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Structure of 4-*tert*-Butyl-2,6-dimethylacetophenone and Comparison with its $FeCl_3$ Complex

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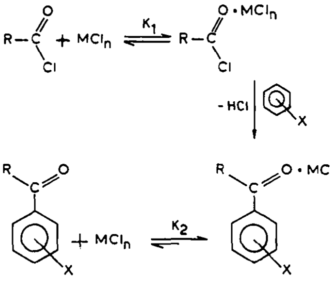
Abstract. $C_{14}H_{20}O$, $M_r = 204{\cdot}31$, triclinic, $P\bar{1}$, $a = 6{\cdot}523\,(1)$, $b = 11{\cdot}106\,(2)$, $c = 10{\cdot}140\,(2)$ Å, $\alpha = 99{\cdot}17\,(2)$, $\beta = 94{\cdot}95\,(2)$, $\gamma = 116{\cdot}03\,(2)°$, $V = 641{\cdot}5$ Å^3, $Z = 2$, $D_x = 1{\cdot}058$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}069$ mm^{-1}, $F(000) = 224$, $T = 290$ K, $R = 0{\cdot}067$ for 1539 unique observed reflections. The dihedral angle between the acetyl plane and the aromatic-ring plane is 80·6 (5)°; the C=O bond length is 1·202 (5) Å. These values differ significantly from the corresponding values [43·7 (5)° and 1·243 (3) Å] in the ligand.$FeCl_3$ complex. It is concluded that the differences are caused by an increased tendency to restore the conjugation between the acetyl group and the aromatic ring upon $FeCl_3$ coordination. The *t*-Bu group adopts a position deviating ~ 12° from the, energetically most favourable, position in which a C—C bond of the *t*-Bu group lies in the aromatic-ring plane.

Introduction. Friedel–Crafts acylations generally require a stoichiometric amount of catalyst (MCl_n with M=Fe, Sn, Al, *etc.*) because of poisoning of the Lewis-acid catalyst by relatively strong complexation with the ketone product (K_2) *versus* the acyl chloride reactant (K_1).



Experiments indicate that alkyl-substituted benzenes, delivering *o*-alkylacetophenones upon acylation, favour the formation of free-product ketone. The carbonyl group in these ketones is rotated out of the plane of the benzene ring.

It is believed that the rotation of the acetyl moiety with respect to the aromatic-ring plane, controlling the degree of conjugation with the ring π system, mainly governs the carbonyl–MCl_n complex strength. Recently the structure of 4-*tert*-butyl-2,6-dimethylacetophenone–iron trichloride (Lig.$FeCl_3$) was published (van Koningsveld, Scheele & Jansen, 1986). Conclusions concerning the stability of the $FeCl_3$.carbonyl complex could hardly be drawn because no literature data on O—$FeCl_3$ coordination bond lengths were available. To study the influence of the 'out-of-plane' rotation of the acetyl group on the O—$FeCl_3$ bond strength in more detail, comparison of the structure of Lig.$FeCl_3$ with the structure of the free ligand (Lig) seemed promising. Therefore the X-ray analysis of Lig was started.

Experimental. Rather poor crystal, approximate size 0·4 × 0·3 × 0·2 mm, grown from methanol/water at 273 K. Enclosed in glass capillary to minimize sublimation. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo$K\alpha$, lattice parameters from setting angles for 25 reflections with $10 < \theta < 18°$. 2792 unique reflections (h: 0 → 8, k: −14 → 12, l: −12 → 12) with $\theta_{max} = 28{\cdot}0°$, 1539 with $I > 2{\cdot}85\sigma(I)$ used in refinement process together with 'less-than' reflections [$I \le 2{\cdot}85\sigma(I)$] with $F_c > F_o$ (2340 contributing reflections). $\omega/2\theta$ scan, scan angle = $(0{\cdot}95 + 0{\cdot}35\tan\theta)°$. Max. counting time 120 s or time spent to obtain 2% accuracy. Standard reflections $05\bar{3}$, $20\bar{5}$ and $\bar{2}\bar{3}0$ used for orientation control every 100 reflections and for intensity control every 3600 s of X-ray exposure time; standard intensity variations <1·7% of mean value. Lp correction, absorption ignored. Structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). Full-matrix least-squares refinement of anisotropic non-H atoms; positional H parameters from $\Delta\rho$ map, but included (except for the aromatic H atoms) in idealized positions [sp^3, d(C—H) = 1·00 Å] with isotropic parameter set to 1·1 times that of the parent atom, positional parameters of

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aromatic H refined. $\sum w(\Delta F)^2$ minimized, final $R = 0{\cdot}067$, $wR = 0{\cdot}069$, $w = 1/\sigma^2(F_o)$, $S = 9{\cdot}96$. Ratio of maximum least-squares shift to e.s.d. in final refinement cycle $= 0{\cdot}038$ [U_{33} of C(10)]. Final ΔF synthesis has $\rho < 0{\cdot}22$ e Å^{-3}. Calculations performed on the Delft University Amdahl 470/V7B computer with programs of the *XRAY72* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and scattering factors for C, O and H from Cromer & Mann (1968).

Discussion. Positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1.* The molecular structure and atom-numbering scheme are shown in Fig. 1. Bond lengths, bond angles, and selected torsion angles, involving non-hydrogen atoms only, are listed in Table 2.

Table 1. *Final fractional coordinates and equivalent isotropic temperature factors*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\rm eq}$ (Å^2)
C(1)	0·0826 (5)	0·0068 (3)	0·2468 (3)	0·055 (3)
C(2)	0·2798 (5)	0·1259 (3)	0·3123 (3)	0·056 (3)
C(3)	0·2901 (5)	0·2524 (3)	0·3023 (3)	0·051 (2)
C(4)	0·1120 (5)	0·2618 (3)	0·2273 (3)	0·050 (2)
C(5)	−0·0780 (5)	0·1413 (3)	0·1602 (3)	0·057 (3)
C(6)	−0·0966 (5)	0·0124 (3)	0·1684 (3)	0·055 (3)
C(7)	0·1336 (5)	0·4038 (3)	0·2187 (3)	0·060 (3)
C(8)	0·2096 (9)	0·4953 (4)	0·3580 (4)	0·146 (8)
C(9)	−0·0935 (6)	0·3946 (4)	0·1546 (5)	0·111 (6)
C(10)	0·3106 (7)	0·4665 (4)	0·1307 (5)	0·116 (6)
C(11)	0·0652 (6)	−0·1304 (3)	0·2634 (3)	0·072 (4)
C(12)	−0·0711 (7)	−0·1949 (4)	0·3653 (4)	0·121 (6)
C(13)	0·4817 (6)	0·1237 (3)	0·3958 (3)	0·081 (4)
C(14)	−0·3086 (5)	−0·1146 (3)	0·0903 (4)	0·073 (4)
O(1)	0·1624 (5)	−0·1834 (2)	0·1996 (3)	0·125 (5)

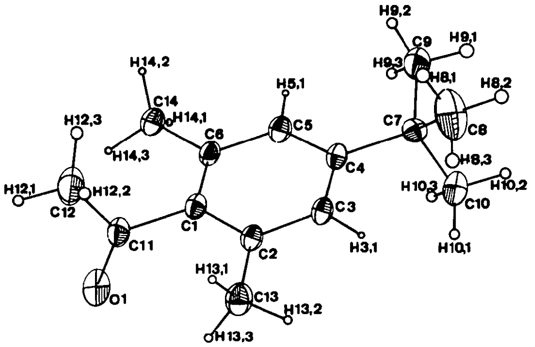

Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(1)–C(2)	1·388 (3)	C(5)–C(6)	1·400 (5)
C(1)–C(6)	1·386 (5)	C(6)–C(14)	1·507 (3)
C(1)–C(11)	1·515 (5)	C(7)–C(8)	1·501 (5)
C(2)–C(3)	1·398 (5)	C(7)–C(9)	1·519 (6)
C(2)–C(13)	1·515 (5)	C(7)–C(10)	1·511 (5)
C(3)–C(4)	1·384 (4)	C(11)–C(12)	1·485 (6)
C(4)–C(5)	1·378 (3)	C(11)–O(1)	1·202 (5)
C(4)–C(7)	1·538 (4)		
C(2)–C(1)–C(6)	121·0 (3)	C(1)–C(6)–C(14)	122·7 (3)
C(2)–C(1)–C(11)	118·7 (3)	C(5)–C(6)–C(14)	118·8 (3)
C(6)–C(1)–C(11)	120·3 (2)	C(4)–C(7)–C(8)	110·0 (3)
C(1)–C(2)–C(3)	118·5 (3)	C(4)–C(7)–C(9)	112·1 (2)
C(1)–C(2)–C(13)	122·5 (3)	C(4)–C(7)–C(10)	108·8 (3)
C(3)–C(2)–C(13)	119·0 (2)	C(8)–C(7)–C(9)	108·8 (4)
C(2)–C(3)–C(4)	122·0 (2)	C(8)–C(7)–C(10)	109·6 (3)
C(3)–C(4)–C(5)	117·9 (3)	C(9)–C(7)–C(10)	107·4 (3)
C(3)–C(4)–C(7)	119·8 (2)	C(1)–C(11)–C(12)	117·3 (3)
C(5)–C(4)–C(7)	122·3 (3)	C(1)–C(11)–O(1)	121·6 (3)
C(6)–C(5)–C(4)	122·0 (3)	C(12)–C(11)–O(1)	121·1 (4)
C(1)–C(6)–C(5)	118·5 (2)		
C(2)C(1)C(11)O(1)	79·6 (5)	C(3)C(4)C(7)C(10)	71·8 (5)
C(3)C(4)C(7)C(8)	48·3 (5)	C(5)C(4)C(7)C(9)	11·9 (5)

The *t*-Bu group adopts a position (Table 2) deviating ~ 12° from the energetically most favourable position, as found for *tert*-butylbenzene (Beckhaus, 1983), in which one of the C—C bonds lies in the aromatic-ring plane. In Lig.FeCl$_3$ this angle is 30°. Apparently packing forces easily influence the rotation of the *t*-Bu group.

The dihedral angle between the C(1)C(11)O(1)-C(12) plane and the aromatic-ring plane is 80·6 (5)°. The corresponding angles in acetophenone (Tanimoto, Kobayashi, Nagakura & Saito, 1973) and in Lig.FeCl$_3$ (van Koningsveld, Scheele & Jansen, 1986) are ~ 0° and 43·7 (5)°, respectively. The torsion angle C(2)C(1)-C(11)O(1) is 79·6 (5)°. On complexation with Lig, FeCl$_3$ induces a positive charge on the acetyl group. This charge can be compensated by delocalization of electrons of the aromatic π system. The delocalization of electrons in Lig.FeCl$_3$ is apparently effected by decreasing the out-of-plane rotation of the acetyl group, thus increasing the conjugation in the complex. However, steric interaction with the *o*-methyl group prevents the acetyl group from being completely in-plane, unlike acetophenone. Further evidence of conjugational effects in Lig.FeCl$_3$ is obtained from a comparison of the bond lengths of the compounds listed in Table 3. The bond distances of acetophenone and the acetophenone-part of Lig are hardly influenced by the rotational position of the acetyl group, although the C(1)—C(11) and C(11)—O(1) bonds might indicate a small contribution of the resonance structure depicted in Fig. 2(*a*). Complexation of Lig with FeCl$_3$, however, significantly influences the bond lengths. This influence can be understood by considering the resonance structure of Lig. FeCl$_3$ given in Fig. 2(*b*).

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* Lists of H-atom parameters, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43373 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of relevant bond lengths* (Å), *in connection with conjugation, in acetophenone, in Lig and in Lig.* $FeCl_3$

	Acetophenone	Lig	Lig. $FeCl_3$
C(1)–C(2)	1·389 (2)	1·388 (3)	1·415 (4)
C(2)–C(3)	1·391 (2)	1·398 (5)	1·379 (4)
C(3)–C(4)	1·383 (3)	1·384 (4)	1·392 (4)
C(4)–C(5)	1·382 (3)	1·378 (3)	1·386 (4)
C(5)–C(6)	1·385 (3)	1·400 (5)	1·380 (4)
C(1)–C(6)	1·392 (2)	1·386 (5)	1·406 (4)
C(1)–C(11)	1·494 (2)	1·515 (5)	1·461 (4)
C(11)–O(1)	1·216 (2)	1·202 (5)	1·243 (3)

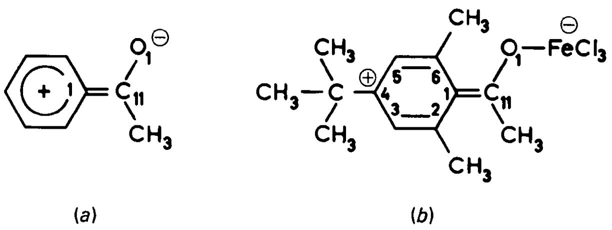

Fig. 2. Resonance structures of (*a*) acetophenone and (*b*) Lig.$FeCl_3$.

Because of the increasing double-bond character, the bond lengths C(2)–C(3), C(5)–C(6) and C(1)–C(11) in Lig.$FeCl_3$ will be shorter than the corresponding values in Lig and, because of the increasing single-bond character, the bond lengths C(1)–C(2), C(3)–C(4), C(4)–C(5), C(6)–C(11) and C(11)–O(1) will be longer. These conjugational effects are confirmed by the distances given in Table 3. Apparently, the resonance structure depicted in Fig. 2(*b*) has an important influence. In acetophenone, without *o*-alkyl substituents, the acetyl moiety coincides with the ring plane (Tanimoto *et al.*, 1973), and strong conjugation is possible. On complexation, more negative charge is available on the carbonyl oxygen atom. Hence, a stronger complexation with $FeCl_3$ can be expected. This may clarify why poisoning of the $FeCl_3$ catalyst, *i.e.* complexation of $FeCl_3$ with the product acetophenones, will be less pronounced in Friedel–Crafts acylations producing *o*-methylacetophenones (Scheele, 1986). It is planned to substantiate this proposal by determining the structure of the $FeCl_3$ complex of *p*-*tert*-butylacetophenone.

References

Beckhaus, H. D. (1983), *Chem. Ber.* **116**, 86–96.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Johnson, C. K. (1965). *ORTEP*. Report ORNL–3794, revised June 1970. Oak Ridge National Laboratory, Tennessee.

Koningsveld, H. van, Scheele, J. J. & Jansen, J. C. (1986). *Acta Cryst.* C**42**, 41–43.

Scheele, J. J. (1986) Thesis, Delft Univ. of Technology. To be published.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY72* system. Tech. Rep. TR–192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Tanimoto, Y., Kobayashi, H., Nagakura, S. & Saito, Y. (1973). *Acta Cryst.* B**29**, 1822–1826.

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Hydrated Proton Complexes in Methyl 3-Sulfoorsellinate Tetrahydrate*†

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Abstract. $C_9H_{10}O_7S.4H_2O$, $M_r = 334{\cdot}3$, triclinic, $P\bar{1}$, $Z = 2$, Cu $K\alpha_1$, $\lambda = 1{\cdot}54056$ Å, $F(000) = 352$, $T = 293$ K. Form *A*: $a = 7{\cdot}941$ (2), $b = 13{\cdot}753$ (2), $c = 6{\cdot}935$ (1) Å, $\alpha = 99{\cdot}68$ (2), $\beta = 91{\cdot}71$ (2), $\gamma = 98{\cdot}35$ (2)°, $V = 737{\cdot}5$ Å^3, $D_x = 1{\cdot}505$ g cm^{-3}, $\mu = 24{\cdot}2$ cm^{-1}, final $R = 0{\cdot}041$ for 1294 unique reflections with $I \geq 3\sigma(I)$. Form *B*: $a = 8{\cdot}099$ (1), $b = 13{\cdot}904$ (1), $c = 6{\cdot}974$ (1) Å, $\alpha = 98{\cdot}95$ (1), $\beta = 105{\cdot}80$ (1), $\gamma = 82{\cdot}28$ (1)°, $V = 743{\cdot}0$ Å^3, $D_x = 1{\cdot}494$ g cm^{-3}, $\mu = 24{\cdot}0$ cm^{-1}, final $R = 0{\cdot}031$ for 1965 unique reflections with $I \geq 3\sigma(I)$. In each structure the water molecules and the sulfonic acid oxygen atoms are joined by hydrogen bonds to form continuous sheets. Within these sheets isolated hydrated proton complexes can be recognized. In *A* the complex can be formulated as $H_9O_4^+$, a central oxonium ion joined to three water molecules by bonds of length 2·490 (5), 2·500 (6) and 2·553 (5) Å. In *B* the complex can be formulated as

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[*] 2,6-Dihydroxy-3-methoxycarbonyl-4-methylbenzenesulfonic acid tetrahydrate.

[†] NRCC No. 26527.