

Structure of *N*-(*n*-Butyl)-*N'*-[(*p*-chlorophenoxy)acetyl]urea – A Short Intramolecular N–H...O Hydrogen Bond

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Abstract. C₁₃H₁₇ClN₂O₃, *M_r* = 284.5, triclinic, *P*1, *Z* = 2, *a* = 5.214 (3), *b* = 8.444 (3), *c* = 17.518 (5) Å, α = 95.40 (3), β = 91.90 (3), γ = 113.99 (4)°, *V* = 699.2 Å³, ρ_m = 1.332, ρ_c = 1.34 g cm⁻³, m.p. 423.7 ± 1 K. The structure was determined by direct methods and refined to *R* = 0.067 (837 reflections) by full-matrix least squares. A short intramolecular hydrogen bond of the type N–H...O [2.62 (1) Å] was observed. The formation of this bond closes a part of the molecule to form a six-membered ring. A short intermolecular Cl...Cl distance of 3.361 (4) Å was observed.

Introduction. Crystals suitable for X-ray structure determination were obtained by slow evaporation from a mixture of bromobenzene and methanol. Accurate values of the cell dimensions were obtained by least-squares refinement of the cell parameters measured from photographs taken with a double-radius Straumanis camera. The data were collected using the multiple-film equi-inclination Weissenberg method. The intensities of 837 unique reflections recorded with Cu K α radiation (λ = 1.5418 Å) were estimated visually. Data from different layers along the *a* axis were brought to a common scale by comparison with cross-level photographs. Since the size of the crystal was small (0.28 × 0.18 × 0.15 mm), an absorption correction was not applied ($\mu_{CuK\alpha}$ = 2.49 mm⁻¹).

The signs of 253 normalized structure amplitudes ($|E| \geq 1.5$) were determined using Sayre's equation (Long, 1965). The *E* map with these normalized structure factors revealed a good fraction of the molecule and the complete molecule was obtained in two successive Fourier maps (*R* = 0.412). The refinement of the structure by full-matrix least squares after two cycles of *F_o* synthesis reduced *R* to 0.371 and the structure could not be refined further. Successive Fourier syntheses using one molecule conforming to the space group *P*1 generated the second molecule in the unit cell (*R* = 0.241) and a close inspection of the electron density maps revealed that the two molecules are centrosymmetrically related. The origin was moved to the centre of symmetry and refinement with anisotropic temperature factors reduced *R* to 0.103.

All the H atoms were located in the difference Fourier map obtained with the reflections having $(\sin \theta/\lambda) \leq 0.40 \text{ \AA}^{-1}$ and calculation with all 36 atoms gave *R* = 0.089. As the *F_o* values of 17 intense low-angle reflections were systematically lower than their *F_c* values, Darwin correction for secondary extinction was applied (Stout & Jensen, 1968). The value of the secondary-extinction coefficient *g* was 2×10^{-5} . One cycle of refinement of positional parameters of H atoms and two more cycles of refinement of non-hydrogen atomic positions reduced *R* to 0.067.* The atomic-scattering factors for structure factor calculations were taken from *International Tables for X-ray Crystallography* (1962).

Some of the atoms had non-positive-definite anisotropic temperature factors when the chosen unit cell had one of the angles of the order of 42°. The anisotropic temperature factors, however, became positive when the molecule was refined after transformation of the unit cell.

Discussion. The final positional parameters of all atoms along with their *B_{eq}* values (Willis & Pryor, 1975) are given in Tables 1 and 2. Bond lengths and bond angles are shown in Figs. 1 and 2 respectively. The presence of Cl, an electron-withdrawing substituent in the *para* position, and O have deformed the skeletal geometry of the benzene ring by increasing both the angles C(2)–C(1)–C(6) and C(3)–C(4)–C(5) to 122.0 (8)°. The Cl–C(1) bond does not undergo in-plane or out-of-plane bending. A very short intramolecular hydrogen bond of the type N–H...O [2.62 (1) Å] is observed and closes part of the molecule to form a six-membered ring. This confirms the infrared work on this compound (Jose & Pabrai, 1966). The geometry of the six-membered ring is shown in Fig. 2. Formation of similar N–H...O bonds has been found in 3-diazo-2,3-dihydrophenalene-1,2-dione 1-[(4-bromo-

* Lists of structure factors, anisotropic thermal parameters and bond distances involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36394 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) of the non-hydrogen atoms and their corresponding B_{eq} values

| | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq} (\AA^2) |
|-------|------------|------------|-----------|--------------------------------|
| Cl | 4521 (8) | -6410 (4) | -792 (1) | 7.2 (2) |
| C(1) | 5144 (25) | -6724 (14) | -1743 (5) | 4.3 (4) |
| C(2) | 6640 (25) | -7733 (14) | -1936 (4) | 4.7 (5) |
| C(3) | 7056 (24) | -7988 (13) | -2692 (5) | 4.5 (5) |
| C(4) | 6116 (22) | -7234 (12) | -3221 (4) | 3.0 (4) |
| C(5) | 4653 (24) | -6237 (12) | -3024 (5) | 4.0 (4) |
| C(6) | 4186 (26) | -5987 (12) | -2283 (5) | 4.5 (4) |
| O(1) | 6649 (15) | -7566 (8) | -3943 (3) | 4.3 (3) |
| C(7) | 5927 (20) | -6752 (12) | -4519 (4) | 3.3 (4) |
| C(8) | 7011 (22) | -7079 (12) | -5250 (4) | 3.2 (4) |
| O(2) | 6824 (16) | -6274 (9) | -5769 (3) | 5.2 (3) |
| N(1) | 8292 (18) | -8228 (9) | -5286 (4) | 2.9 (3) |
| C(9) | 9364 (20) | -8756 (12) | -5938 (5) | 3.1 (4) |
| O(3) | 10399 (16) | -9829 (8) | -5893 (3) | 4.4 (3) |
| N(2) | 9197 (19) | -8036 (9) | -6559 (4) | 4.1 (4) |
| C(10) | 10129 (25) | -8523 (13) | -7269 (5) | 4.7 (4) |
| C(11) | 9019 (25) | -7859 (14) | -7912 (5) | 4.9 (5) |
| C(12) | 9932 (28) | -8356 (15) | -8674 (5) | 6.0 (5) |
| C(13) | 8670 (32) | -7831 (19) | -9332 (6) | 8.6 (6) |

Table 2. Fractional coordinates ($\times 10^3$) of the hydrogen atoms

| | <i>x</i> | <i>y</i> | <i>z</i> |
|---------|-----------|-----------|----------|
| H(C2) | 750 (22) | -820 (12) | -150 (5) |
| H(C3) | 796 (21) | -853 (12) | -272 (5) |
| H(C5) | 360 (21) | -574 (11) | -322 (5) |
| H(C6) | 290 (22) | -530 (11) | -203 (5) |
| H1(C7) | 688 (22) | -554 (11) | -436 (4) |
| H2(C7) | 390 (22) | -690 (12) | -464 (4) |
| H(N1) | 879 (20) | -865 (11) | -489 (4) |
| H(N2) | 923 (22) | -710 (11) | -655 (5) |
| H1(C10) | 961 (24) | -973 (13) | -739 (5) |
| H2(C10) | 1200 (24) | -854 (13) | -720 (5) |
| H1(C11) | 683 (22) | -821 (12) | -792 (5) |
| H2(C11) | 990 (22) | -640 (13) | -773 (5) |
| H1(C12) | 899 (25) | -977 (14) | -878 (5) |
| H2(C12) | 1207 (26) | -816 (14) | -864 (5) |
| H1(C13) | 630 (28) | -860 (17) | -936 (6) |
| H2(C13) | 960 (27) | -787 (16) | -987 (6) |
| H3(C13) | 854 (28) | -658 (17) | -925 (6) |

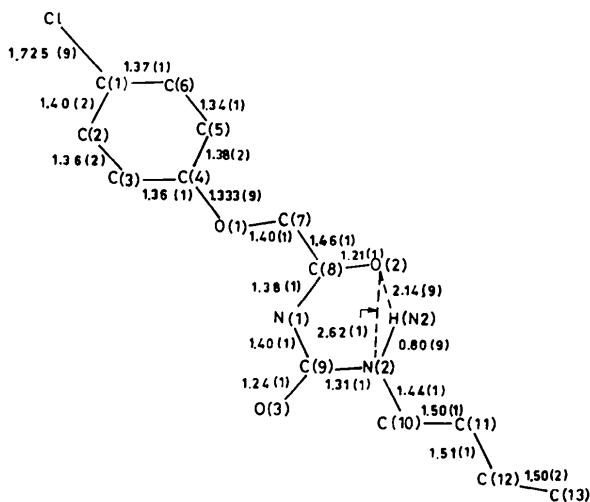


Fig. 1. Bond lengths (\AA) with e.s.d.'s in parentheses.

phenylsulphonylhydrazone] (Maas, 1980), where $N-H \cdots O = 2.56(1)$, $O \cdots H = 1.94(13)$ \AA and $\angle N-H \cdots O = 113(9)^\circ$, and also in methyl phenyl[*syn*- α -(tosylhydrazono)benzyl]phosphinate (Maas & Hoge, 1980). The six-membered group is planar, except for the H atom which deviates by 0.32 (7) \AA from the least-squares plane, and subtends an angle of 10.5 (2) $^\circ$ with the plane of the benzene ring. The bond lengths and angles of the urea group are in good agreement with those of related compounds (Mullen & Hellner, 1978).

The $Cl \cdots Cl$ intermolecular distance is 3.361 (4) \AA , shorter than the usually quoted van der Waals distance of 3.60 \AA . The angle between $C(1)-Cl$ and $Cl \cdots Cl$ is 147.9 (5) $^\circ$ which is close to the orientation-factor condition (Sakurai, Sundaralingam & Jeffrey, 1963). Table 3 gives a few short $Cl \cdots Cl$ intermolecular distances. The average C-H and N-H bond lengths are 1.01 (3) and 0.85 (7) \AA , respectively. The packing of the molecules is shown in Fig. 3 along with principal intermolecular distances.



Fig. 2. Bond angles ($^\circ$) with e.s.d.'s in parentheses.

Table 3. Short intermolecular $Cl \cdots Cl$ distances

| | $Cl \cdots Cl$ (\AA) | $\angle C-Cl \cdots Cl$ ($^\circ$) | References |
|--|------------------------------------|---|---|
| Tetrachlorohydroquinone | 3.37 | 168, 168 | Sakurai (1962) |
| 2,5-Dichloroaniline | 3.37 | 157, 166 | Sakurai, Sundaralingam & & Jeffrey (1963) |
| Dimethyl 3,6-dichloro- 2,5-dihydroxy- terephthalate (form <i>y</i>) | 3.47 | 147, 147 | Byrn, Curtin & Paul (1971) |
| <i>p</i> -Chlorobenzoic acid | 3.44 | 167, 167 | Miller, Paul & Curtin (1974) |
| 1,4-Dichlorobenzene (form β) | 3.38 | 169.5, 169.5 | Wheeler & Colson (1975) |
| <i>p</i> -Chlorophenoxyacetic acid | 3.349 (3) | 177.1 (3), 177.1 (3) | Vijay Kumar & Rao (1982) |
| Title compound | 3.361 (4) | 147.9 (5), 147.9 (5) | |

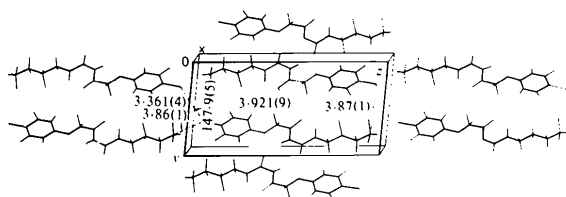


Fig. 3. The packing of the molecules when viewed perpendicular to the *bc* plane, along with some intermolecular distances (Å) and an angle (°).

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References

- BYRN, S. R., CURTIN, D. Y. & PAUL, I. C. (1971). *J. Am. Chem. Soc.* **94**, 890–898.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOSE, C. I. & PABRAI, P. R. (1966). *Spectrochim. Acta Part A*. **23**, 734–736.
- LONG, R. E. (1965). Doctoral dissertation, part III. Univ. of California at Los Angeles.
- MAAS, G. (1980). Unpublished work.
- MAAS, G. & HOGE, R. (1980). *Acta Cryst.* **B36**, 499–502.
- MILLER, S., PAUL, I. C. & CURTIN, D. Y. (1974). *J. Am. Chem. Soc.* **96**, 6334–6339.
- MULLEN, D. & HELLNER, E. (1978). *Acta Cryst.* **B34**, 1624–1627.
- SAKURAI, T. (1962). *Acta Cryst.* **15**, 443–447.
- SAKURAI, T., SUNDARALINGAM, M. & JEFFREY, G. A. (1963). *Acta Cryst.* **16**, 354–363.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 411. London: Macmillan.
- VIJAY KUMAR, S. & RAO, L. M. (1982). *Acta Cryst.* In the press.
- WHEELER, G. L. & COLSON, S. D. (1975). *J. Chem. Phys.* **65**, 1227–1235.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1982). **B38**, 976–978

Reinvestigation of the Structure of Feist's Acid 3-Methylene-*trans*-1,2-cyclopropanedicarboxylic Acid

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Abstract. $C_6H_6O_4$, $M_r = 142$, triclinic, $P\bar{1}$, $a = 4.842$ (1), $b = 7.607$ (1), $c = 9.168$ (3) Å, $\alpha = 98.41$ (2), $\beta = 99.89$ (2), $\gamma = 77.74$ (1)°, $V = 320.9$ Å³, $Z = 2$, $D_m = 1.45$ (floatation), $D_x = 1.470$ g cm⁻³, μ (Mo $K\alpha$, $\lambda = 0.7107$ Å) = 0.63 cm⁻¹, $F(000) = 148$. The structure was solved by direct methods and refined to an R value of 0.038 for 723 intensity measurements. The geometrical changes in the cyclopropane ring are discussed in the light of substituent effects. In the crystal structure the carboxylic groups are disordered.

Introduction. Feist's acid (Feist, 1893) (see Fig. 1), initially thought to embody a methylcyclopropylene system, is now known to be a methylenecyclopropane. The latter structure, suggested by NMR (Ettlinger & Kennedy, 1956; Kende, 1956; Lloyd, 1969), was confirmed by simple X-ray work (Lloyd, Downie & Speakman, 1954*a,b*; Petersen, 1956). We now report a

more precise X-ray study as a part of a programme of investigations of substituent effects on three-membered rings. Our results are of particular relevance to a theoretical interest in such rings (Deakyne, Allen & Laurie, 1976).

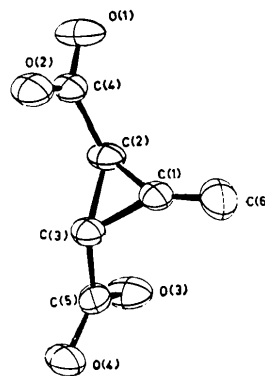


Fig. 1. Perspective view of the molecule viewed down *a*. The H atoms were given numbers corresponding to the bonded C atoms.

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