Data collection

Marresearch Image Plate
95 frames at 2° intervals, counting time 2 min
Absorption correction: none
16 265 measured reflections
9432 independent reflections
6739 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\rm max} = 26.15°$
$h = 0 \rightarrow 15$
$k = -16 \rightarrow 18$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.0831$
$wR(F^2) = 0.2928$
$S = 0.615$
9432 reflections
595 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.2778P)^2 + 11.3102P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.438$
$\Delta\rho_{\rm max} = 0.562$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.446$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection used rotation about a single axis, giving 85.6% data completeness. Interframe scaling indicated no significant intensity decay. H atoms were constrained to ideal positions with a riding model including torsional freedom for methyl groups and with isotropic displacement parameters [$U(\rm H) = 1.2U_{\rm eq}(\rm C)$]. One *tert*-butyl group was disordered. The *tert*-butyl groups in general had high displacement parameters with significant anisotropy; this could indicate further disorder, but it could not be resolved. The highest Δ/σ ratio is for atoms in the disordered groups and these are probably responsible for the high final residuals.

Data collection: *XDS* (Kabsch, 1988). Cell refinement: *XDS*. Data reduction: *XDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*94 (Spek, 1994).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Arnaud-Neu, F. (1994). *Chem. Soc. Rev.* pp. 235–241.
Beer, P. D., Drew, M. G. B., Gale, P. A., Leeson, P. B. & Ogden, M. I. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3479–3485.
Beer, P. D., Drew, M. G. B., Kan, M., Leeson, P. B., Ogden, M. I. & Williams, G. (1996). *Inorg. Chem.* **35**, 2202–2211.
Beer, P. D., Drew, M. G. B., Leeson, P. B. & Ogden, M. I. (1995). *J. Chem. Soc. Dalton Trans.* pp. 1273–1283.
Beer, P. D., Drew, M. G. B., Leeson, P. B. & Ogden, M. I. (1996). *Inorg. Chim. Acta*, **246**, 133–141.
Böhmer, V. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 713–745.
Bünzli, J. C. G. & Harrowfield, J. M. (1991). *Calixarenes: A Versatile Class of Macrocyclic Compounds*, edited by J. Vicens & V. Böhmer, pp. 211–231. Dordrecht: Kluwer Academic Publishers.
Casnati, A., Pochini, A., Ungaro, R., Ugozzili, F., Arnaud, F., Fanni, S., Schwing, M.-J., Egberink, R. J. M., de Jong, F. & Reinhoudt, D. N. (1995). *J. Am. Chem. Soc.* **117**, 2767–2777.
Delaigue, X., Hosseini, M. W., Kyritsakas, N., De Cian, A. & Fischer, J. (1995). *J. Chem. Soc. Chem. Commun.* pp. 609–610.
Harrowfield, J. M., Ogden, M. I., Richmond, W. R., Skelton, B. W. & White, A. H. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2427–2433.
Kabsch, W. (1988). *J. Appl. Cryst.* **21**, 916–932.
Loeber, C., Matt, D., Briard, P. & Grandjean, D. (1996). *J. Chem. Soc. Dalton Trans.* pp. 513–524.
McKervey, M. A., Collins, E. M., Madigan, E., Moran, M. B., Owens, M., Ferguson, G. & Harris, S. (1991). *J. Chem. Soc. Perkin Trans.* 1, pp. 3137–3142.
McKervey, M. A., Schwing, M.-J. & Arnaud-Neu, F. (1996). *Comprehensive Supramolecular Chemistry*, Vol. 1, edited by G. W. Gokel, ch. 15, pp. 537–603. Oxford: Elsevier Science Ltd.
Roundhill, D. M. (1995). *Prog. Inorg. Chem.* **43**, 533–593.
Scheibye, S., Pedersen, B. S. & Lawesson, S.-O. (1978). *Bull. Soc. Chim. Belg.* **87**, 229–238.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1994). *PLATON94. Molecular Graphics Program.* University of Utrecht, The Netherlands.
Xu, W., Vittal, J. J. & Puddephatt, R. J. (1996). *Can. J. Chem.* **74**, 766–774.

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meta-Nitroacetophenone at 173 K

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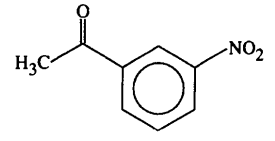
Abstract

The title compound, methyl 2-nitrophenyl ketone, $C_8H_7NO_3$, crystallizes as a nearly planar molecule. Layers parallel to the $(\bar{2}02)$ plane are stabilized by intermolecular C—H···O contacts. The molecular geometry is very similar to that of *para*-nitroacetophenone, but some bond lengths of the aromatic ring are significantly different. The molecular geometry agrees well with a recent room-temperature structure determination.

Comment

The crystal structure of *m*-nitroacetophenone, (I), has been determined. The structure agrees well with the recent room-temperature structure determination of *m*-nitroacetophenone (Feeder, Jones, Chorlton & Docherty, 1996); a least-squares fit of all non-H atoms shows an r.m.s. deviation of 0.018 Å. Bond lengths and angles are as expected.



(I)

In *p*-nitroacetophenone (Kim, Boyko & Carpenter, 1973), the bonds between the non-substituted aromatic C atoms are significantly shortened compared with the other aromatic bonds, but no such effect is found here, consistent with the resonance theory. The entire molecule is approximately planar [r.m.s. deviation 0.066 (2) Å]. While the nitro group forms an angle of 1.8 (1)° with the plane of the phenyl ring [1.8 (2)° for the structure at 295 K and −3.6° in *p*-nitroacetophenone], the acetyl group is twisted by 8.95 (9)° from the central ring [9.4 (2)° for the structure at 295 K and −2.5° in *p*-nitroacetophenone]. For each of the O atoms, one short contact to an aromatic H atom can be found; O11···H6^{i} 2.433 (2), O31···H5^{ii} 2.664 (2), O32···H4^{ii} 2.730 (2) Å, O11···H6^{i}—C6^{i} 131.55 (4), O31···H5^{ii}—C5^{ii} 154.13 (4) and O32···H4^{ii}—C4^{ii} 137.32 (3)° [symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$].

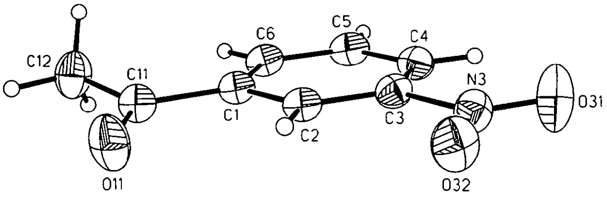


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are plotted at the 50% probability level.

Experimental

The title compound was obtained by slowly adding nitrating acid to a mixture of acetophenone and concentrated sulfuric acid. After stirring for 10 min at 273 K, the reaction product was isolated by filtration and suitable crystals were obtained by slow evaporation of an ether/petrol ether solution.

Crystal data

$C_8H_7NO_3$
$M_r = 165.15$
Monoclinic
$P2_1/n$
$a = 7.3045\,(2)$ Å
$b = 9.8633\,(3)$ Å
$c = 10.7436\,(4)$ Å
$\beta = 98.608\,(1)°$
$V = 765.32\,(4)$ Å^3
$Z = 4$
$D_x = 1.433$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5382 reflections
$\theta = 2$–$25°$
$\mu = 0.112$ mm^{-1}
$T = 173$ K
Block
0.60 × 0.50 × 0.40 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: *SADABS* (Sheldrick, 1996*a*)
$T_{\min} = 0.692$, $T_{\max} = 1.000$
6481 measured reflections
1402 independent reflections

1217 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0391$
$\theta_{\max} = 26.06°$
$h = -8 \rightarrow 9$
$k = -12 \rightarrow 11$
$l = -13 \rightarrow 13$
208 standard reflections
frequency: 420 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0354$
$wR(F^2) = 0.1027$
$S = 1.044$
1402 reflections
109 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.0948P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.168$ e Å^{-3}
$\Delta\rho_{\min} = -0.191$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The data collection nominally covered over a sphere of reciprocal space by a combination of four sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 98% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. The program *SADABS* (Sheldrick, 1996*a*) was able to correct for other effects, such as crystal movement in a slightly inhomogeneous beam, as well as absorption. All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U({\rm H}) = 1.5U_{\rm eq}({\rm C_{methyl}})$ or $U({\rm H}) = 1.2U_{\rm eq}({\rm C})$] using a riding model with C—H(aromatic) = 0.95 or C—H(methyl) = 0.98 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Feeder, N., Jones, W., Chorlton, A. P. & Docherty, R. (1996). *Acta Cryst.* C**52**, 1454–1456.

Kim, J. K. S., Boyko, E. R. & Carpenter, G. B. (1973). *Acta Cryst.* B**29**, 1141–1144.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996*a*). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1996*b*). *SHELXL96. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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2-Methylamino-5-chlorobenzophenone

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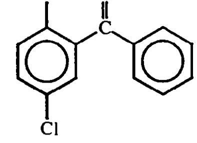
Abstract

Intramolecular hydrogen bonding is present in 2-methylamino-5-chlorophenyl phenyl ketone, $C_{14}H_{12}ClNO$, and the phenyl rings are inclined by 54.39 (8)° with respect to one another. The Cl···Cl intermolecular separation of 3.355 (2) Å is considerably less than the sum of the van der Waals radii.

Comment

Diazepam is a well known benzodiazepine drug prescribed for the short-term relief of severe anxiety: its crystal structure has been determined previously (Camerman & Camerman, 1972). The drug is hydrolyzed to the title compound, 2-methylamino-5-chlorobenzophenone (MACB), and the hydrolysis kinetics have been investigated by a number of workers (Han, Yakatan & Maness, 1977; Nakano, Inotsume, Kohri & Arita, 1979; Anisuzzaman, 1995). The two phenyl rings of MACB are inclined by 54.39 (8)° with respect to one another such that the H6···H9 distance is 2.455 (3) Å. In benzophenone (Fleischer, Sung & Hawkinson, 1968), this angle is 56°, which is in reasonable agreement with the energy minimum conformation predicted using *ab initio* molecular-orbital calculations (Kendrick, 1990).



MACB

The N···O separation is 2.674 (3) Å and the geometry of the intramolecular hydrogen bonding is N—H1 0.880 (3), H1···O 1.994 (3) Å and N—H1···O 133.13 (6)°. The Cl···Cl($2-x$, $1-y$, $1-z$) separation is 3.355 (2) Å, which is less than the sum of the van der Waals radii (3.50 Å; Bondi, 1964). Recent surveys (Gavezzotti & Filippini, 1993; Rowland & Taylor, 1996) of halogen-containing crystal structures in the Cambridge Structural Database (Allen & Kennard, 1993) show a significant number of Cl···Cl non-bonded contacts of < 3.5 Å. It has been suggested (Pedireddi *et al.*, 1994) that polarization and anisotropic electron distribution are important factors in the formation of these short contacts. A short intermolecular distance C10···O($\frac{1}{2}+x$, $\frac{1}{2}-y$, z) of 3.172 (3) Å may involve a weak hydrogen-bonded contact; the C—H···O angle is 124.30 (6)° and the H10···O distance is 2.538 (3)°. Interactions of this type may influence the packing of molecules in the crystal. Reference to the Cambridge Structural Database for 3762 aromatic-C—H···O=C contacts less than the sum of the C···O van der Waals radii (3.22 Å) shows a mean C···O distance of 2.800 (4) Å, with an angular range of 74–179° [mean 134.3 (3)°].

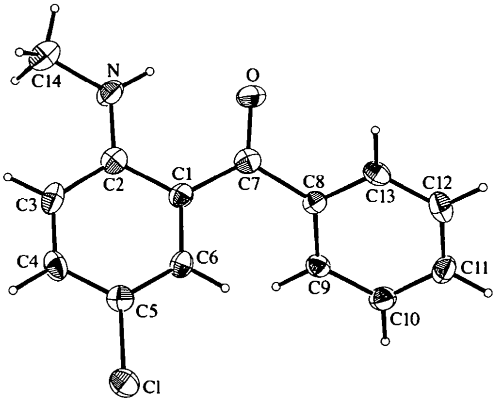


Fig. 1. The atomic arrangement in the title molecule. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

Diazepam was hydrolyzed with aqueous HCl to give the title compound, which was then recrystallized from aqueous ethanol.

Crystal data

$C_{14}H_{12}ClNO$
$M_r = 245.70$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å