. These three antischizophrenia drugs each form dimers by paired intermolecular O···H(N) hydrogen bonds at the carbamoyl moieties. The ethylene radical in the dibenzazepine ring is in plane with one benzene ring and is out of plane for the other. The Cl atom of the first compound is connected to the out-of-plane benzene ring at the position *meta* to the N atom. That of the second compound is connected to the in-plane benzene ring at the same position.

**Introduction.** Compounds (*A*), (*B*) and (*C*) are very similar as shown in Fig. 1. However, the pharmacological spectra and activities for antischizophrenia are remarkably different. The X-ray analyses were carried out to study these pharmacological differences from the viewpoint of the molecular conformations.

**Experimental.** Experimental data are shown in Table 1. Density measured by flotation in KI solution. Colorless crystals of these compounds ground manually to spheres of diameters of about 0·5 mm. Rigaku AFC-5 four-circle automated diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Cell dimensions derived from least-squares treatment of the setting angles for 20 reflexions. $\omega$–$2\theta$ scan technique, scan rate 8° min$^{-1}$ for $\omega$. Three standard reflexions measured every 100 reflexions: no significant variations in

Table 1. *Experimental data*

| Compound | (*A*) | (*B*) | (*C*) |
|---|---|---|---|
| Maximum $2\theta$ (°) | 45 | 50 | 50 |
| Range of $h,k,l$ | $\pm h,k,l$ | $h,\pm k,\pm l$ | $h,k,\pm l$ |
| Standard reflections | $\bar{2}04$, 020, $\bar{6}02$ | $11\bar{2}$, 111, 121 | 220, 022, $20\bar{4}$ |
| Intensities measured | 3248 [$F > \sigma(F)$] | 3636 (all) | 3630 [$F > \sigma(F)$] |
| Unique intensities | 2847 [$F > \sigma(F)$] | 3546 (all) | 3328 [$F > \sigma(F)$] |
| Intensities $>2\cdot5\sigma(F)$ | 2566 | 3114 | 2851 |
| $R$ | 0·0639 | 0·0658 | 0·0620 |
| $wR$ ($w = 1\cdot0$) | 0·0586 | 0·0747 | 0·0623 |
| $S$ | 3·12 | 1·18 | 2·57 |
| Residual density (e Å$^{-3}$) | <0·95 | <0·62 | <0·22 |
| $(\Delta/\sigma)_{\max}$ for non-H atoms | 0·87 | 0·25 (except disordered parts) | 0·67 |

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* IUPAC name: 1′-[3-(3-chloro-10,11-dihydro-5*H*-dibenz[*b*,*f*]-azepin-5-yl)propyl][1,4′-bipiperidine]-4′-carboxamide.

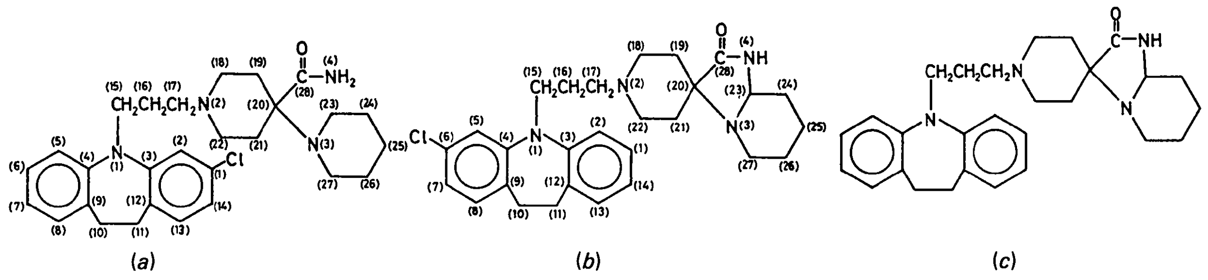

Fig. 1. The chemical structures of (*a*) compound (*A*), (*b*) compound (*B*) and (*c*) compound (*C*), with the atom-numbering schemes.

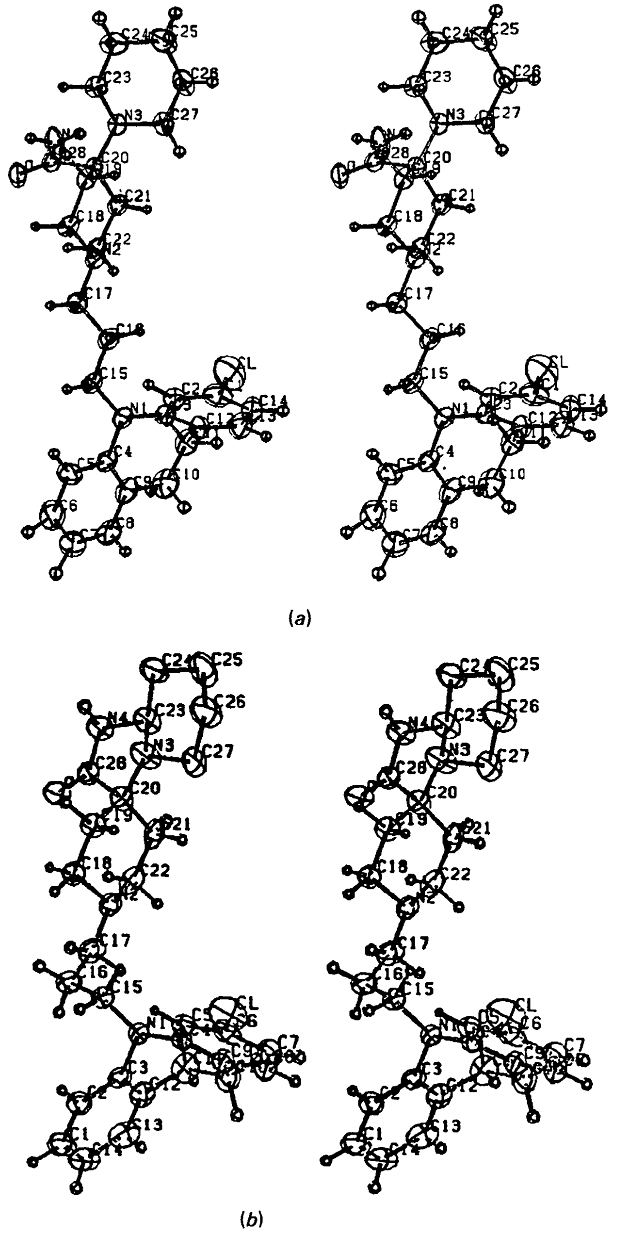

Fig. 2. Stereoscopic views of (*a*) compound (*A*), (*b*) compound (*B*).

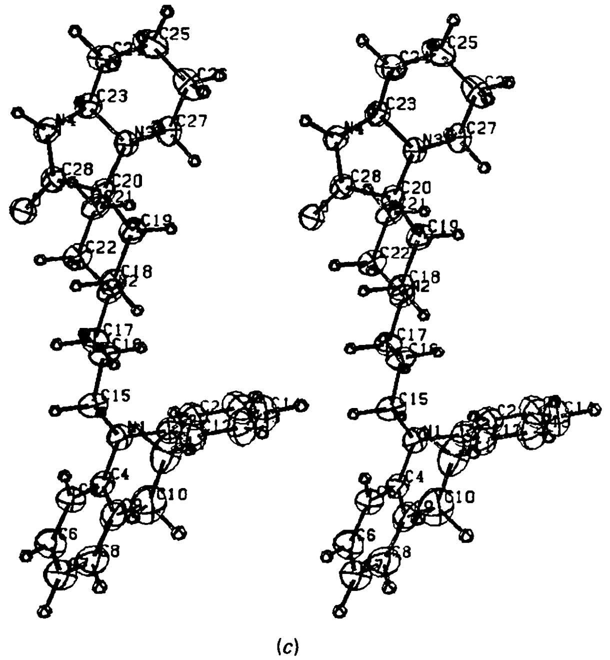

Fig. 2 (*cont.*). (*c*) Stereoscopic view of compound (*C*).

intensities. Lorentz and polarization corrections applied, but absorption ignored. Structures for all compounds solved using *MULTAN* (Germain, Main & Woolfson, 1971). All coordinates, anisotropic thermal parameters for non-H and isotropic ones for H atoms refined by block-diagonal least squares; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1{\cdot}0$. The large residual electron densities of compound (*A*) are due to the trace of the Cl atom of the opposite side in the dibenzazepine ring; those of compound (*B*) are due to the H atoms which were not introduced for the disordering of the terminal piperidino rings. Atomic scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). No corrections for secondary extinction. Calculations performed on a FACOM M-200 computer at the Computer Center of Kyushu University using the *UNICS*III program system (Sakurai & Kobayashi, 1979).

Table 2. *Fractional coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å²) *for non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| Compound (*A*) | | | | |
| Cl | 2093 (1) | 509 (2) | 3556 (1) | 6·81 (5) |
| O | 168 (1) | −2181 (4) | 6758 (1) | 3·89 (9) |
| N(1) | 1111 (1) | 4370 (4) | 4563 (2) | 3·64 (10) |
| N(2) | 930 (1) | −393 (4) | 5735 (2) | 3·25 (10) |
| N(3) | 1342 (1) | −3798 (4) | 7180 (2) | 3·13 (10) |
| N(4) | 688 (1) | −2253 (6) | 7682 (2) | 4·96 (13) |
| C(1) | 2053 (2) | 2179 (6) | 3980 (2) | 4·75 (16) |
| C(2) | 1600 (2) | 2583 (6) | 4089 (2) | 3·75 (13) |
| C(3) | 1563 (2) | 3889 (5) | 4427 (2) | 3·33 (12) |
| C(4) | 896 (2) | 5725 (5) | 4240 (2) | 3·48 (13) |
| C(5) | 432 (2) | 5634 (6) | 3845 (3) | 4·79 (16) |
| C(6) | 202 (2) | 6922 (7) | 3524 (3) | 6·61 (21) |
| C(7) | 438 (2) | 8295 (7) | 3581 (3) | 6·59 (21) |
| C(8) | 896 (2) | 8421 (6) | 3955 (3) | 5·19 (17) |
| C(9) | 1133 (2) | 7156 (6) | 4302 (2) | 4·22 (14) |
| C(10) | 1633 (2) | 7498 (7) | 4714 (3) | 5·71 (18) |
| C(11) | 1916 (2) | 6208 (6) | 5064 (2) | 4·82 (15) |
| C(12) | 1979 (2) | 4815 (6) | 4660 (2) | 4·20 (14) |
| C(13) | 2419 (2) | 4386 (7) | 4529 (3) | 5·15 (16) |
| C(14) | 2468 (2) | 3095 (7) | 4187 (2) | 4·95 (16) |
| C(15) | 780 (2) | 3124 (5) | 4675 (2) | 3·77 (13) |
| C(16) | 1026 (2) | 2107 (6) | 5212 (2) | 3·91 (13) |
| C(17) | 681 (2) | 801 (6) | 5309 (2) | 3·64 (13) |
| C(18) | 626 (2) | −1808 (5) | 5668 (2) | 3·17 (12) |
| C(19) | 869 (2) | −3094 (5) | 6095 (2) | 3·12 (12) |
| C(20) | 1036 (1) | −2612 (5) | 6775 (2) | 2·84 (11) |
| C(21) | 1313 (2) | −1063 (5) | 6804 (2) | 3·40 (12) |
| C(22) | 1024 (2) | 140 (5) | 6375 (2) | 3·51 (13) |
| C(23) | 1096 (2) | −5322 (6) | 7144 (2) | 4·36 (15) |
| C(24) | 1361 (2) | −6377 (7) | 7664 (3) | 5·63 (18) |
| C(25) | 1895 (2) | −6597 (7) | 7632 (3) | 5·68 (18) |
| C(26) | 2135 (2) | −5024 (7) | 7614 (3) | 5·04 (16) |
| C(27) | 1849 (2) | −4003 (6) | 7102 (2) | 4·45 (15) |
| C(28) | 585 (2) | −2339 (5) | 7069 (2) | 3·08 (12) |
| Compound (*B*) | | | | |
| Cl | 2871 (1) | 4645 (1) | 1434 (2) | 5·95 (5) |
| O | −4325 (4) | 5919 (3) | −8626 (3) | 4·50 (12) |
| N(1) | −1378 (4) | 8066 (3) | −1724 (4) | 3·05 (12) |
| N(2) | −2804 (4) | 6667 (3) | −4962 (4) | 3·21 (12) |
| N(3) | −2475 (5) | 3236 (4) | −6447 (4) | 5·70 (18) |
| N(4) | −3974 (5) | 3915 (4) | −8568 (4) | 4·57 (15) |
| C(1) | −1593 (6) | 11274 (5) | −1649 (5) | 4·55 (19) |
| C(2) | −1117 (5) | 10036 (4) | −1745 (5) | 3·55 (16) |
| C(3) | −1819 (5) | 9348 (4) | −1601 (4) | 3·04 (15) |
| C(4) | −725 (5) | 7297 (4) | −485 (4) | 2·94 (15) |
| C(5) | 566 (5) | 6433 (4) | −156 (5) | 3·20 (15) |
| C(6) | 1227 (5) | 5682 (4) | 1041 (5) | 3·94 (17) |
| C(7) | 633 (6) | 5760 (5) | 1952 (5) | 4·48 (19) |
| C(8) | −641 (6) | 6626 (5) | 1616 (5) | 4·42 (20) |
| C(9) | −1367 (5) | 7404 (4) | 416 (5) | 3·55 (17) |
| C(10) | −2782 (6) | 8260 (5) | 211 (6) | 4·80 (22) |
| C(11) | −3644 (5) | 9088 (5) | −1124 (6) | 4·82 (20) |
| C(12) | −2965 (5) | 9885 (5) | −1345 (5) | 3·79 (17) |
| C(13) | −3429 (6) | 11133 (5) | −1252 (5) | 4·82 (19) |
| C(14) | −2729 (6) | 11815 (5) | −1412 (6) | 5·24 (21) |
| C(15) | −882 (5) | 7672 (4) | −2795 (5) | 3·54 (17) |
| C(16) | −1922 (6) | 8322 (5) | −4177 (5) | 4·76 (22) |
| C(17) | −3134 (6) | 7951 (5) | −4754 (5) | 4·53 (19) |
| C(18) | −2168 (5) | 6333 (4) | −5928 (4) | 3·23 (15) |
| C(19) | −1762 (5) | 4988 (4) | −6081 (5) | 3·45 (16) |
| C(20) | −2962 (5) | 4563 (4) | −6497 (4) | 3·53 (15) |
| C(21) | −3783 (5) | 5100 (6) | −5641 (5) | 4·44 (20) |
| C(22) | −4063 (5) | 6422 (5) | −5480 (5) | 4·19 (19) |
| C(23)† | −3545 (8) | 2944 (7) | −7493 (7) | 4·68 (27) |
| C(24)† | −2943 (9) | 1679 (7) | −7853 (8) | 5·28 (33) |
| C(25)† | −2375 (11) | 779 (9) | −6575 (9) | 6·48 (39) |
| C(26)† | −1351 (10) | 1182 (8) | −5367 (9) | 6·35 (37) |
| C(27)† | −2019 (8) | 2509 (7) | −5138 (7) | 4·61 (27) |
| C(28) | −3837 (5) | 4907 (4) | −8029 (4) | 3·37 (15) |
| C(23′)‡ | −2884 (18) | 2710 (15) | −7802 (16) | 4·79 (61) |
| C(24′)‡ | −3603 (21) | 1953 (17) | −7699 (17) | 5·44 (73) |
| C(25′)‡ | −2596 (26) | 934 (15) | −6463 (18) | 7·14 (95) |
| C(26′)‡ | −2124 (26) | 1507 (19) | −5169 (17) | 6·81 (95) |
| C(27′)‡ | −1442 (21) | 2293 (17) | −5317 (18) | 6·07 (76) |

† Population parameter 0·7.

‡ Population parameter 0·3.

Table 2 (*cont.*)

| | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| Compound (*C*) | | | | |
| O | 4631 (1) | 1020 (3) | 2542 (1) | 4·69 (8) |
| N(1) | 3561 (1) | −5673 (3) | 2819 (2) | 4·15 (9) |
| N(2) | 4010 (1) | −2129 (3) | 1826 (2) | 3·81 (8) |
| N(3) | 4180 (1) | 1442 (3) | 681 (2) | 4·04 (9) |
| N(4) | 4765 (1) | 2236 (3) | 1529 (2) | 4·36 (9) |
| C(1) | 2792 (2) | −6244 (6) | 1007 (3) | 7·78 (19) |
| C(2) | 3181 (2) | −6314 (4) | 1575 (2) | 5·43 (13) |
| C(3) | 3152 (2) | −5671 (4) | 2246 (2) | 4·44 (11) |
| C(4) | 3513 (1) | −6399 (4) | 3476 (2) | 4·42 (11) |
| C(5) | 3879 (2) | −7305 (5) | 3726 (3) | 5·45 (13) |
| C(6) | 3870 (2) | −7989 (5) | 4390 (3) | 7·07 (17) |
| C(7) | 3495 (2) | −7797 (6) | 4804 (3) | 7·99 (20) |
| C(8) | 3134 (2) | −6932 (6) | 4560 (3) | 7·48 (19) |
| C(9) | 3124 (2) | −6203 (5) | 3898 (3) | 5·67 (14) |
| C(10) | 2702 (2) | −5276 (7) | 3713 (3) | 8·25 (21) |
| C(11) | 2719 (2) | −4307 (6) | 3089 (3) | 7·16 (18) |
| C(12) | 2740 (2) | −4959 (5) | 2360 (3) | 5·62 (14) |
| C(13) | 2344 (2) | −4907 (6) | 1777 (3) | 7·92 (20) |
| C(14) | 2381 (2) | −5554 (7) | 1115 (3) | 8·68 (21) |
| C(15) | 4057 (1) | −5614 (4) | 2584 (2) | 4·59 (12) |
| C(16) | 4114 (2) | −4502 (4) | 2046 (2) | 4·67 (12) |
| C(17) | 4002 (2) | −3191 (4) | 2368 (2) | 4·23 (11) |
| C(18) | 3773 (1) | −975 (4) | 2097 (2) | 4·03 (10) |
| C(19) | 3740 (1) | 111 (4) | 1518 (2) | 4·15 (11) |
| C(20) | 4240 (1) | 465 (4) | 1279 (2) | 3·50 (9) |
| C(21) | 4510 (1) | −784 (4) | 1092 (2) | 4·16 (11) |
| C(22) | 4515 (1) | −1809 (4) | 1699 (2) | 4·39 (11) |
| C(23) | 4627 (1) | 2206 (4) | 728 (2) | 4·19 (11) |
| C(24) | 4532 (2) | 3493 (4) | 349 (2) | 5·48 (14) |
| C(25) | 4330 (2) | 3221 (5) | −468 (3) | 6·42 (16) |
| C(26) | 3891 (2) | 2303 (6) | −528 (3) | 7·20 (17) |
| C(27) | 4004 (2) | 1061 (5) | −85 (2) | 5·98 (14) |
| C(28) | 4565 (1) | 1252 (4) | 1868 (2) | 3·59 (9) |

Table 3. *Bond lengths* (Å) *involving non*-H *atoms*

| | (*A*) | (*B*) | (*B′*)* | (*C*) |
|---|---|---|---|---|
| Cl—C(1) | 1·733 (6) | — | | — |
| Cl—C(6) | — | 1·738 (5) | | — |
| O—C(28) | 1·218 (6) | 1·215 (6) | | 1·234 (4) |
| N(1)—C(3) | 1·418 (7) | 1·437 (6) | | 1·426 (5) |
| N(1)—C(4) | 1·427 (6) | 1·420 (6) | | 1·423 (5) |
| N(1)—C(15) | 1·469 (6) | 1·460 (8) | | 1·470 (4) |
| N(2)—C(17) | 1·461 (6) | 1·460 (7) | | 1·468 (5) |
| N(2)—C(18) | 1·470 (6) | 1·452 (7) | | 1·463 (5) |
| N(2)—C(22) | 1·457 (6) | 1·471 (8) | | 1·463 (4) |
| N(3)—C(20) | 1·493 (5) | 1·464 (6) | | 1·469 (5) |
| N(3)—C(23) | 1·472 (6) | 1·451 (9) | 1·53 (2) | 1·443 (4) |
| N(3)—C(27) | 1·469 (7) | 1·488 (9) | 1·48 (2) | 1·463 (5) |
| N(4)—C(23) | — | 1·476 (9) | 1·52 (1) | 1·453 (5) |
| N(4)—C(28) | 1·326 (6) | 1·322 (7) | | 1·333 (5) |
| C(1)—C(2) | 1·379 (8) | 1·385 (7) | | 1·384 (7) |
| C(1)—C(14) | 1·389 (8) | 1·350 (10) | | 1·361 (8) |
| C(2)—C(3) | 1·366 (7) | 1·390 (9) | | 1·393 (5) |
| C(3)—C(12) | 1·405 (7) | 1·370 (8) | | 1·378 (8) |
| C(4)—C(5) | 1·391 (7) | 1·382 (6) | | 1·397 (6) |
| C(4)—C(9) | 1·388 (7) | 1·405 (9) | | 1·398 (7) |
| C(5)—C(6) | 1·393 (8) | 1·374 (7) | | 1·395 (8) |
| C(6)—C(7) | 1·343 (8) | 1·377 (10) | | 1·357 (8) |
| C(7)—C(8) | 1·361 (7) | 1·368 (8) | | 1·358 (8) |
| C(8)—C(9) | 1·408 (7) | 1·391 (7) | | 1·410 (8) |
| C(9)—C(10) | 1·513 (7) | 1·510 (8) | | 1·498 (8) |
| C(10)—C(11) | 1·477 (8) | 1·528 (8) | | 1·510 (9) |
| C(11)—C(12) | 1·528 (7) | 1·505 (10) | | 1·487 (8) |
| C(12)—C(13) | 1·370 (8) | 1·395 (8) | | 1·414 (7) |
| C(13)—C(14) | 1·368 (9) | 1·389 (11) | | 1·384 (8) |
| C(15)—C(16) | 1·512 (6) | 1·516 (6) | | 1·520 (6) |
| C(16)—C(17) | 1·523 (8) | 1·509 (10) | | 1·512 (6) |
| C(18)—C(19) | 1·513 (6) | 1·513 (7) | | 1·524 (6) |
| C(19)—C(20) | 1·531 (6) | 1·540 (9) | | 1·526 (4) |
| C(20)—C(21) | 1·533 (6) | 1·525 (8) | | 1·536 (5) |
| C(20)—C(28) | 1·554 (7) | 1·541 (5) | | 1·529 (5) |
| C(21)—C(22) | 1·510 (6) | 1·499 (9) | | 1·520 (6) |
| C(23)—C(24) | 1·522 (8) | 1·511 (11) | 1·46 (4) | 1·495 (6) |
| C(24)—C(25) | 1·515 (8) | 1·547 (13) | 1·59 (2) | 1·538 (6) |
| C(25)—C(26) | 1·513 (9) | 1·572 (14) | 1·51 (3) | 1·517 (8) |
| C(26)—C(27) | 1·513 (7) | 1·538 (12) | 1·47 (4) | 1·516 (8) |

* Compound (*B′*) concerns that part of the terminal piperidine rings of molecule (*B*) whose occupancies are 0·3.

**Discussion.** The atomic parameters for the non-H atoms are given in Table 2.* The bond lengths and angles are respectively listed in Tables 3 and 4. Stereoscopic views of molecules (*A*), (*B*) and (*C*) are shown in Fig. 2 with the atom-numbering schemes (*ORTEP*, Johnson, 1965). For all compounds, pairs of racemic molecules are connected by paired O···H(N4) hydrogen bonds around the centers of symmetry. The O···N(4) distances are 2·919 (5), 2·860 (5) and 2·837 (4) Å for molecules (*A*), (*B*) and (*C*) respectively. These paired molecules are held together by van der Waals forces to form the crystals.

Table 4. *Bond angles* (°) *involving non-*H *atoms*

| | (*A*) | (*B*) | (*B'*) | (*C*) |
|---|---|---|---|---|
| C(3)–N(1)–C(4) | 115·1 (4) | 115·6 (4) | | 117·6 (3) |
| C(3)–N(1)–C(15) | 116·2 (4) | 116·1 (4) | | 117·0 (3) |
| C(4)–N(1)–C(15) | 118·1 (3) | 117·9 (3) | | 116·6 (3) |
| C(17)–N(2)–C(18) | 109·7 (3) | 112·0 (5) | | 109·4 (3) |
| C(17)–N(2)–C(22) | 111·4 (4) | 108·8 (4) | | 111·4 (3) |
| C(18)–N(2)–C(22) | 109·5 (4) | 108·7 (4) | | 109·7 (3) |
| C(20)–N(3)–C(23) | 112·3 (3) | 106·8 (4) | | 108·1 (3) |
| C(20)–N(3)–C(27) | 116·5 (4) | 118·7 (5) | | 120·7 (3) |
| C(23)–N(3)–C(27) | 109·5 (4) | 109·9 (6) | 112·3 (10) | 112·1 (3) |
| C(23)–N(4)–C(28) | — | 110·4 (5) | | 112·0 (3) |
| Cl–C(1)–C(2) | 118·3 (4) | — | | — |
| Cl–C(1)–C(14) | 120·0 (5) | — | | — |
| C(2)–C(1)–C(14) | 121·6 (5) | 120·5 (7) | | 119·3 (5) |
| C(1)–C(2)–C(3) | 119·1 (5) | 119·6 (6) | | 120·1 (5) |
| N(1)–C(3)–C(2) | 122·3 (5) | 121·5 (5) | | 120·6 (4) |
| N(1)–C(3)–C(12) | 117·0 (4) | 118·2 (6) | | 118·1 (4) |
| C(2)–C(3)–C(12) | 120·7 (5) | 120·4 (5) | | 121·2 (4) |
| N(1)–C(4)–C(5) | 119·8 (4) | 119·5 (5) | | 118·8 (4) |
| N(1)–C(4)–C(9) | 122·5 (4) | 121·1 (4) | | 122·5 (3) |
| C(5)–C(4)–C(9) | 117·8 (4) | 119·4 (4) | | 118·7 (4) |
| C(4)–C(5)–C(6) | 122·2 (5) | 120·8 (6) | | 121·6 (5) |
| Cl–C(6)–C(5) | — | 119·0 (5) | | — |
| Cl–C(6)–C(7) | — | 119·4 (4) | | — |
| C(5)–C(6)–C(7) | 119·4 (5) | 121·5 (5) | | 120·0 (5) |
| C(6)–C(7)–C(8) | 119·9 (5) | 117·0 (5) | | 118·8 (5) |
| C(7)–C(8)–C(9) | 122·2 (5) | 124·2 (6) | | 124·0 (5) |
| C(4)–C(9)–C(8) | 118·4 (4) | 117·1 (5) | | 117·0 (5) |
| C(4)–C(9)–C(10) | 125·8 (5) | 126·9 (4) | | 125·7 (5) |
| C(8)–C(9)–C(10) | 115·8 (5) | 116·0 (6) | | 117·3 (5) |
| C(9)–C(10)–C(11) | 118·8 (5) | 117·9 (6) | | 119·3 (5) |
| C(10)–C(11)–C(12) | 113·5 (4) | 111·7 (5) | | 112·1 (5) |
| C(3)–C(12)–C(11) | 117·8 (5) | 118·2 (5) | | 119·6 (4) |
| C(3)–C(12)–C(13) | 118·1 (5) | 119·2 (6) | | 118·0 (5) |
| C(11)–C(12)–C(13) | 124·0 (5) | 122·6 (6) | | 122·4 (5) |
| C(12)–C(13)–C(14) | 122·7 (5) | 120·1 (6) | | 119·8 (5) |
| C(1)–C(14)–C(13) | 117·7 (5) | 120·3 (6) | | 121·6 (5) |
| N(1)–C(15)–C(16) | 111·3 (4) | 112·0 (4) | | 112·8 (3) |
| C(15)–C(16)–C(17) | 110·4 (4) | 114·7 (6) | | 112·2 (3) |
| N(2)–C(17)–C(16) | 112·7 (4) | 114·4 (5) | | 112·4 (3) |
| N(2)–C(18)–C(19) | 112·0 (4) | 111·6 (5) | | 110·5 (3) |
| C(18)–C(19)–C(20) | 114·4 (4) | 112·8 (4) | | 113·0 (3) |
| N(3)–C(20)–C(19) | 114·5 (4) | 110·1 (4) | | 110·5 (3) |
| N(3)–C(20)–C(21) | 110·7 (3) | 114·6 (5) | | 114·7 (3) |
| N(3)–C(20)–C(28) | 104·9 (4) | 99·8 (3) | | 99·0 (3) |
| C(19)–C(20)–C(21) | 108·4 (4) | 109·7 (4) | | 109·6 (3) |
| C(19)–C(20)–C(28) | 110·9 (3) | 110·2 (5) | | 112·9 (3) |
| C(21)–C(20)–C(28) | 107·2 (4) | 112·1 (4) | | 110·0 (3) |
| C(20)–C(21)–C(22) | 112·1 (4) | 114·7 (6) | | 112·2 (3) |
| N(2)–C(22)–C(21) | 110·6 (4) | 111·4 (4) | | 110·2 (3) |
| N(3)–C(23)–N(4) | — | 98·9 (7) | | 100·5 (3) |
| N(3)–C(23)–C(24) | 110·4 (4) | 109·1 (6) | 106·4 (15) | 110·8 (3) |
| N(4)–C(23)–C(24) | — | 113·6 (7) | 106·0 (13) | 116·6 (3) |
| C(23)–C(24)–C(25) | 110·8 (5) | 107·7 (7) | 107·6 (17) | 107·6 (3) |
| C(24)–C(25)–C(26) | 109·4 (5) | 108·7 (9) | 110·4 (14) | 111·5 (5) |
| C(25)–C(26)–C(27) | 112·1 (4) | 111·3 (7) | 110·4 (20) | 112·2 (4) |
| N(3)–C(27)–C(26) | 109·9 (4) | 105·3 (6) | 105·4 (15) | 107·4 (4) |
| O–C(28)–N(4) | 122·4 (5) | 126·3 (4) | | 125·7 (3) |
| O–C(28)–C(20) | 122·4 (4) | 125·6 (4) | | 126·0 (4) |
| N(4)–C(28)–C(20) | 115·2 (4) | 108·1 (4) | | 108·3 (3) |

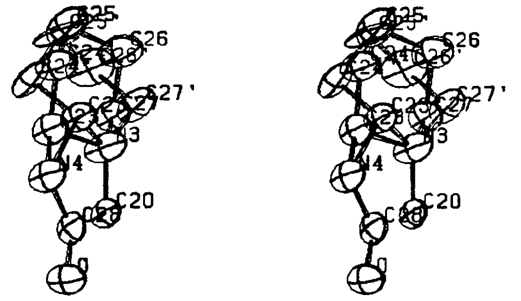

Fig. 3. Stereoscopic view of the terminal piperidine rings of compound (*B*).

The conformation of the dibenzazepine ring is asymmetric: the C(10)—C(11) bond of the ethylene moiety is in plane with one benzene ring and is out of plane with the other. The Cl atom of compound (*A*) is connected to the position *meta* to N(1) of the out-of-plane benzene ring. On the other hand, the Cl atom of compound (*B*) is connected to the same position of the in-plane benzene ring. The tilt angles between these benzene rings are 120·1, 119·3 and 128·5° for compounds (*A*), (*B*) and (*C*) respectively. These angles are closer to the results of Post, Kennard & Horn (1975) than to those of Reboul, Cristau, Estienne & Astier (1980). The conformations of the propylene moieties from N(1) to N(2) are quite different for these compounds, as shown in Fig. 2 and by the torsion angles (deposited). For compound (*A*), the conformations of C(15) – C(17) are *trans* and *trans*. For compound (*B*), they are *gauche* and *gauche*. For compound (*C*), they are *gauche* and *trans*. By these twistings, the Cl atoms of compounds (*A*) and (*B*) and H(Cl) of compound (*C*) have approximately the same coordinations to the face of each middle piperidine ring. On the backs of the rings, the carbamoyl moieties are situated by the spiro conformations of C(20). The two piperidine rings for each compound have chair forms. The terminal piperidine ring of compound (*B*) consists of two antipodal parts, C(23) – C(27) and C(23′) – C(27′), whose occupancies are respectively 0·7 and 0·3 as shown in Table 2 and Fig. 3. The geometrical isomerism is caused by the triangular-pyramidal configurations of N(3) and N(4). The short bond lengths of N(4)—C(28) for all compounds suggest charge transfer from N(4) to O and affect the formation of hydrogen bonds.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, coordinates and isotropic thermal parameters for H atoms and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38958 (60 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (2,2′-Bipyridine)chloro(triphenylphosphine)copper(I) Monohydrate,* $C_{28}H_{23}ClCuN_2P.H_2O$

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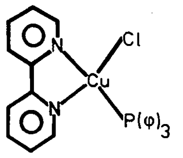
(*Received* 14 *June* 1983; *accepted* 12 *October* 1983)

**Abstract.** $M_r = 535{\cdot}5$, triclinic, $P\bar{1}$, $a = 16{\cdot}967\,(10)$, $b = 9{\cdot}426\,(5)$, $c = 8{\cdot}712\,(5)$ Å, $\alpha = 65{\cdot}50\,(4)$, $\beta = 88{\cdot}23\,(5)$, $\gamma = 89{\cdot}53\,(5)°$, $V = 1267\,(1)$ Å$^3$, $Z = 2$, $D_m = 1{\cdot}39$, $D_x = 1{\cdot}40\,(3)$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}09$mm$^{-1}$, $F(000) = 552$, $T = 298$ K, $R = 0{\cdot}049$ for 2371 unique reflections. The metal atom is tetrahedrally coordinated to 2,2′-bipyridine [Cu—N 2·076 (5), 2·087 (6) Å; N—Cu—N 79·2 (2)°] Cl [Cu—Cl 2·330 (2) Å] and triphenylphosphine [Cu—P 2·180 (2) Å], and is distorted [N—Cu—Cl 102·9 (2), 104·5 (2)°; N—Cu—P 122·8 (2), 123·2 (1)°; and Cl—Cu—P 117·1 (1)°]. The water molecule is hydrogen bonded to Cl [Cl···O 3·25 (1), 3·30 (1) Å].

**Introduction.** Complexes of the type $Cu^{I}(XYZ)$, with $X$ = ligands containing an N—C—C—N group, $Y = Cl^-$ or $BH_4^-$, and $Z$ = triphenylphosphine, are currently being investigated. The title compound, $[Cu(bpy)Cl(tpp)].H_2O$, (I), where bpy = 2,2′-bipyridine and tpp = triphenylphosphine, is the first member of this series. bpy and tpp are used to stabilize $Cu^{I}$ (Jardine, Rule & Vohra, 1970).



(I)

**Experimental.** (I) prepared by reacting $[(tpp)CuCl]_4$ with bpy in absolute alcohol (Jardine *et al.*, 1970), and recrystallized from a chloroform–xylene mixture as yellow crystals. Crystal 0·25 × 0·20 × 0·13 mm. $D_m$ by flotation. Syntex $P2_1$ four-circle diffractometer. 15 reflections used for lattice-parameter determination. No absorption or extinction correction. $2\theta_{max} = 50°$. Standard reflections: $I_{400} = 302\,(7) \times 10^3$; $I_{020} = 129\,(2) \times 10^3$; $I_{003} = 108\,(3) \times 10^3$. 3058 reflections measured, 2371 unique [$I > 2{\cdot}5\sigma(I)$], 687 unobserved. Cu atom obtained using the *TANG* direct method of *SHELX* (Sheldrick, 1976). Remaining atoms located from a weighted difference-Fourier synthesis. H atoms located at the end of the refinement, and set at fixed positions with $U = 0{\cdot}05$ Å$^2$. Full-matrix least-squares refinement based on $F$ reduced $R$ to 0·049 and $wR$ to 0·049; $w = 2{\cdot}26/[\sigma^2(F_o) + 0{\cdot}0003F_o^2]$ (determined by least squares). Maximum and average $\Delta/\sigma$ ratios 2·4 and 0·6. Final difference electron density maximum 0·12, minimum $-0{\cdot}12$ e Å$^{-3}$. Scattering factors: non-hydrogens (Cromer & Mann, 1968), H (Stewart, Davidson & Simpson, 1965).

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* Stereochemistry of Rigid Chelate–Metal Complexes. VII. Part VI: Green, Kennard, Smith, James & White (1981).

0108-2701/84/030426-03$01.50