

- EILAND, P. F. & PEPINSKY, R. (1955). *Z. Kristallogr.* **106**, 273–298.  
 GEORGE, R. S., CADY, H. H., ROGERS, R. N. & ROHWER, R. K. (1965). *Ind. Eng. Chem. Prod. Res. Dev.* **4**, 209–214.  
 HALLER, T. M., RHEINGOLD, A. L. & BRILL, T. B. (1983). In preparation.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LANDERS, A. G., APPLE, T. M., DYBOWSKI, C. & BRILL, T. B. (1983). Submitted to *Org. Magn. Reson.*  
 MCCRONE, W. C. (1950). *Anal. Chem.* **22**, 1225.  
 SELIG, W. (1982). *Propellants Explos.* **7**, 70–77.  
 SHELDRIK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen.  
 STALS, J. (1969). *Aust. J. Chem.* **22**, 2505–2514.

*Acta Cryst.* (1983). **C39**, 1563–1565

## Methyl 3-(4-Chlorobenzoyl)-4-(4-chlorophenyl)-1-cyano-4-hydroxy-2,6-diphenylcyclohexanecarboxylate, $C_{34}H_{27}Cl_2NO_4$

BY A. KIRFEL AND M. EL KORDY\*

*Mineralogisches Institut der Universität Bonn, Lehrstuhl für Mineralogie und Kristallographie, Poppelsdorfer Schloss, D-5300 Bonn, Federal Republic of Germany*

AND R. TROSCHÜTZ

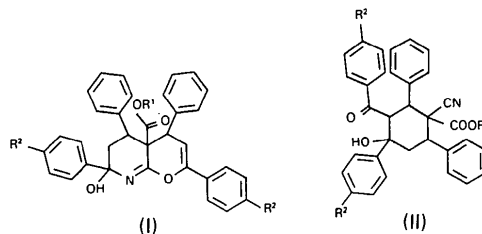
*Pharmazeutisches Institut der Universität Bonn, An der Immenburg, D-5300 Bonn, Federal Republic of Germany*

(Received 9 May 1983; accepted 7 July 1983)

**Abstract.**  $M_r = 584.5$ , triclinic,  $P\bar{1}$ ,  $a = 11.246$  (3),  $b = 12.265$  (3),  $c = 13.029$  (3) Å,  $\alpha = 86.41$  (2),  $\beta = 72.22$  (2),  $\gamma = 115.71$  (2)°,  $Z = 2$ ,  $V = 1501.7$  (7) Å<sup>3</sup>,  $D_x = 1.292$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.252$  mm<sup>-1</sup>,  $F(000) = 608$ ,  $T = 293$  K. Final  $R = 0.059$  for 2323 observed reflections. The structure proposed from chemical and spectroscopic considerations could be fully corroborated. The cyclohexane ring is in the chair conformation and is slightly strained, probably due to steric reasons. The phenyl rings are essentially planar and approximately perpendicular to the cyclohexane least-squares plane. There is an intramolecular hydrogen bond between the benzoyl O and the hydroxyl group.

**Introduction.** For the 2:1 reaction product from chalcone (1,3-diphenyl-2-propen-1-one) and esters of cyanoacetic acid there are different structures proposed in the literature. One is a non-cyclic structure (Kohler, Graustein & Merrill, 1922), whereas in another case the product from chalcone ( $R^2 = \text{H}$ ) and ethyl cyanoacetate ( $R^1 = \text{Et}$ ) is proposed as (I) (Degny, Zard, Pastor & Cambon, 1981). In the course of syntheses of pteridine analogues (Troschütz & Roth, 1978) the reaction was reinvestigated. From spectroscopic data (<sup>1</sup>H, <sup>13</sup>C, UV) the product from 4-chlorochalcone ( $R^2 = \text{Cl}$ ) and methyl cyanoacetate ( $R^1 = \text{Me}$ ) prepared according to Kohler *et al.* was concluded to possess the monocyclic structure (II). This is also supported by the finding of an

analogous monocyclic product obtained from chalcone and malononitrile (Soto, Seoane & Ciller, 1980). Since, however, (I) could not be discarded unambiguously from the spectroscopic investigations an X-ray analysis had to be undertaken in order to establish the true stereochemistry of the title compound.



**Experimental.** Colourless needles, crystal size  $0.25 \times 0.25 \times 0.3$  mm. Syntex  $P2_1$ , diffractometer, Mo  $K\alpha$  radiation, graphite monochromator. Lattice constants from angular settings of 24 independent reflections ( $15 < 2\theta < 30^\circ$ ). Range of  $hkl$ :  $-10-10$ ,  $-11-11$ ,  $0-13$ .  $2\theta_{\text{max}} = 42^\circ$  ( $2^\circ$  plus  $\alpha_1$ ,  $\alpha_2$  dispersion scan range, variable scan speed  $2-10^\circ \text{ min}^{-1}$ ). One check reflection after every 33 records. 3318 total reflections (omitting standards), adjustment of individual intensities to fluctuations of the standard intensities, 3117 unique reflections, 792 with  $|F| < 3\sigma$ .  $R_{\text{int}} = 0.02$ . No absorption correction. Analysis of normalized structure amplitudes clearly showed structure to be centrosymmetric ( $\langle E^2 - 1 \rangle = 0.97$ ); solved by use of direct-methods program *MULTAN* (Germain, Main &

\* Guest from the National Research Center, Cairo, Egypt.

Woolfson, 1971) employing 264  $|E|$ 's  $> 1.76$ . Least-squares structure refinement on  $F$  carried out in alternating cycles (max. 100 parameters) with neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974),  $w = [\sigma^2(F)]^{-1}$ , and anisotropic temperature factors for non-H atoms. All H atoms except H(O4) treated as riding on their carrier atoms with fixed bond distances of 0.96 Å and with isotropic temperature factors  $B(H) = 1.2B_{eq}(C)$ ; H(O4) could be clearly located from a difference density map, and was refined for its positional parameters only. Refinement converged at  $R = 0.059$ ,  $R_w = 0.039$  (omitting unobs.),

Table 1. Atom coordinates ( $\times 10^4$ ; for H  $\times 10^3$ ) and equivalent isotropic temperature factors ( $\text{Å}^2 \times 10^4$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U$  tensor.

|       | x         | y        | z         | $U_{eq}$ |
|-------|-----------|----------|-----------|----------|
| Cl(1) | 11800 (2) | 3623 (2) | -5025 (1) | 131 (1)  |
| Cl(2) | 6115 (2)  | 1993 (2) | -5898 (1) | 124 (1)  |
| O(1)  | 3792 (3)  | 3257 (3) | 2501 (2)  | 55 (2)   |
| O(2)  | 3134 (3)  | 1240 (3) | 2996 (2)  | 61 (2)   |
| O(3)  | 7425 (3)  | 5204 (2) | -1568 (2) | 54 (2)   |
| O(4)  | 4527 (3)  | 4088 (3) | -1311 (2) | 47 (2)   |
| N     | 3906 (4)  | -64 (3)  | 1029 (3)  | 62 (2)   |
| C(1)  | 4010 (4)  | 2115 (4) | 1087 (3)  | 35 (2)   |
| C(2)  | 5506 (4)  | 3177 (3) | 310 (3)   | 34 (2)   |
| C(3)  | 5816 (4)  | 3052 (4) | -887 (3)  | 34 (2)   |
| C(4)  | 4641 (4)  | 2974 (4) | -1320 (3) | 36 (2)   |
| C(5)  | 3187 (4)  | 1960 (4) | -526 (3)  | 42 (3)   |
| C(6)  | 2860 (4)  | 2122 (4) | 654 (3)   | 37 (2)   |
| C(7)  | 3665 (4)  | 2290 (4) | 2262 (3)  | 45 (3)   |
| C(8)  | 2580 (6)  | 1238 (5) | 4146 (3)  | 103 (5)  |
| C(9)  | 3968 (4)  | 878 (4)  | 1073 (3)  | 43 (2)   |
| C(10) | 6709 (4)  | 3283 (4) | 689 (3)   | 38 (3)   |
| C(11) | 7365 (4)  | 4281 (4) | 1103 (3)  | 51 (3)   |
| C(12) | 8500 (5)  | 4438 (5) | 1407 (4)  | 69 (4)   |
| C(13) | 8975 (5)  | 3580 (5) | 1293 (4)  | 71 (4)   |
| C(14) | 8325 (6)  | 2579 (5) | 892 (4)   | 67 (4)   |
| C(15) | 7202 (4)  | 2422 (4) | 583 (4)   | 54 (3)   |
| C(16) | 7235 (4)  | 4162 (4) | -1631 (3) | 41 (3)   |
| C(17) | 8359 (4)  | 3984 (4) | -2449 (3) | 39 (3)   |
| C(18) | 8331 (5)  | 2843 (4) | -2482 (4) | 61 (3)   |
| C(19) | 9381 (5)  | 2734 (5) | -3256 (4) | 76 (4)   |
| C(20) | 10498 (5) | 3776 (5) | -4015 (4) | 72 (3)   |
| C(21) | 10591 (5) | 4926 (5) | -4010 (4) | 73 (3)   |
| C(22) | 9511 (5)  | 5019 (4) | -3221 (4) | 53 (3)   |
| C(23) | 4941 (4)  | 2719 (4) | -2461 (3) | 43 (3)   |
| C(24) | 5101 (5)  | 3493 (4) | -3347 (4) | 56 (3)   |
| C(25) | 5449 (5)  | 3259 (5) | -4413 (4) | 75 (4)   |
| C(26) | 5607 (5)  | 2237 (5) | -4570 (4) | 74 (3)   |
| C(27) | 5407 (5)  | 1422 (5) | -3692 (4) | 70 (3)   |
| C(28) | 5063 (5)  | 1652 (4) | -2648 (4) | 56 (3)   |
| C(29) | 1356 (4)  | 1202 (4) | 1428 (3)  | 45 (3)   |
| C(30) | 710 (5)   | -23 (5)  | 1382 (4)  | 61 (3)   |
| C(31) | -653 (6)  | -841 (5) | 2092 (5)  | 74 (4)   |
| C(32) | -1422 (6) | -434 (6) | 2845 (5)  | 81 (4)   |
| C(33) | -813 (6)  | 797 (6)  | 2897 (4)  | 79 (4)   |
| C(34) | 577 (5)   | 1609 (4) | 2189 (4)  | 60 (3)   |
| H(O4) | 537 (4)   | 472 (3)  | -166 (3)  | 50*      |

\*  $U_{iso}$ .

Table 2. Selected bond distances (Å) and angles ( $^\circ$ )

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Cl(1)—C(20) | 1.733 (6) | Cl(2)—C(26) | 1.738 (6) |
| O(1)—C(7)   | 1.205 (6) | O(2)—C(7)   | 1.326 (5) |
| O(2)—C(8)   | 1.436 (5) | O(3)—C(16)  | 1.214 (6) |
| O(4)—C(4)   | 1.427 (6) | N—C(9)      | 1.133 (6) |
| C(1)—C(2)   | 1.564 (4) | C(1)—C(6)   | 1.563 (7) |
| C(1)—C(7)   | 1.513 (6) | C(1)—C(9)   | 1.498 (7) |
| C(2)—C(3)   | 1.523 (5) | C(2)—C(10)  | 1.534 (7) |
| C(3)—C(4)   | 1.557 (7) | C(3)—C(16)  | 1.531 (4) |
| C(4)—C(5)   | 1.527 (4) | C(4)—C(23)  | 1.505 (6) |
| C(5)—C(6)   | 1.515 (6) | C(6)—C(29)  | 1.520 (5) |
| C(16)—C(17) | 1.493 (7) |             |           |

$S = 2.56$ .  $\Delta/\sigma_{av} = 0.06$ ,  $\Delta/\sigma_{max} = 0.31$ . Final difference Fourier map peaks below  $0.3 \text{ e Å}^{-3}$ . All calculations performed using *SHELX76* (Sheldrick, 1976).

**Discussion.** The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.\* Table 2 summarizes selected bond distances.

An *ORTEP* drawing (Johnson, 1965) of the molecule is depicted in Fig. 1 clearly showing it to be identical with the alternative structure (II). The cyclohexane ring is in the chair conformation, and the C—C single bonds in the ring vary between 1.515 (6) and 1.564 (4) Å. The longest bonds are C(1)—C(2) 1.564 (4), C(1)—C(6) 1.563 (7), and C(3)—C(4) 1.557 (7) Å indicating some strain in the six-membered ring probably due to steric reasons.

\* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, hydrogen positions, and results of least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38711 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

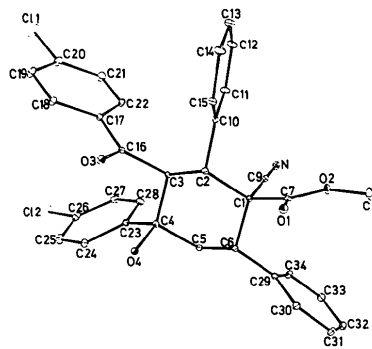


Fig. 1. Numbering scheme and *ORTEP* plot of the molecule.

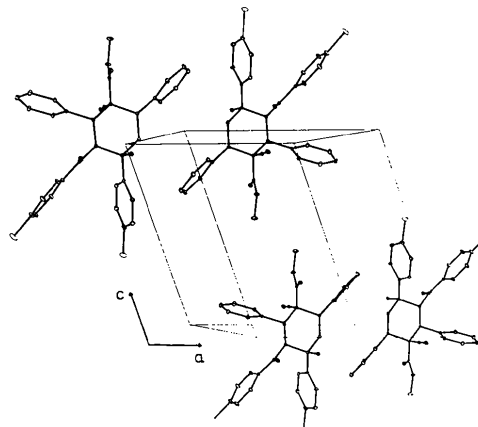


Fig. 2. The arrangement of the molecules viewed approximately along  $b_0$ .

The mean C—C bond distances in the other four six-membered rings are 1.375 (10) [C(10) to C(15)], 1.377 (11) [C(17) to C(22)], 1.379 (21) [C(23) to C(28)], and 1.378 (8) Å [C(29) to C(34)], where the e.s.d.'s are based on the variations of the lengths. The corresponding mean values for the C—C—C bond angles are 120.0 (1.0), 120.0 (1.8), 120.0 (1.6), and 120.0 (1.3)°. The least-squares-planes' calculations show the phenyl rings to be essentially planar, and they are all approximately perpendicular to the cyclohexane least-squares plane forming angles of 80.0, 91.6, 85.8, and 110.7°.

The H atom H(O4) can be regarded as providing a hydrogen bond within the molecule with O(4)···O(3) 2.831 (4), O(4)—H(O4) 0.87 (3), H(O4)···O(3) 2.16 (4) Å, O(4)—H(O4)···O(3) 133 (4)°, and simultaneously another somewhat weaker interaction with O(1<sup>i</sup>) of an adjacent molecule, O(4)···O(1<sup>i</sup>) 2.970 (4), H(O4)···O(1<sup>i</sup>) 2.29 (3) Å, O(4)—H(O4)···O(1<sup>i</sup>) 134 (3)°. The angle O(3)···H(O4)···O(1<sup>i</sup>) is 90 (1)°, and thus H(O4) lies in the plane through the three O atoms O(4), O(3), and O(1<sup>i</sup>). The intramolecular hydrogen bond is therefore somewhat weakened due to

the attractive force exerted by the next O(1) atom of the molecule related by the symmetry operation  $1-x, 1-y, -z$ . For the molecule in solution, however, one can expect that the intramolecular hydrogen bond gains importance.

The packing of the molecules viewed along  $b_0$  is depicted in Fig. 2.

#### References

- DEGNY, E., ZARD, S. Z., PASTOR, R. & CAMBON, A. (1981). *Tetrahedron Lett.* **22**, 2169–2170.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KOHLER, E. P., GRAUSTEIN, A. & MERILL, D. R. (1922). *J. Am. Chem. Soc.* **44**, 2536–2556.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SOTO, J. L., SEOANE, C. & CILLER, J. A. (1980). *An. Quim. Ser. C*, **76** (3), 281–285.  
 TROSCHÜTZ, R. & ROTH, H. J. (1978). *Arch. Pharm. (Weinheim, Ger.)*, **311**, 406–414.

*Acta Cryst.* (1983). **C39**, 1565–1568

## A Reinvestigation of the Structure of Bis(2-fluoro-2,2-dinitroethyl)nitramine, $C_4H_4F_2N_6O_{10}$

BY HERMAN L. AMMON AND SOVAN K. BHATTACHARJEE

*Department of Chemistry, University of Maryland, College Park, Maryland 20742, USA*

AND SYDNEY R. HALL AND BRIAN SKELTON

*Crystallography Center, University of Western Australia, Nedlands 6009, Australia*

(Received 7 June 1982; accepted 13 July 1983)

**Abstract.**  $M_r = 334.1$ , monoclinic,  $P2_1$ ,  $a = 5.972$  (1),  $b = 18.180$  (4),  $c = 10.669$  (3) Å,  $\beta = 92.25$  (1)°,  $V = 1157.5$  (8) Å<sup>3</sup>,  $D_x = 1.917$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 1.904$  mm<sup>-1</sup>,  $T = 294$  K,  $F(000) = 672$ . Final  $R = 0.027$  for 1916 observed reflections. The two crystallographically independent molecules have distinct conformations and symmetries ( $C_2$  and  $C_s$ ). A previous crystal structure report [Atovmyan, Gafurov, Golovina & Eremenko (1978). *Sov. Phys. Dokl.* **23**, 539–540] indicated that the conformer with the shorter intramolecular contacts was involved with the longer intermolecular contacts and *vice versa*, in support of the authors' hypothesis that 'van der Waals bonds possess the property of saturability'. The present investigation was carried out

to examine further this interesting hypothesis. On the basis of a 0.4 Å<sup>3</sup> difference in the calculated molecular volumes and a comparison of the inter- and intramolecular contacts, it is concluded that there are no significant differences in the molecular environments of the two molecules.

**Introduction.** We are investigating the crystal structures of a number of high-density, CF(NO<sub>2</sub>)<sub>2</sub>-containing compounds, which are of interest as possible organic explosives. Our crystallographic work on the title compound (I)

