Donor-Acceptor Complexes between Organoamines and Phosphorus Tribromide

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Lewis acid-base adducts between NMe₃, tmeda (N,N',N',N'-tetramethylethlenediamine), and 1,4-dimethylpiperazine as donors and PBr₃ as acceptor have been prepared and structurally characterized. NMe₃ and tmeda form 1:1 adducts (Me₃N)PBr₃ (1) and (tmeda)PBr₃ (2), respectively, while 1,4-dimethylpiperazine adds 2 molecules of PBr₃ leading to [(1,4-dimethylpiperazine)(PBr₃)₂] (3). Adduct 2 is found in two modifications 2a and 2b with different crystal and molecular structures. (Crystal data of 1: monoclinic P₂₁/n, a = 5.983(3), b = 10.821(2), c = 13.877(5) Å, β = 99.70(2)°, Z = 4. 2a: monoclinic P₂₁/c, a = 7.891(1), b = 12.826(1), c = 12.218(2) Å, β = 102.162(6)°, Z = 4. 2b: monoclinic P₂₁/n, a = 11.687(2), b = 8.375(1), c = 12.668(1) Å, β = 102.74(1)°, Z = 4. 3: monoclinic P₂₁/c, a = 6.383(3), b = 16.36(3), c = 8.407(3) Å, β = 101.49(2)°, Z = 2). The molecular structures of 1 and 2 indicate a partially ionic character with a strongly bonded amine and one (1) or two (2) weakly bonded bromine atoms. In 2 the donor tmeda is bonded through both nitrogen atoms to one phosphorus atom. In 3 the 1,4-dimethylpiperazine ring is in chair conformation, the methyl and PBr₃ substituents being in equatorial and axial positions, respectively. Due to axial-axial repulsion the N-P donor-acceptor bonds are long while the P-Br bonds are rather uniform in length.