Complex Formation Involving 4,4′-Bis(dimethylamino)benzophenone (Michler's Ketone). The Crystal Structures of the 1:1 Hydrogen-Bonded Complexes with Trifluoromethanesulfonic Acid and Pentafluorophenol

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The 1:1 complexes between 4,4′-bis(dimethylamino)benzophenone, and trifluoromethanesulfonic acid (**1**) and pentafluorophenol (**2**) have been prepared by mixing the components in CH_2Cl_2 and evaporating to dryness. The crystal structures of the two complexes have been determined at −135 °C from X-ray diffraction data: $(p\text{-}Me_2NPh)_2CO \cdot HO_3SCF_3$ (**1**): a = 6.190(2), b = 8.837(3), c = 18.989(5) Å, α = 76.59(2), β = 85.48(2), γ = 70.63(2)°, Z = 2, space group $P\bar{1}$, final R = 0.042 for 4047 observed reflections. $(p\text{-}Me_2NPh)_2CO \cdot HOC_6F_5$ (**2**): a = 6.785(2), b = 20.250(7), c = 15.484(5) Å, β = 101.55(2)°, Z = 4, space group $P2_1/n$, final R = 0.068 for 3493 observed reflections. In adduct **1**, one of the two nitrogen atoms has been protonated by the acid, and this hydrogen is strongly hydrogen-bonded to its parent trifluoromethanesulfonate anion. There is no proton transfer in adduct **2**, where the pentafluorophenol hydroxy group forms a relatively strong hydrogen bond to the ketonic carbonyl group. The different modes of interaction between proton donors and acceptors in the two complexes are discussed.

During our studies of hydrogen bonding in organic complexes, we found proton transfer during adduct formation between trifluoromethanesulfonic acid and *N,N,N′,N′*-tetramethylglutaramide;[1] the proton transfer was from the acid to the carbonyl groups and not to the amino groups. We then decided to study complex formation between 4,4′-bis(dimethylamino)benzophenone and both the strong acid trifluoromethanesulfonic acid and the weaker acid pentafluorophenol. Also here there should be two different types of sites available for accepting a proton or, alternatively, a hydrogen bond from an acid.

Experimental

Syntheses. $(p\text{-}Me_2NPh)_2CO \cdot HO_3SCF_3$ (**1**): Trifluoromethanesulfonic acid (0.4186 g, 0.0028 mol) was dissolved in 10 ml of CH_2Cl_2 and the solution was added dropwise to a stirred solution of the ketone (0.7485 g, 0.0028 mol) in 10 ml of CH_2Cl_2. During the reaction the temperature was kept between 0 and 5 °C. Upon addition of the first drop the solution turned orange–yellow. After all the acid had been added, the orange–yellow solution was evaporated to dryness under a low pressure of nitrogen. The residue was recrystallized from CH_2Cl_2; yield 1.04 g (89 %) of faintly yellow crystals, m.p. 130–131 °C.

$(p\text{-}Me_2NPh)_2CO \cdot HOC_6F_5$ (**2**): Pentafluorophenol (0.2281 g, 0.0012 mol) was dissolved in 10 ml of CH_2Cl_2. The resulting solution was added dropwise to a solution of the ketone (0.3338 g, 0.0012 mol) in 10 ml of CH_2Cl_2 kept at temperatures between 0 and 8 °C. The yellow solution was evaporated under vacuum. The residue was recrystallized from CH_2Cl_2 to give yellow crystals; yield 0.47 g (86 %), m.p. 114–115 °C (decomp.).

Table 1. Positional parameters and their estimated standard deviations.

Atom	*x*	*y*	*z*	*B*/Å^2
1				
S	1.1674(6)	0.21729(4)	0.13270(2)	2.333(7)
O1	1.1947(2)	0.3620(1)	0.08596(6)	3.42(3)
O2	1.3703(2)	0.0931(1)	0.16461(7)	3.34(3)
O3	0.9767(2)	0.2527(1)	0.18240(6)	3.04(2)
C	1.0719(3)	0.1206(2)	0.0718(1)	3.73(4)
F1	1.0206(2)	−0.0109(1)	0.10716(7)	5.32(3)
F2	0.8881(2)	0.2232(1)	0.03517(7)	6.11(3)
F3	1.2338(3)	0.0718(2)	0.02403(6)	6.28(4)
O	−0.2410(2)	0.6622(1)	0.33804(6)	2.81(2)
N1	−0.0349(2)	0.0587(1)	0.60853(7)	2.31(2)
N2	0.6614(2)	0.5653(1)	0.14898(6)	2.19(2)
C1	−0.2461(3)	0.0329(2)	0.63875(8)	2.48(3)
C2	0.1805(3)	−0.0517(2)	0.64144(9)	2.81(3)
C3	−0.0388(2)	0.1731(2)	0.54629(7)	2.07(3)
C4	−0.2471(2)	0.2763(2)	0.51199(8)	2.34(3)
C5	−0.2490(2)	0.3941(2)	0.45054(8)	2.25(3)
C6	−0.0469(2)	0.4151(2)	0.41856(7)	2.07(3)
C7	0.1596(2)	0.3129(2)	0.45200(8)	2.19(3)
C8	0.1655(2)	0.1948(2)	0.51422(8)	2.20(3)
C9	−0.0632(2)	0.5482(2)	0.35434(8)	2.15(3)
C10	0.1413(2)	0.5459(2)	0.30590(7)	2.04(3)
C11	0.1737(2)	0.6952(2)	0.27461(8)	2.31(3)
C12	0.3482(2)	0.7038(2)	0.22515(8)	2.30(3)
C13	0.4839(2)	0.5612(2)	0.20537(7)	1.99(3)
C14	0.4534(3)	0.4108(2)	0.23413(8)	2.25(3)
C15	0.2829(2)	0.4037(2)	0.28550(8)	2.24(3)
C16	0.5677(3)	0.5850(2)	0.07586(8)	2.96(3)
C17	0.7754(3)	0.6907(2)	0.14818(9)	2.80(3)
H	0.768(3)	0.473(2)	0.1557(8)	2.3(3)*
2				
O′	0.4692(3)	0.29686(9)	0.5831(1)	3.67(5)
F2	0.4456(3)	0.28329(8)	0.4100(1)	3.78(4)
F3	0.3881(3)	0.16454(9)	0.3296(1)	3.92(4)
F4	0.3553(3)	0.05395(8)	0.4251(1)	4.25(4)
F5	0.3845(3)	0.06394(8)	0.6026(1)	4.31(4)
F6	0.4437(3)	0.18186(8)	0.6833(1)	3.93(4)
C1′	0.4417(4)	0.2359(1)	0.5487(2)	2.82(6)
C2′	0.4272(4)	0.2290(1)	0.4579(2)	2.86(6)
C3′	0.3988(4)	0.1690(1)	0.4171(2)	3.00(6)
C4′	0.3822(4)	0.1132(1)	0.4643(2)	3.12(6)
C5′	0.3973(4)	0.1182(1)	0.5547(2)	3.12(6)
C6′	0.4271(4)	0.1786(1)	0.5948(2)	2.96(6)
O	0.4500(3)	0.3163(1)	0.7461(1)	3.56(4)
N1	0.0765(4)	0.5803(1)	0.5617(2)	4.01(6)
N2	0.4297(4)	0.3442(1)	1.1493(2)	3.53(6)
C1	0.1697(6)	0.5996(2)	0.4890(2)	4.54(8)
C2	−0.0950(5)	0.6167(2)	0.5769(2)	4.31(8)
C3	0.1552(5)	0.5300(1)	0.6173(2)	3.06(6)
C4	0.3275(5)	0.4953(1)	0.6066(2)	3.24(6)

contd

Table 1. (contd)

Atom	*x*	*y*	*z*	*B*/Å^2
C5	0.3975(4)	0.4425(1)	0.6593(2)	3.06(6)
C6	0.3049(4)	0.4227(1)	0.7281(2)	2.71(6)
C7	0.1377(4)	0.4583(1)	0.7408(2)	2.82(6)
C8	0.0645(4)	0.5103(1)	0.6871(2)	3.04(6)
C9	0.3824(4)	0.3638(1)	0.7811(2)	2.77(6)
C10	0.3806(4)	0.3609(1)	0.8757(2)	2.52(5)
C11	0.4052(4)	0.2996(1)	0.9177(2)	2.80(6)
C12	0.4202(4)	0.2940(1)	1.0070(2)	2.90(6)
C13	0.4116(4)	0.3498(1)	1.0600(2)	2.78(6)
C14	0.3861(4)	0.4115(1)	1.0177(2)	2.76(6)
C15	0.3704(4)	0.4164(1)	0.9279(2)	2.60(5)
C16	0.4603(6)	0.2803(2)	1.1920(2)	4.46(8)
C17	0.4271(6)	0.4025(2)	1.2034(2)	4.42(8)
H	0.463(6)	0.297(2)	0.639(3)	8(1)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given with an isotropic equivalent thermal parameter.

X-ray data. Intensities were recorded on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Mo*K*α radiation was used for the determination of unit cell dimensions and recording of intensity data. During measurements, the crystal site was kept at −135 °C. The crystal dimensions were 0.48×0.64×0.80 mm for **1** and 0.26×0.29×0.48 mm for **2**. Cell parameters were calculated from a least-squares fit to the diffractometer settings of 25 general reflections for both compounds. **1**: Triclinic, a = 6.190(2), b = 8.837(3), c = 18.989(5) Å, α = 76.59(2), β = 85.48(2), γ = 70.63(2)°, Z = 2, d_x = 1.458 g cm^{-3}, μ(Mo*K*α) = 2.153 cm^{-1}, space group $P\bar{1}$. **2**: Monoclinic, a = 6.785(2), b = 20.250(7), c = 15.484(5) Å, β = 101.55(2)°, Z = 4, d_x = 1.442 g cm^{-3}, μ(Mo*K*α = 1.163 cm^{-1}, space group $P2_1/n$.

For both **1** and **2** the intensities were recorded using the ω-scan technique with a constant scan rate of 7° min^{-1} and a minimum scan width of 1.80°, including background scans of 0.30° at both ends of each scan. Crystal orientation was checked at intervals of 200 recordings and the intensities of three standard reflections were measured every 2 h; no significant variations were observed. For **1**, 4575 unique reflections with $2\theta \leq 56°$ were measured. Of these, 4047 were observed and 528 had $I \leq 2\sigma(I)$ and were regarded as unobserved. For **2**, the corresponding numbers with $2\theta \leq 56$ are 5014, 3493 and 1521. Both sets of intensities were corrected for Lorentz and polarization effects, but not for absorption. The computer programs used in these investigations were supplied by Enraf-Nonius (SPD–plus 1983 and CAD4–OS11).

Structure determination

The structure of (p-Me$_2$NPh)$_2$CO · HO$_3$SCF$_3$ (**1**) was solved using conventional heavy atom methods, while the structure of (p-Me$_2$NPh)$_2$ CO · HOC$_6$F$_5$ (**2**) was solved using direct methods (MULTAN). Both structures were refined as described in Ref. 2 with $w = [\sigma(F)^2 + (0.03F)^2 + 5.0]^{-1}$. All hydrogen atoms were included in the refinements with isotropic temperature parameters. The other atoms were refined with anisotropic temperature parameters. Final refinement parameters are: **1**: R = 0.0422, R_w = 0.0543, S = 2.371; **2**: R = 0.0680, R_w = 0.0751, S = 2.615. The final difference maps showed maxima of 0.44 and 0.35 eÅ^{-3} for **1** and **2**, respectively. Atomic parameters are listed in Table 1. Calculated and observed structure factors, atomic coordinates and temperature factors for hydrogen atoms not participating in hydrogen bonding, and anisotropic temperature factors are

Table 2. Bond lengths(Å) and angles (°) in the two adducts **1** and **2**, with e.s.d.'s in parentheses.

Bond lengths

4,4'-Bis(dimethylamino)benzophenone

	1	**2**
O–C9	1.224(1)	1.236(2)
N1–C1	1.452(1)	1.451(3)
N1–C2	1.451(1)	1.436(3)
N1–C3	1.361(1)	1.371(2)
C3–C4	1.413(1)	1.402(3)
C4–C5	1.369(1)	1.370(3)
C5–C6	1.397(1)	1.400(2)
C6–C7	1.396(1)	1.392(2)
C7–C8	1.377(1)	1.372(3)
C8–C3	1.412(1)	1.405(3)
C6–C9	1.468(1)	1.482(2)
N2–H	0.852(12)	
N2–C16	1.489(1)	1.450(3)
N2–C17	1.495(1)	1.449(3)
N2–C13	1.476(1)	1.368(2)
C12–C13	1.380(1)	1.405(2)
C11–C12	1.384(1)	1.372(3)
C10–C11	1.388(1)	1.396(2)
C10–C15	1.392(1)	1.393(2)
C14–C15	1.387(1)	1.378(2)
C13–C14	1.383(1)	1.405(2)
C9–C10	1.502(1)	1.469(2)

Other bonds

	1
S–O1	1.431(1)
S–O2	1.431(1)
2–O3	1.448(1)
S–C	1.821(1)
C–F1	1.323(1)
C–F2	1.323(1)
C–F3	1.329(2)
O3···N2	2.766(1)
O3···H	1.921(12)
	2
O–C1'	1.343(2)
O'–H	0.88(3)
C1'–C2'	1.397(2)
C2'–C3'	1.365(2)
C3'–C4'	1.363(3)
C4'–C5'	1.387(3)
C5'–C6'	1.367(3)
C6'–C1'	1.376(2)
C3'–F3	1.344(2)
C4'–F4	1.341(2)
C5'–F5	1.339(2)
C6'–F6	1.355(2)
O'···O	2.583(2)
O···H	1.72(3)

Angles

4,4'-Bis(dimethylamino)benzophenone

	1	**2**		**1**	**2**
C1–N1–C2	118.54(9)	118.8(2)	C16–N2–C17	110.98(9)	118.7(2)
C1–N1–C3	120.25(8)	120.8(2)	C16–N2–C13	110.83(8)	120.6(2)
C2–N1–C3	120.86(9)	120.4(2)	C17–N2–C13	114.33(8)	120.6(2)
N1–C3–C4	121.40(9)	121.9(2)	H–N2–C16	104.3(8)	
N1–C3–C8	121.13(9)	121.2(2)	H–N2–C17	105.9(8)	
C3–C4–C5	120.82(9)	121.2(2)	H–N2–C13	109.9(9)	
C4–C5–C6	121.76(9)	121.5(2)	N2–C13–C12	120.59(9)	121.2(2)
C5–C6–C7	117.69(9)	117.5(2)	N2–C13–C14	117.11(9)	121.4(2)
C6–C7–C8	121.55(9)	121.2(2)	C11–C12–C13	118.38(9)	121.3(2)
C7–C8–C3	120.71(9)	121.6(2)	C10–C11–C12	121.00(9)	121.4(2)
C8–C3–C4	117.46(9)	116.9(2)	C11–C10–C15	119.25(9)	117.5(2)
C5–C6–C9	118.58(9)	119.2(2)	C10–C15–C14	120.53(9)	121.7(2)
C7–C6–C9	123.65(9)	123.2(2)	C13–C14–C15	118.56(9)	120.7(2)
C6–C9–O	121.91(9)	120.4(2)	C12–C13–C14	122.22(9)	117.3(2)
C6–C9–C10	120.08(8)	120.7(2)	C9–C10–C11	117.85(9)	123.9(2)
C10–C9–O	118.00(9)	118.9(2)	C9–C10–C15	122.54(9)	118.4(2)

contd

Table 2 (contd)

Other angles

1

O1–S–O2	117.04(5)
O1–S–O3	113.02(5)
O2–S–O3	114.33(5)
O1–S–C	103.49(5)
O2–S–C	103.63(5)
O3–S–C	103.06(6)
S–C–F1	111.92(9)
S–C–F2	111.34(9)
S–C–F3	111·1(1)
F1–C–F2	107.6(1)
F1–C–F3	107.0(1)
F2–C–F3	107.6(1)
O3···H–N2	171(1)
S–O3···H	113.3(5)

2

C1′–C2′–C3′	122.0(2)
C2′–C3′–C4′	120.6(2)
C3′–C4′–C5′	118.9(2)
C4′–C5′–C6′	119.9(2)
C5′–C6′–C1′	122.5(2)
C6′–C1′–C2′	116.1(2)
C1′–C2′–F2	118.6(2)
C3′–C2′–F2	119.5(2)
C2′–C3′–F3	120.0(2)
C4′–C3′–F3	119.4(2)
C3′–C4′–F4	121.2(2)
C5′–C4′–F4	119.9(2)
C4′–C5′–F5	119.9(2)
C6′–C5′–F5	120.2(2)
C1′–C6′–F6	118.9(2)
C5′–C6′–F6	118.6(2)
C2′–C1′–O′	117.8(2)
C6′–C1′–O′	126.0(2)
C1′–O′–H	111(2)
O′–H···O	166(3)
C9–O···H	134(1)

available from one of the authors (K.M.-M.) upon request.

Results and discussion

Atomic parameters are listed in Table 1, interatomic distances and angles in Table 2, and molecular planes and interplanar angles in Table 3. Fig. 1 shows the structure of **1** and Fig. 2 shows the structure of **2**. In **1**, there has been a proton transfer from the strong acid CF_3SO_3H to the nitrogen atom of one of the two equivalent dimethylamino groups of the ketone. The same proton is then involved in a N-H···O bond to the resulting $CF_3SO_3^-$ ion. There is no proton transfer in **2**; instead, a hydrogen bond is formed between the OH group of C_6F_5OH and the ketonic oxygen.

The hydrogen bonds. **1** has an N–H···O hydrogen bond between the protonated amino group and the trifluoromethanesulfonate anion, with N2–H = 0.852(12), H···O3 = 1.921(12), N2···O3 = 2.766 Å and $\angle$N2–H··O3 = 171(1)°. The N···O separation is less than 2.80 Å and thus corresponds to a strong hydrogen bond according to Emsley *et al.*[3] It may be compared to the corresponding distance of 2.75 Å in the 2:1 adduct between 6-aza-2-thiothymine and triethylamine.[4] It is significantly longer than the average N···O distance of 2.661 Å found for N–H···O bonding in 2-acetylcyclopentadienone 1-phenylhydrazone.[5] In **2**, there is a O–H···O hydrogen bond connecting the pentafluorophenol and the oxygen atom of the ketone, with O′–H = 0.88(3), H···O = 1.72(3), O′···O = 2.583(2) Å and $\angle$O′–H···O = 166(3)°. This is a relatively strong hydrogen bond. The O··O distance is significantly shorter than the corresponding distances of 2.645(2) and 2.647(1) Å found in the hydrogen-bonded complexes of pentafluorophenol/triphenylphosphine oxide (1:1) and pentafluorophenol/dioxane (2:1), respectively.[6,7] An S–O3···H angle of 113.3(5)° in **1** indicates that the direction of the H···O3 bond is towards an sp^3 lone-pair of electrons on O3. For **2**, the corresponding C=O···H angle is 134(1)°. This is in the general direction of an sp^2 lone-pair on oxygen, but the deviation from 120° is considerable. Why do the two acids, trifluoromethanesulfonic acid and pentafluorophenol, behave so differently towards the same base, 4,4′-bis(dimethylamino)-benzophenone? It is well known that increasing

Table 3. Molecular planes and interplanar angles (°).

Plane No.	Atoms included	Δ^a/Å	Interplanar angles	
(p-$Me_2NPh)_2CO \cdot HO_3SCF_3$ complex (**1**)				
1	C6, C9, C10, 0	−0.004(C9)	1–2	18.3
2	C3, C4, C5, C6, C7, C8	0.005(C4)	1–3	38.9
3	C10, C11, C12, C13, C14, C15	0.014(C15)	2–3	52.7
4	N1, C1, C2, C3	−0.036(N1)	2–4	0.9
5	C13, C16, C17	0	3–5	66.7
(p-$Me_2NPh)_2CO \cdot HOC_6F_5$ complex (**2**)				
1	C6, C9, C10, 0	0.000	1–2	36.4
2	C3, C4, C5, C6, C7, C8	−0.016(C4)	1–3	19.0
3	C10, C11, C12, C13, C14, C15	0.004(C15)	2–3	52.1
4	N1, C1, C2, C3	0.014(N1)	2–4	2.2
5	N2, C13, C16, C17	0.014(N2)	3–5	1.7
6	C_6F_5O'	−0.022(F6)	3–6	13.2

Distances of atoms from planes

1	1:	C5, 0.36; C7, −0.40; C11, −0.70; C15, 0.78
	2:	N1, −0.029
	3:	N2, 0.071
	5:	N2, −0.45; H, −1.34
2	1:	C5, −0.70; C7, 0.71; C11, 0.34; C15, −0.42; H, 0.13
	2:	N1, −0.07
	3:	N2, −0.021
	6:	H, 0.11; O, 0.34

[a] Max. deviation of constituent atoms from plane.

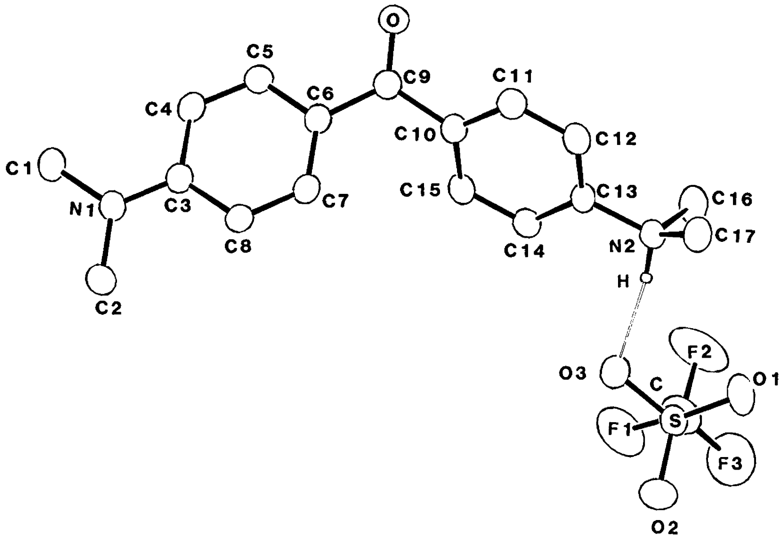


Fig. 1. The complex (p-$Me_2NPh)_2CO \cdot HO_3SCF_3$ (**1**) as seen along the normal to the plane defined by C6, C9 and C10.

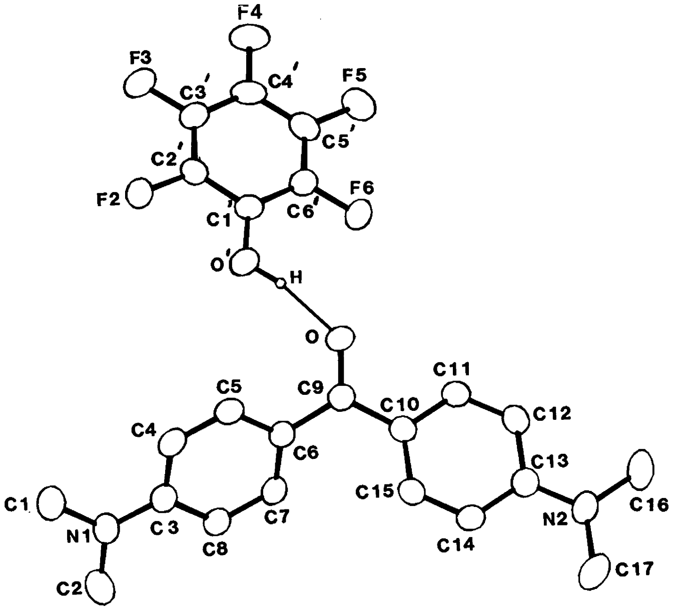
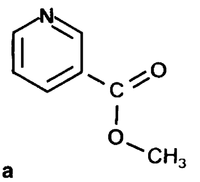


Fig. 2. The complex (p-$Me_2NPh)_2CO \cdot HOC_6F_5$ (**2**) as seen along the normal to the plane defined by C6, C9 and C10.

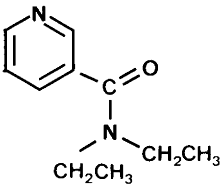
acidity of a hydrogen bond donor increases the probability of proton transfer interaction with a hydrogen bond acceptor as compared to normal hydrogen bonding.[8,9] Thus, it is not surprising that there is proton transfer in **1** but a normal hydrogen bond in **2**. Trifluoromethanesulfonic acid is also known to participate in proton transfer in another hydrogen bonded complex.[1]

In the complexes **1** and **2**, the preferred site of protonation is one of the dimethylamino nitrogens, while the preferred site of hydrogen bonding is the carbonyl oxygen. Molecular orbital calculations on protonation of DNA bases indicated that nitrogen was preferred as the protonation site rather than carbonyl oxygen.[10] These nitrogen atoms were also found to be the main contributors to the highest occupied n-orbitals.[10] The above may be visualized in the following manner: Protonation occurs with strong acids. The dissociated proton actively seeks an acceptor site with an available (loosely bonded) lone-pair of electrons. Such electron pairs are generally localized in the highest occupied n-orbitals, which themselves are localized mostly on the N atoms. With weak acids like phenols the degree of dissociation is very low. The partially positively charged hydrogen of the hydroxy group seeks out the acceptor site with the highest partial negative charge (carbonyl oxygen in the present case) for the formation of a normal hydrogen bond. The fact that protonation takes place at carbonyl in *N,N,N',N'*-tetramethylglutaramide and other amides is due to the conjugation between the amino group and carbonyl which makes carbonyl oxygen the most basic site.[1,11] In the present case, such conjugation effects are weakened by the phenyl groups.

IR studies of protonation and hydrogen bonding in methyl nicotinate (**a**) and the corresponding diethylamide (**b**) also show that nitrogen (pyridine N) is the preferred protonation site and that carbonyl oxygen is the preferred hydrogen bonding site.[12,13] Another study of complex formation between phenols and bases with nitrogen and carbonyl as acceptor sites has given similar results.[14]

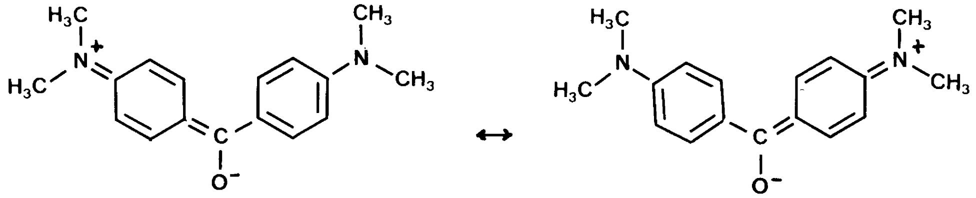


a



b

The structure of 4,4'-bis(dimethylamino)benzophenone. In **2**, the ketone has the expected struc-



ture with the dimethylamino groups (excluding hydrogens) approximately coplanar with the benzene rings. The interplanar angle between the two benzene rings is 52.1°, as compared to 52.7 in **1** and 56° in benzophenone itself.[15] This deviation from coplanarity is mostly due to repulsion between hydrogens bonded to C7 and C10. The bond lengths indicate a small contribution from the above resonance forms in **2**. This implies weak conjugation between N and O. Thus, the average N$\overset{...}{-}$C bond length is 1.370 Å, as compared to 1.47 Å, the sum of the respective covalent radii.[16] The average central C$\overset{...}{-}$C bond length in the benzene rings is 1.373 Å, as compared to 1.400 Å for the average of the four other bond lengths in each ring. The C–C(O) bonds have very little double bond character since their average length is 1.476 Å as compared to a C(sp^2)–C(sp^2) bond length of 1.48 Å.[16,17] However, they are significantly shorter than the corresponding bond length in **1** [1.502(1)Å], involving the benzene ring with the protonated dimethylamino group. The C=O double bond length in **2** is 1.236(2) Å, as compared to 1.224(1) Å in **1** in which there is no hydrogen bond to the oxygen atom, and to ca. 1.23 Å which is normal for ketones.[5]

Relative to hydrogen bonding in **2**, protonation in **1** has a much greater structural effect. There is no conjugation through the benzene ring bearing the protonated substituent, and thus only one of the resonance forms shown above contributes. This is best evidenced by the observation of a normal N2–C13 single bond of 1.476(1) Å, ca. 0.1 Å greater than the N1–C3 bond length of 1.361(1) Å and the corresponding bond lengths in **2**. Protonation also has made N2 sp^3 hybridized in **1**.

The angles are normal in both complexes, indicating sp^2 hybridization on the nitrogens (except N2 in **2**) and the carbon atoms (except methyl carbons). Hydrogen bonding leads to the observed asymmetry in the C–C–N2 and C–C–O angles in **1** and **2**.

The approximately parallel planes of the pentafluorophenol and the C10–C15 phenyl groups

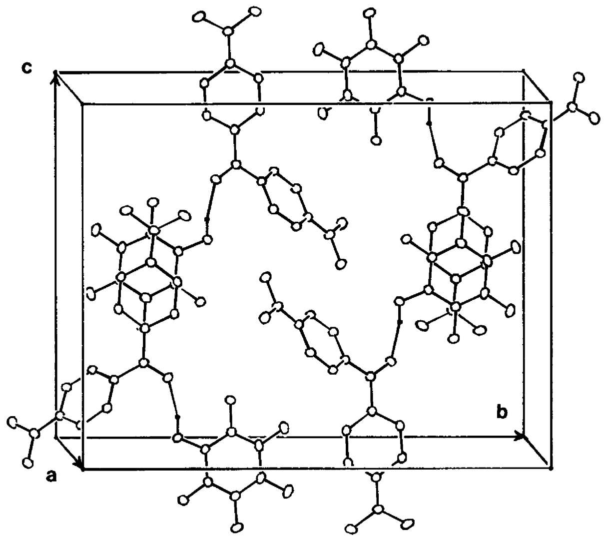


Fig. 3. Molecular packing in **1**.

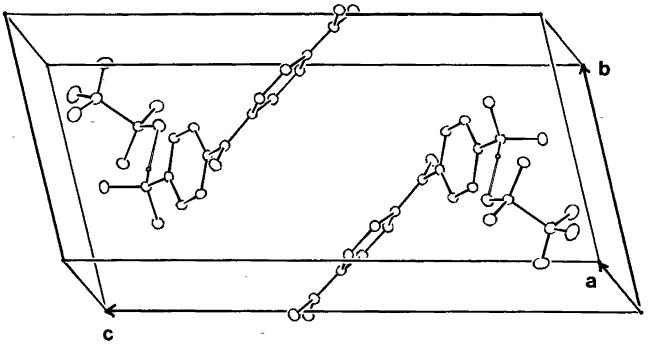


Fig. 4. Molecular packing in **2**.

are only 3.4 Å apart in neighbour adducts. Since these groups partially "overlap" (Fig. 4), there may be a weak charge transfer interaction between them.

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