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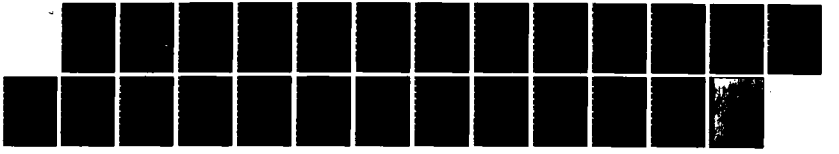

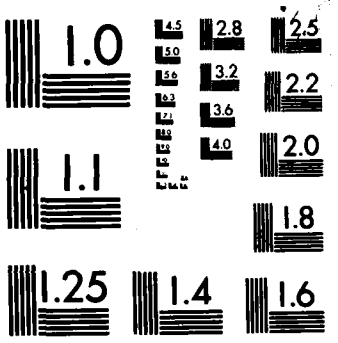

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Studies on B-(Pyrazol-1'-yl)pyrazaboles

by

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The pyrazaboles $H_2B(\mu\text{-pz})_2BRR'$ (pz - pyrazolyl = $N_2C_3H_3$; R = R' = H; R = H, R' = pz; R = R' = pz) have been prepared by reaction of poly(pyrazol-1-yl)-borate ions with $(CH_3)_3NBH_2I$. Also the preparation of the pyrazoboles $Hpz'B(\mu\text{-pz}')_2BHpz'$ and $pz'_2B(\mu\text{-pz}')_2Bpz'_2$ (pz' = N_2C_3H-3,5-$(CH_3)_2$) is reported. The latter compound forms a thermally very stable and unusual monohydrate.

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Studies on the interaction of $H_2B(\mu\text{-pz})_2BH_2$ with Hpz' suggest that, in contrast to electrophilic substitutions, the condensation to yield B-pyrazolylpyrazaboles occurs via opening of the initial central B_2N_4 ring of the pyrazabole.

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

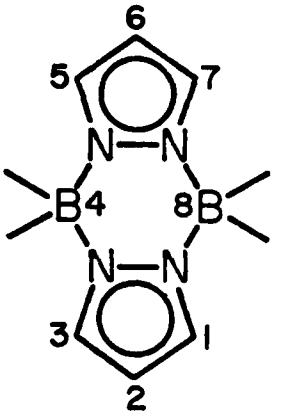
Studies on B-(Pyrazol-1'-yl)pyrazaboles[1]

Kurt Niedenzu* and Philipp M. Niedenzu

The pyrazaboles $H_2B(\mu\text{-pz})_2BRR'$ (pz = pyrazolyl = $N_2C_3H_3$; R = R' = H; R = H, R' = pz; R = R' = pz) have been prepared by reaction of poly(pyrazol-1-yl)borate ions with $(CH_3)_3NBH_2I$. Also, the preparation of the pyrazaboles $Hpz'B(\mu\text{-pz}')_2BHpz'$ and $pz'_2B(\mu\text{-pz}')_2Bpz'_2$ (pz' = $N_2C_3H\text{-}3,5\text{-}(CH_3)_2$) is reported. The latter compound forms a thermally very stable and unusual monohydrate. Studies on the interaction of $H_2B(\mu\text{-pz})_2BH_2$ with Hpz' suggest that, in contrast to electrophilic substitutions, the condensation to yield B-pyrazolylpyrazaboles occurs via opening of the initial central B_2N_4 ring of the pyrazabole.

Introduction

Poly(pyrazol-1-yl)borate anions of the general formula $[Bpz_{4-n}R_n]^-$ (pz = pyrazol-1-yl = $N_2C_3H_3$ or C-substituted derivatives thereof; R = non-coordinating substituent, n = 0, 1, 2) feature electronic and geometric factors that have led to their extensive use as ligands in coordination chemistry.[2-4] In contrast, neutral species containing a terminal Bpz_2 group have received little attention although their coordinating ability should equal that of the poly(pyrazol-1-yl)borate anions. Such a neutral Bpz_2 ar gement is present in the three known 4,4-bis(pyrazol-1'-yl)pyrazaboles $pz_2B(\mu\text{-}pz)_2Bpz_2$,[5] $pz_2B(\mu\text{-}pz)_2B(C_2H_5)_2$,[6] and $pz_2B(\mu\text{-}pz)_2Bpz[N(CH_3)_2]$,[7] all of which feature two additional bridging pyrazolyl groups in a pyrazabole skeleton $B(\mu\text{-}pz)_2B$, 1, to which exocyclic pyrazolyl groups are B-bonded in the 4 (and 8) terminal position(s).



Trofimenko briefly illustrated the potential coordinating functions of the terminal Bpz_2 groups in $pz_2B(\mu\text{-}pz)_2Bpz_2$ and $pz_2B(\mu\text{-}pz)_2B(C_2H_5)_2$ but no experimental details have been presented.[8] Additional work on 4,4-bis(pyrazol-1'-yl)-pyrazaboles has been limited to some NMR spectroscopic studies.[9] The present paper describes some investigations on the formation and characterization of 4,4-bis(pyrazol-1'-yl)pyrazaboles and other B-(pyrazol-1'-yl)pyrazabole species.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block. Mass spectral data were obtained on a PE-Hitachi RMU-7 or VG ZAB-2F spectrometer. - ^1H NMR spectra were recorded on a Varian EM-390 instrument and on a Varian XL-200 pulse FT spectrometer operating at 200 MHz (Me_4Si reference). The latter instrument was also used for the recording of the additional spectra, operating at 64.185 MHz for ^{11}B (external Et_2OBF_3 refrence) and at 50.300 MHz for ^{13}C (Me_4Si reference). Conditions for HOMCOR-2D and HETCOR-2D experiments have been described elsewhere.[9] All chemical shift data are given in ppm with positive

values indicating downfield from the reference; s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet; an asterisk denotes a broad signal. Coupling constants are given in Hz. - Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer under standard operating conditions; frequencies in cm^{-1}; s = strong, m = medium, w = weak, br = broad, v = very, sh = shoulder.

Pyrazoles were commercial products. - $K[Bpz_4]$ and $K[HBpz_3]$ were prepared by literature procedures.[10] Materials thus obtained were slightly impure. The salt $K[Bpz_4]$ ($\delta(^1H)$ = 7.68, 7.38, 6.33; $\delta(^{11}B)$ = -1.0.[11] $\delta(^{11}B)$ = +3.2; $\delta(^{13}C)$ = 140.9, 135.0, 104.5.[9] This work: $\delta(^1H)$ (solution in D_2O) = 7.51, 7.21, 6.17) was contaminated by a small amount of polyborate evidenced by a signal $\delta(^{11}B)$ = +12.6 (even after recrystallization from ethanol). Similarly, $K[HBpz_3]$ ($\delta(^1H)$ = 7.57, 7.18, 6.15; $\delta(^{11}B)$ = +1.3.[11] This work (solution in D_2O): $\delta(^1H)$ = 7.44, 7.10, 6.06; $\delta(^{11}B)$ = +0.8; $\delta(^{13}C)$ = 140.5 (d, J = 176, of t, J = 10), 134.4 (d, J = 184, of t, J = 7), 104.5 (d, J = 183, of t, J = 7) exhibited an additional signal at $\delta(^{11}B)$ = +9.4. - Pyrazabole and 1,3,5,7-tetramethylpyrazabole were prepared from $(CH_3)_3NBH_3$ and the required pyrazole.[10] 4,4-Di-n-butylpyrazabole[6] and 1,3,5,7-tetramethyl-4,4-diethylpyrazabole[6] were provided by Dr. S. Trofimenko. - Trimethylamine-monoiodoborane was prepared by the literature procedure.[12] It was repurified prior to use by dissolving it in benzene, decanting the clear solution and precipitation of $(CH_3)_3NBH_2I$ with petroleum ether.

4,4-Bis(pyrazol-1'-yl)pyrazabole. A mixture of 16.86 g (53 mmol) of $K[Bpz_4]$, 9.94 g (50 mmol) of $(CH_3)_3NBH_2I$ and 125 mL of toluene was heated with stirring for 12 h to 70°C, another 12 h to 80°C (oil-bath temperature) and finally 4 h to reflux. After cooling to room temperature, the mixture was filtered and solvent was evaporated from the filtrate. The resultant large crystals were crushed and stirred for 10 min each with three 25-mL portions of water (for removal of pyrazole) and, after drying, three 25-mL portions of petroleum ether (from the combined latter solutions about 3 g of pyrazabole can be recovered). For a final purification the product was sublimed under vacuum or recrystallized from cyclohexane or toluene to yield 5.98 g (41% yield calculated for $(CH_3)_3NBH_2I$) as colorless crystals, mp 152-153°C. Anal. Calcd. for $C_{12}H_{14}B_2N_8$ (291.92): C, 49.37; H, 4.83; B, 7.41; N, 38.39. Found: C, 49.57; H, 5.05; B, 7.51; N, 38.34.

NMR data: $\delta(^1H)$ (solution in $CDCl_3$) = 7.74 (2H, d, J = 1.7), 7.40 (1H, d, J = 2.6), 7.05 (1H, d, J = 2.5), 6.44 (1H, t, J = 2.4), 6.28 (1H, 2 overlapping d, J = 2.3), 3.5* (1H); (solution in CD_3CN) = 7.87 (1H, d), 7.63 (1H, d), 7.34 (1H, d), 7.03 (1H, d), 6.49 (1H, t), 6.30 (1H, unsym t), 3.5* (1H); $\delta(^{11}B)$ (solution in $CDCl_3$) = -0.1 (s, $h_{\frac{1}{2}}$ = 60 Hz), -8.6* ($h_{\frac{1}{2}}$ = 420 Hz (proton-decoupled), = 680 Hz (proton-coupled)), area ratio 1:1; $\delta(^{13}C)$ (solution in $CDCl_3$) = 142.8 (d, J = 184, of t, J = 7), 137.2 (d, J = 191, of t, J = 7), 136.6 (d, J = 193, of t, J = 7), 134.2 (d, J = 190, of t, J = 7), 106.8 (t, J = 183), 105.7 (two overlapping d, J = 179). Based on HOMCOR and

HETCOR 2D experiments, the signals $\delta(^1H)/\delta(^{13}C)$ = 7.74/142.8, 7.05/134.2, 6.28/105.7 and 7.74/137.2, 7.40/136.6, 6.44/106.8 are assigned to the two different types of pyrazolyl groups. - Infrared spectrum (KBr pellet): 3100(w), 3090(sh), 2450(m), 2400(m), 2350(vw), 2320(sh), 2240(vw), 2220(vw), 2060(vw), 1790(vw, br), 1760 (vw, br), 1630(vw), 1553(sh), 1538(sh), 1530(sh), 1518(sh), 1506(m), 1462(w), 1457(sh), 1438(sh), 1427(s), 1418(sh), 1409(s), 1381(s), 1340(m), 1329(s), 1292(s), 1288(sh), 1245(s), 1233(sh), 1230(s), 1217(vs), 1210(sh), 1188(ms), 1182(ms), 1179(sh), 1153(m), 1143(ms), 1129(m), 1113(s), 1095(sh), 1092(s), 1081(vs), 1078(sh), 1049(ms), 1040(ms), 1034(sh). 1022(w), 1015(w), 972(sh), 967(vw), 929(m), 919(sh), 917(w), 905(m), 891(m), 873(m), 858(s), 847(sh), 841(s), 827(s), 819(vs), 813(sh), 810(sh), 776(vs), 764(vs), 757(vs), 725(vw), 711(w), 673(w), 667(w). - Mass spectrum: M/z (relative abundance) = 292 (12), 291 (68), 290 (34), 225 (18), 224 (54), 223 (100), 222 (42), 221 (6), 196 (10), 195 (7), 157 (33), 156 (17), 155 (6), 147 (5), 130 (7), 129 (6), 112 (7), 98.5 (14), 98 (11), 79 (26), 78 (5), 52 (5). 1st ionization potential (by mass spectrometry): 9.2 $\pm$ 0.1 eV.

4-(Pyrazol-1'-yl)pyrazabole. A mixture of 12.60 g (50 mmol) of $K[HBpz_3]$, 9.45 g (45 mmol) of $(CH_3)_3NBH_2I$ and 200 mL of toluene was heated with stirring for 4 h in an oil-bath of 65°C and subsequently gently refluxed for 8 h. After cooling to room temperature the mixture was filtered and toluene was evaporated from the filtrate. On prolonged standing of the colorless liquid residue, crystals of pyrazole and pyrazabole

(including 4,4-bis(pyrazol-1'-yl)pyrazabole, if the $K[HBpz_3]$ contained some $K[Bpz_4]$) formed and were filtered off. Remaining traces of pyrazole and, mostly, pyrazabole were sublimed from the product under vacuum (bath temperature of about 65°C). The remaining oil was dissolved in a small amount of $CHCl_3$, insolubles were filtered off and the solvent was evaporated to leave 4.7 g (48% yield based on $(CH_3)_3NBH_2I$) of the desired compound as a colorless oil, identical (NMR spectra) with the previously described material.[13]

IR spectrum (neat, NaCl plates): 3110(m), 3040(sh), 3026(w), 2890(vw), 2620(vw), 2464(ms), 2410(sh), 2360(sh), 2260(w), 2110(vw), 2060(vw), 1760(w, br), 1620(vw), 1542(sh), 1510(ms), 1490(sh), 1460(w), 1428(s), 1419(sh), 1410(sh), 1384(m), 1326(s), 1304(m), 1234(sh), 1222(ms), 1185(m), 1156(sh), 1138(s), 1128(sh), 1104(wm), 1076(s), 1038(wm, br), 960(sh), 949(wm), 930(w), 915(w), 900(sh), 888(m), 875(w), 854(w), 841(wm), 822(wm), 761(s, br), 730(sh), 698(w).

4,4-Di-n-butylpyrazabole. NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 7.56 (2H, d, J = 2.4), 6.29 (1H, unsym t, J = 2.4), 3.2* (1H), 1.25 to 0.79 (9H, m); $\delta(^{11}B)$ = 2.1*, -8.5*, area ratio 1:1; $\delta(^{13}C)$ = 134.6 (d, J = 188, of t, J = 7.5), 133.8 (d, J = 188, of t, J = 7), 105.2 (d, J = 180, of t, J = 8.5), 27.5, 26.2, 22*, 14.1.

1,3,5,7-Tetramethylpyrazabole. NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 5.85 (1H, s), 3.1* (2H, t, J ca. 120), 2.29 (6H, s); $\delta(^{11}B)$ = -12.5* (t, J ca. 90); $\delta(^{13}C)$ = 143.8 (s), 105.8 d, J = 175, of m, J = 3.5), 12.0 (q, J = 129). - Mass

spectrum (70 eV): M/z (relative abundance) = 216 (13), 215 (100), 214 (70), 213 (48), 212 (20), 211 (6), 172 (6), 158 (5), 119 (5), 107 (27), 106.5 (14), 96 (15), 95 (11), 78 (5), 76 (11), 66 (9), 65 (5), 63 (7), 62 (5), 54 (9), 53 (5), 52 (7), 51 (6), 41 (7), 39 (12), 38 (10), 28 (9).

1,3,5,7-Tetramethyl-4,8-bis(3',5'-dimethylpyrazol-1'-yl)pyrazabole. A mixture of 10.8 g (0.05 mol) of 1,3,5,7-tetramethylpyrazabole and 9.6 g (0.1 mol) 3,5-dimethylpyrazole was carefully molten and then the temperature was slowly increased to provide for gentle reflux (bath temperature of about 220°C). When the theoretical amount of hydrogen was evolved (approximately 4 to 5 h reaction time), the product was cooled to room temperature, crushed and washed with hot methanol and then with hot toluene. There remained 15.4 g (76% yield) of colorless crystals, mp (after recrystallization from chloroform/cyclohexane) 286-288°C. Anal. Calcd. for $C_{20}H_{30}B_2N_8$ (404.14): C, 59.44; H, 7.48; B, 5.35; N, 27.73. Found: C, 59.53; H, 7.36; B, 5.26; N, 27.72.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 5.97 (1H, s), 5.68 (1H, s), 2.19 (3H, s), 2.08 (6H, s), 1.76 (3H, s); $\delta(^{11}B)$ = -4.9 (d, J = 105); $\delta(^{13}C)$ = 148.7, 147.8, 143.1, 109.1 (d, J = 177), 105.8 (d, J = 170), 13.7 (q, J = 127), 12.2 (q, J = 130), 11.3 (q, J = 128).

1,3,5,7-Tetramethyl-4,4,8,8-tetrakis(3',5'-dimethylpyrazol-1'-yl)pyrazabole. A mixture of 10.8 g (0.05 mol) of 1,3,5,7-tetramethylpyrazabole and 21.1 g (0.22 mol) of 3,5-di-

methylpyrazole was molten and then the temperature was slowly increased to 240 to 260°C (oil-bath) which was maintained for 48 h. After cooling to room temperature, the solid product was crushed and washed with water to remove excess 3,5-dimethylpyrazole. The residue was then recrystallized from ethanol/cyclohexane (1/1 by volume) or benzene and dried in vacuum for 4 h at 60°C to give 11.2 g (76% yield) of the desired compound as the monohydrate, mp 248-252°C. (Note: Some changes in the material were observed near 160 and 220°C, respectively, but no melting occurred.) Anal. Calcd. for $C_{30}H_{44}B_2N_{12}O$ (610.39): C, 59.03; H, 7.27; B, 3.54; N, 27.54; O, 2.62. Found: C, 59.19; H, 7.23; B, 3.50; N, 27.22.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 5.94 (1H, s), 5.69 (1H, s), 5.32 (1H, s), 4.13 (1H, s), 2.15 (3H, s), 2.02 (3H, s), 1.81 (3H, s), 1.45 (3H, s), 1.42 (3H, s), 1.17 (3H, s); $\delta(^{11}B)$ = -0.7 ($h_{\frac{1}{2}}$ = 50 Hz); $\delta(^{13}C)$ = 152.1, 151.0, 149.1, 148.5, 147.4, 144.2, 111.7 (d, J = 180), 107.1 (d, J = 170), 106.6 (d, J = 170), 13.4 (q, J = 127), 13.2 (q, J = 126), 12.5 (q, 130), 11.8 (q, J = 130), 10.4 (q, J = 128), 10.1 (q, J = 128). - Infrared spectrum (KBr pellet): 3520(sh), 3448(ms, br), 3400(sh), 3245(vw), 3132(w), 3084(w), 2980(m), 2930(m), 2862(sh), 1652(vw), 1562(vs), 1506(vw), 1474(sh), 1454(s), 1422(vs), 1381(s), 1360(s), 1348(sh), 1250(sh), 1221(s, br), 1202(sh), 1164(w), 1142(w), 1111(m), 1098(s), 1064(sh), 1024(s), 1020(sh), 975(wm, br), 9ss(sh), 908(s), 888(wm), 878(sh), 868(vs), 848(w), 817(w, br), 774(sh), 768(s), 758(sh), 726(m), 721(sh), 708(ms).

In an alternate procedure, a mixture of 7.15 g (0.05 mol) of tris(dimethylamino)borane and 16.3 g (0.17 mol) of 3,5-dimethylpyrazole was slowly heated to reflux. Reflux was maintained for about 6 h after which time the evolution of dimethylamine had ceased. After cooling to room temperature, the solid material was crushed and washed with three 50-mL portions of water. The residue was recrystallized (after drying) as described above to yield 10.8 g (73%) of the desired material as the monohydrate as described above.

In order to prepare the anhydrous material, the monohydrate was heated for 8 h under vacuum at a bath temperature of 160-170°C. (Note: Essentially no water was lost at 100°C; after 6 h at 120°C, only partial removal of water was accomplished.) This temperature is sufficiently low to avoid sublimation. The remaining material exhibited the same mp 248-252°C as noted for the monohydrate but the elemental analysis and NMR spectral data showed it to be the anhydrous material. Anal. Calcd. for $C_{30}H_{42}B_2N_{12}$ (592.37): C, 60.83; H, 7.15; B, 3.65; N, 28.37. Found: C, 60.81; H, 7.17; B, 3.61; N, 28.33.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 5.88 (1H, s), 5.61* (1H, s), 5.26* (1H, s), 3.05* (6H, s), 1.6* (6H, unsym s), 1.28 (6H, s); $\delta(^{11}B)$ = -0.6 ($h_{\frac{1}{2}}$ = 46 Hz); $\delta(^{13}C)$ (proton decoupled) = 151.8, 150.6, 149.1, 148.1, 147.5, 143.6, 111.1, 107.3, 13.4, 12.4, 11.8, 10.7, 9.8. - The infrared spectrum of the material (KBr pellet) is essentially identical to that of the monohydrate except that the band of medium to strong intensity at 3448 cm^{-1} and its accompanying shoulders are missing.

1,3,5,7-Tetramethyl-4,4-diethylpyrazabole. NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 5.95(1H, s), 3.4* (1H), 2.43 (3H, s), 2.30 (3H, s), 0.82 (2H, q, J = 7.5), 0.38 (3H, t, J = 7.5); $\delta(^{11}B)$ = +5.6 ($h_{\frac{1}{2}}$ = 160 Hz), -11.2 (t, J = 106), area ratio 1:1; $\delta(^{13}C)$ = 144.5, 143.5, 108.4 (d, J = 175), 14.5 (q, J = 129), 14.4* (boron-bonded C), 12.2 (q, J = 129), 9.0 (q, J = 123; from ethyl group).

Reaction of Pyrazabole with 3-Methylpyrazole. A mixture of 16.0 g (0.1 mol) of pyrazabole and 32.8 g (0.4 mol) of 3-methylpyrazole (= Hpz') was heated to boiling until the calculated amount of hydrogen had been evolved and reaction ceased (which is usually recognized by a yellow taint of the reaction mixture; the reaction requires about 12 h). The material could be distilled under vacuum (ca. 3 Torr) from an oil-bath of 260-280°C to give a glassy material, mp 75-76°C. Mass spectrum (region above M/z 460 only): M/z (relative abundance, calcd. monoisotopic ion) = 509 (10), 508 (17, $B_2pz'_6$), 507 (13), 496 (8), 495 (24), 494 (71, $B_2pzpz'_5$), 493 (39), 492 (10), 482 (9), 481 (30), 480 (100, $B_2pz_2pz'_4$), 479 (51), 478 (13), 468 (7), 467 (20), 466 (63, $B_2pz_3pz'_3$), 465 (35), 464 (10).

Reaction of Pyrazabole with 3,5-Dimethylpyrazole. A mixture of 16.0 g (0.1 mol) of pyrazabole and 38.5 g (0.4 mol) of 3,5-dimethylpyrazole (= Hpz') was reacted as described above. The crude product, mp 103-107°C, could not be distilled without

noticeable decomposition. Mass spectrum (region above M/z 460 only): M/z (relative abundance, calcd. monoisotopic ion) = 593 (10), 592 (26, $B_2pz'_6$), 591 (15), 590 (3), 566 (5), 565 (25), 564 (67, $B_2pzpz'_5$), 563 (33), 562 (7), 550 (3), 549 (5), 548 (3), 538 (5), 537 (26), 536 (82, $B_2pz_2pz'_4$), 535 (43), 534 (18), 522 (3), 521 (7), 520 (3), 510 (5), 509 (28), 508 (93, $B_2pz_3pz'_3$), 507 (48), 506 (12) 500 (5), 499 (30), 498 (100), 497 (66), 496 (18), 495 (5), 494 (3), 492 (3).

Results and Discussion

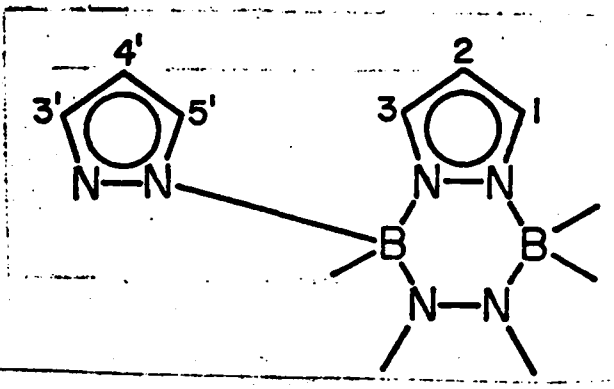
Preparation and Characterization of 4,4-Bis(pyrazol-1'-yl)-pyrazabole. The compound 4,4-bis(pyrazol-1'-yl)pyrazabole, $pz_2B(\mu\text{-}pz)_2BH_2$, has been found to be readily accesible by the reaction of trimethylamine-monoiodoborane with potassium tetrakis(pyrazol-1-yl)borate in accordance with eq (1), whereby the former undergoes both base and iodide ion displacement.

$$K[Bpz_4] + (CH_3)_3NBH_2I \longrightarrow pz_2B(\mu\text{-}pz)_2BH_2 + N(CH_3)_3 + KI \quad (1)$$

It should be noted that pyrazabole, $H_2B(\mu\text{-}pz)_2BH_2$, is a substantial by-product in this reaction (usually about 1/3 of the quantity of the desired product) as is pyrazole. Based on NMR spectroscopic data, intermediates of the type $pz_3B(\mu\text{-}pz)BH_2\text{-}N(CH_3)_3$ appear to be formed (though were not isolated) and only careful control of the reaction conditions

promotes the formation of the desired $pz_2B(\mu\text{-}pz)_2BH_2$ in reasonable yield.

The latter compound is stable to moisture and air and is soluble in many common organic solvents but insoluble in water. The NMR spectral data of $pz_2B(\mu\text{-}pz)_2BH_2$ are in complete consonance with the suggested structure. Based on HOMCOR and HETCOR 2D experiments analogous to those described previously[9] for a number of pyrazaboles, $\delta(^1H)/\delta(^{13}C)$ signals at 7.74/142.8, 7.05/134.2 and 6.28/105.7 ppm belong to one (the terminal) type of pyrazole moiety, those at 7.74/137.2, 7.40/136.6 and 6.44/106.8 ppm to the other (bridging). Based on these findings, NMR assignments for the numbered positions in 2 of some B-pyrazolylpyrazaboles are listed below.



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$\delta(^1H)/\delta(^{13}C)$ in position (see 2)	$pz_2B(\mu\text{-}pz)_2Bpz_2$	$pz_2B(\mu\text{-}pz)_2BH_2$	$pz_2B(\mu\text{-}pz)_2BEt_2$
1	7.67/139.0	7.40/136.6	7.46/136.6
2	6.70/107.8	6.44/106.8	6.52/106.8
3	7.67/139.0	7.74/137.2	7.75/136.3
5'	6.81/133.6	7.05/134.2	7.46/133.6
4'	6.16/105.7	6.28/105.7	6.26/105.6
3'	7.70/142.5	7.74/142.8	7.73/142.6

The ready base and iodide ion displacement from trimethylamine-monoiodoborane by Bpz_2 groups is also observed on reaction of potassium hydrotris(pyrazol-1-yl)borate with the cited reagent according to eq (2).

$$K[HBpz_3] + (CH_3)_3NBH_2I \longrightarrow HpzB(\mu\text{-}pz)_2BH_2 + N(CH_3)_3 + KI \quad (2)$$

The resultant 4-pyrazol-1'-ylpyrazabole has been obtained earlier in low yield by a condensation of pyrazabole with an equimolar amount of pyrazole.[13] However, the present method is less cumbersome and provides better yields. Similarly, $K[H_2Bpz_2]$ reacts with $(CH_3)_3NBH_2I$ to give the parent pyrazabole. But this latter reaction offers no advantage as compared to the standard preparation of the compound from pyrazole and trimethylamine-borane.[10]

It is interesting to note that the position of the ^{11}B NMR signal of the BH_2 group in pyrazaboles of the type $RR'B(\mu\text{-}pz)_2BH_2$ is essentially unaffected by the nature of R and R'. This is illustrated by the following data.

compound	$\delta(^{11}B)$ of the BH_2 group (ppm)
$H_2B(\mu\text{-}pz)_2BH_2$[9]	-8.6
$HBrB(\mu\text{-}pz)_2BH_2$[13]	-8.4
$HpzB(\mu\text{-}pz)_2BH_2$[13]	-8.6
$F_2B(\mu\text{-}pz)_2BH_2$[6]	-8.2
$pz_2B(\mu\text{-}pz)_2BH_2$	-8.6
$(C_2H_5)_2B(\mu\text{-}pz)_2BH_2$[6]	-8.3
$(n\text{-}C_4H_9)_2B(\mu\text{-}pz)_2BH_2$	-8.5

On the other hand, the only known unsymmetrical pyrazabole in which the bridging pyrazolyl groups are C-substituted, i.e., $(C_2H_5)_2B(\mu\text{-pz}')_2BH_2$ (pz' = 3,5-dimethylpyrazolyl), exhibits the signal for the BH_2 group at $\delta(^{11}B)$ = -11.2 ppm. This datum seems to be somewhat unusual inasmuch as the influence of C-substitution is much less apparent in symmetrical pyrazaboles.[9]

Condensation Reactions of Pyrazabole with C-Substituted Pyrazoles. Electrophilic-induced substitution at the boron sites of pyrazabole occurs readily even at low temperatures. Based on NMR data and experiments involving ^{10}B-labelled reagents, the reaction proceeds in stepwise fashion, without opening of the central B_2N_4 ring, and seems to involve a three-coordinate boron cation as an intermediate.[13] In contrast, the condensation of pyrazabole with active hydrogen compounds requires high reaction temperatures. Relevant substitutions have been described for the reaction of pyrazabole with pyrocatechol,[5] phenol,[5] pyrazole[5,13] and α,ω-dithiols.[14] The reaction with o-phenylenediamine resulted in a complete breakdown of the pyrazabole skeleton, in which the formation of an intermediate by symmetrical cleavage of the central B_2N_4 ring has been postulated.[5] Indeed, such a symmetrical cleavage has been observed on reaction of pyrazaboles with α,ω-diamines, in which case the resultant monomeric pyrazol-1-ylboranes were thermally stable species which could be isolated and characterized.[14]

The preceding data suggest that, in contrast to the electrophilic-induced substitution of pyrazabole, substitution via reaction with active hydrogen compounds, HL, may involve

at least a B_2N_4-ring opened intermediate if not the HL adduct of a complete symmetrical cleavage product, i.e., a monomeric pyrazol-1-ylborane. These assumptions are supported by a study of the interaction of pyrazabole with C-substituted pyrazoles, Hpz' (= 3-methylpyrazole, 3,5-dimethylpyrazole). If this reaction were to occur by means analogous to the electrophilic substitution, condensation of pyrazabole with Hpz' in 1:4 molar ratio should yield the pyrazabole $pz'_2B(\mu\text{-}pz)_2Bpz'_2$. However, mass spectral data of the reaction product clearly showed it to be a mixture and the species observed as the parent ion in the spectrum was the pyrazabole $pz'_2B(\mu\text{-}pz')_2Bpz'_2$. In addition, ion peaks were observed for all possible pyrazabole species of the composition $B_2pz_{6-n}pz'_n$ (with n = 0 to 6). The formation of a mixture of compounds was also confirmed by ^{11}B NMR spectral data: For a BN_4 structural unit one expects a sharp resonance signal due to the low field gradient at the boron. This is, indeed, generally observed. In contrast, the ^{11}B NMR spectrum of the above product exhibited a broad resonance line centered near 0 ppm with several maxima but which could not be resolved. This observation suggests that the product is a mixture of compounds with similar ^{11}B chemical shifts, as is expected since there are at least 17 isomeric species possible (disregarding possible cis-trans conformations). Hence, one must assume intermediate opening of the central B_2N_4 ring during the reaction, presumably by thermal dissociation of the pyrazabole into monomeric pyrazol-1-ylborane vis symmetrical cleavage. It seems reasonable that this cleavage

is promoted by the presence of free Hpz' which may, initially, lead to the formation of an adduct Hpz'-BH_2pz containing four-coordinate boron. (Similar adducts of monomeric pyrazol-1-ylboranes have been observed in the reaction of pyrazole with dimethylaminoboranes.[7]) Subsequently, the cited adduct may lose hydrogen to yield a monomeric pyrazol-1-ylborane, pz'BHpz, containing trigonal boron. The latter then may undergo renewed adduct formation and subsequent dehydrogenation although ligand scrambling may also be possible. Ultimately, $Bpz_{3-n}pz'_n$ species recombine (=dimerize) in random fashion to form the observed mixture of B-pyrazolylpyrazaboles. This interpretation is supported by the fact that even on reaction of pyrazabole with Hpz' in only 1:2 molar ratio again all possible pyrazabole species $B_2pz_{6-n}pz'_n$ are observed in the mass spectrum of the reaction product. When $H_2B(\mu\text{-pz})_2BH_2$ is reacted with a large excess of 3,5-dimethylpyrazole, the process can be directed to yield $pz'_2B(\mu\text{-pz}')_2Bpz'_2$ as the major product, since pyrazole can be slowly sublimed out of the reaction mixture.

It is noteworthy that these observations illustrate the existence of a pyrazabole in which a boron atom is bonded to four presumably bulky 3,5-dimethylpyrazolyl groups. Such species have so far been elusive and attention was directed to their preparation and characterization.

Preparation and Characterization of 1,3,5,7-Tetramethyl-bis(3',5'-dimethylpyrazol-1'-yl)pyrazabole and 1,3,5,7-Tetramethyl-4,4,8,8-tetrakis(3',5'-dimethylpyrazol-1'-yl)pyrazabole. The X-ray crystal structure of Hpz'B(μ-pz')$_2$BHpz' (pz' = 3,5-dimethylpyrazolyl) has previously been reported,[15] but no details on the preparation or properties of the compound were given. In the present work, the material was prepared by reacting $H_2B(\mu\text{-pz}')_2BH_2$ with Hpz' in 1:2 molar ratio. As expected, the compound is high melting but is readily soluble in many common organic solvents. The NMR spectra of Hpz'B(μ-pz')$_2$BHpz' were tentatively assigned on the basis of intensity considerations and coupling constants in conjunction with the corresponding data for $H_2B(\mu\text{-pz}')_2BH_2$ and $(C_2H_5)_2B(\mu\text{-pz}')_2BH_2$. The ^{13}C chemical shift of the N-bonded carbon atoms 1, 3, 5 and 7 of the bridging pyrazolyl groups in $H_2B(\mu\text{-pz}')_2BH_2$ is 143.8 ppm. Based on line intensity, $\delta(^{13}C)$ of these same atoms in Hpz'B(μ-pz')$_2$BHpz' is assigned at 147.8 ppm. Also based on the line intensity, the signals of the CH_3 groups bonded to the cited carbon atoms are assigned at $\delta(^{13}C)$ = 12.2 ppm (J = 130 Hz), which is in good agreement with the datum $\delta(^{13}C)$ = 12.0 ppm (J = 129 Hz) for these same signals in $H_2B(\mu\text{-pz}')_2BH_2$. The $\delta(^1H)/\delta(^{13}C)$ values (in ppm) of the CH groups in 2 and 6 position migrate from 5.85/105.8 (J = 175 Hz) to 5.95/108.4 (J = 175 Hz) to 5.97/109.1 (J = 177 Hz) within the series $H_2B(\mu\text{-pz}')_2BH_2$ - $(C_2H_5)_2B(\mu\text{-pz}')_2BH_2$ - Hpz'B(μ-pz')$_2$BHpz'. In studies on $pz_2B(\mu\text{-pz})_2Bpz_2$ and

$HpzB(\mu\text{-}pz)_2BHpz$, the carbon signal for the atom bonded to the two-coordinate nitrogen of the terminal pyrazolyl groups (3' in 2, above) was found to be the one with the largest chemical shift value.[9] Hence, the corresponding carbon atom in $Hpz'B(\mu\text{-}pz')_2BHpz'$ is assigned to $\delta(^{13}C) = 148.7$ ppm. No effort was made to assign the methyl groups of the terminal pyrazolyl moieties.

The compound $pz'_2B(\mu\text{-}pz')_2Bpz'_2$ was most readily obtained when tris(dimethylamino)borane was reacted with excess Hpz'. It is likely that this latter reaction proceeds via several intermediates as was illustrated for the reaction of the cited borane with pyrazole.[7] However, no effort was made to isolate and identify any of the intermediates. The ready formation of $pz'_2B(\mu\text{-}pz')_2Bpz'_2$ in good yield confirms that four bulky pz' substituents can, indeed, be bonded to the same central boron atom. It is of interest to note that, due to the work-up procedure, the compound is initially obtained as its monohydrate. This monohydrate is thermally extremely stable. The water molecule can only be removed by prolonged heating of the species under vacuum at temperatures near 160°C. This observation in conjunction with the compound being a monohydrate rather than a dihydrate or tetrahydrate suggests some unusual coordination of the water molecule. Unfortunately, the low quality of the available crystals did not yet permit a study of the crystal and molecular structure by X-ray diffraction.

The ^1H NMR spectrum of the monohydrate clearly shows the presence of three different types of pyrazolyl groups by exhibiting three sharp signals for the protons in the 4 position of the various rings with $\delta(^1H)$ = 5.94, 5.69 and 5.32 ppm, respectively. The observation of six different methyl resonances with sharp signals at $\delta(^1H)$ = 2.15, 2.02, 1.81, 1.45 and 1.17 ppm illustrates that even the methyl groups of the bridging pyrazolyl moieties are not equivalent. In addition, the water signal is evident with $\delta(^1H)$ = 4.13 ppm. When the temperature is increased to 57°C, the methyl signals 2.15/2.02 and 1.45/1.42 ppm collapse to singlets each, of which the latter is very sharp whereas the remaining signals except for the one with $\delta(^1H)$ = 5.94 ppm broaden considerably. Decreasing the temperature to -40°C results in a sharpening of the individual signals. Interestingly, the line shape of the water signal is essentially unaffected by the temperature changes but migrates from 3.64 ppm (at 57°C) to 4.86 ppm (at -50°C). Based on the above observations the signals at $\delta(^1H)$ = 5.94 and 1.45/1.42 ppm, respectively, are assigned to the bridging pyrazolyl groups.

In the ^1H NMR spectrum of the anhydrous material, only the signals with δ = 5.88 and 1.28 ppm are sharp; they are assigned to the bridging pyrazolyl groups. All others are extremely broad, particularly the one at 1.6 ppm with $h_{\frac{1}{2}}$ = ca. 30 Hz. Similarly, the $\delta(^{13}C)$ signals in the 140-150 ppm region are unusually broad. Based on intensity considerations, the signal $\delta(^{13}C)$ = 111.1 ppm must be assigned to the bridging

pyrazolyl groups. Also, the signal $\delta(^{13}C)$ = 13.4 ppm is sharp but those at 12.4/11.8 and 10.7/9.8 ppm, respectively, are broad and seem to be merging.

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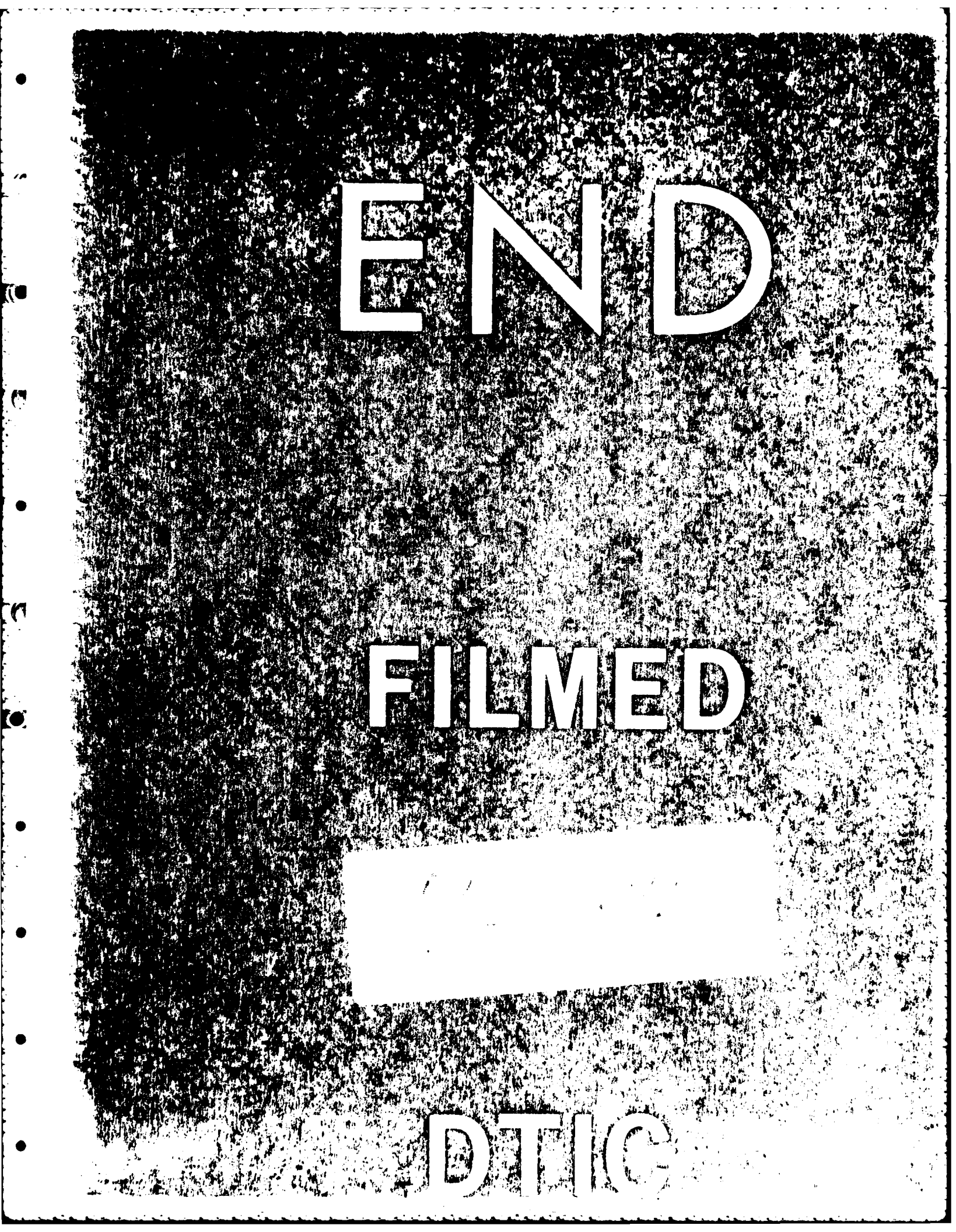
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