Table 4. *Main torsion angles (°) for three known fentanyl derivatives*
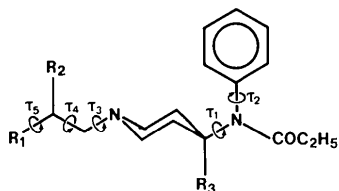
	R_1	R_2	R_3
R4333	Phenyl	—OH	—H
R30490	Phenyl	—H	—C—O—CH₃
R30730	Thienyl	—H	—C—O—CH₃

	τ_1	τ_2	$\tau_3{}^*$	τ_4	τ_5
R4333	−169	−95	22	167	128
R30490	−180	−83	43	170	101
R30730	−162	−87	49	163	35

* From the orientation of the nitrogen lone pair.

as R30490* (Koch, De Ranter, Rolies & Dideberg, 1976) and R30730* (Peeters, Blaton & De Ranter, 1979).

Packing is only governed by van der Waals interactions. Surprisingly, the Cl^- ion does not contribute to the formation of intermolecular hydrogen bonds. Indeed, Cl^- is bound to the piperidyl nitrogen |Cl—N(15) 3·120 (20) Å|, which is of course protonated, and to the hydroxy group |Cl—O(20)

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* Janssen Pharmaceutica internal code number.

3·002 (9) Å| of the same molecule by means of an intramolecular bridge. No other hydrogens are available for hydrogen bonding; moreover, all contact distances from Cl^- are greater than 3·50 Å.

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Tetrachlorophthalic Anhydride (TCPA), a Refinement

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Abstract. $C_8Cl_4O_3$, $M_r = 285 \cdot 9$, monoclinic, $P2_1/n$, $a = 13 \cdot 459$ (4), $b = 5 \cdot 789$ (1), $c = 12 \cdot 342$ (2) Å, $\beta = 91 \cdot 18$ (1)°, $V = 961 \cdot 4$ (6) Å^3 at 294 K, $Z = 4$, $D_m = 2 \cdot 00$, $D_x = 2 \cdot 00$ Mg m^{-3}, μ(Mo $K\alpha$) = $1 \cdot 217$ mm^{-1}. The atomic parameters of tetrachlorophthalic anhydride (TCPA), which had been determined photographically [Rudman (1971). *Acta Cryst.* B27, 262–269], were refined with diffractometer data. The refinements by block-diagonal least squares gave a final R value of 0·050 for 1835 independent reflections. All the chemically equivalent bond distances are almost equal within the e.s.d.'s. The results are in agreement

with Rudman's own refinement within the e.s.d.'s [Sake Gowda & Rudman (1982). *Acta Cryst.* B38, 2842–2845], which has been reported independently of this paper.

Introduction. In a series of structure determinations of electron donor–acceptor complexes containing TCPA as an electron acceptor, it was necessary to refine the atomic parameters of the TCPA molecule, which had been determined by Rudman based on photographic data (Rudman, 1971). After this paper was submitted, we were informed of the independent refinement of

the same compound by Sake Gowda & Rudman (1982, hereafter SG & R), whose results essentially agree with ours (hereafter UN & K).

A b-elongated crystal of dimensions $0.25 \times 0.40 \times 0.45$ mm, obtained from an acetonitrile solution, was mounted on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. Lattice constants were determined by a least-squares procedure with setting angles of 12 reflections with $21.6° < \theta < 29.2°$. The intensities were recorded with an $\omega-2\theta$ step-scan mode. All reflections $h0l$, $h + l$ odd, and $0k0$, k odd, were systematically absent, as required by the space group $P2_1/n$. Of the 2203 independent reflections with $2\theta < 55°$, 1838 with $|F_o| > 3\sigma(F)$ were used for further calculations (SG & R: 1615 reflections with Cu $K\alpha$ radiation). Lorentz and polarization, but no absorption, corrections were made.

The block-diagonal least-squares refinements were started with the parameters described in the literature (Rudman, 1971). After five cycles of refinements with anisotropic temperature parameters, the discrepancy index R was 0.057. At this stage of refinement, three F_o's (204, 21$\bar{3}$, and 21$\bar{2}$) were given zero weights because they were seriously affected by extinction. After four additional cycles, the final R was 0.050 and a weighted R_w was 0.083 for 1835 reflections. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = (F^*/F_o)^2$ for $|F_o| > F^*$, and $w = 1.0$ for $|F_o| < F^*$ ($F^* = 8.2$ on the absolute scale). In the final cycle, the maximum parameter shift/error was less than 0.009. Another refinement by full-matrix least squares with $w = 1.0$ for all the 1835 reflections gave $R = 0.051$ and $R_w = 0.059$. Although this gave a lower R_w value, the block-diagonal refinement yielded a better approximation to the molecular geometry expected on chemical grounds. Thus, the results of the block-diagonal least-squares refinement are described below.

A final difference Fourier synthesis showed no extra peaks. The atomic scattering factors were adopted from *International Tables for X-ray Crystallography* (1974). All computations were carried out on the HITAC M200H computer at the Computer Centre of the University of Tokyo with the *UNICS* (1967) program system.

Discussion. The final atomic parameters are listed in Table 1,† and the bond distances and angles are shown in Fig. 1 with the numbering scheme. They are in good agreement with the results of SG & R within the e.s.d.'s except for a few parameters. However, there are

Table 1. *Positional parameters* ($\times 10^5$ *for* Cl, $\times 10^4$ *for* O *and* C), *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*
Cl(1)	12119 (6)	8961 (15)	57265 (7)	3.67 (2)
Cl(2)	32456 (7)	18810 (17)	69399 (7)	3.94 (2)
Cl(3)	45250 (6)	60734 (18)	63000 (7)	4.06 (2)
Cl(4)	38895 (6)	91653 (17)	43099 (8)	3.99 (2)
O(1)	836 (2)	6539 (5)	3123 (2)	3.80 (6)
O(2)	1930 (2)	9376 (6)	2818 (2)	4.77 (8)
O(3)	25 (2)	3507 (6)	3828 (2)	4.84 (8)
C(1)	1664 (2)	4643 (5)	4523 (2)	2.61 (6)
C(2)	1942 (2)	3184 (5)	5365 (2)	2.61 (6)
C(3)	2852 (2)	3639 (5)	5905 (2)	2.67 (6)
C(4)	3444 (2)	5496 (6)	5591 (2)	2.81 (6)
C(5)	3157 (2)	6939 (5)	4727 (2)	2.71 (6)
C(6)	2254 (2)	6469 (5)	4214 (2)	2.62 (6)
C(7)	1724 (2)	7699 (6)	3314 (2)	3.21 (7)
C(8)	748 (2)	4680 (7)	3826 (3)	3.24 (7)

* The B_{eq} values were calculated with Hamilton's (1959) formula: $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.
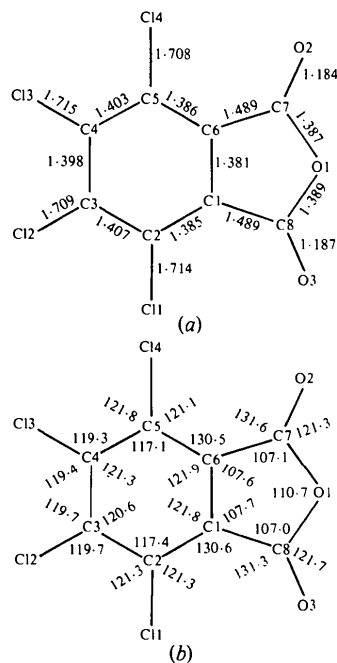

Fig. 1. (a) Bond distances (Å), and (b) angles (°). E.s.d.'s in the bond distances are within 0.003 Å (C—Cl's) and 0.005 Å (excluding Cl's), respectively, and those in bond angles are within $0.3°$.

significant differences in lattice constants, especially for a, between the two groups (SG & R and UN & K), the cause of which is not understandable. UN & K carried out the determination with two sets of least-squares procedures, each with 12 reflections, to give lattice constants in good agreement.

Table 2. *Equations of the planes and deviations of atoms from the planes*

A: TCPA-ring plane; *B*: benzene-ring plane; *C*: furan-ring plane

Equations of the planes

$$A \quad 0.4714X - 0.5934Y - 0.6524Z + 4.2533 = 0$$
$$B \quad 0.4807X - 0.5967Y - 0.6426Z + 4.1664 = 0$$
$$C \quad 0.4611X - 0.5896Y - 0.6632Z + 4.3071 = 0$$

Deviations of atoms from the planes ($\text{Å} \times 10^3$)

	A	B	C		A	B	C
Cl(1)	36	30	0	C(1)	19*	−2*	1*
Cl(2)	−4	29	−81	C(2)	8*	4*	−28
Cl(3)	−110	−76	−187	C(3)	−12*	0*	−66
Cl(4)	51	47	15	C(4)	−18*	−5*	−72
O(1)	−14*	−66	2*	C(5)	10*	6*	−26
O(2)	−46	−92	−34	C(6)	18*	−3*	0*
O(3)	−63	−111	−52	C(7)	−5*	−46	−1*
				C(8)	−6*	−47	−2*

Orthogonal coordinates, *X*, *Y* and *Z* (in Å), are defined parallel to the **a**, **b** and **c*** axial directions. Least-squares planes were calculated through the atoms marked with asterisks. E.s.d.'s in the atom-plane distances are about 0.001 Å for Cl and 0.003–0.004 Å for C and O atoms.

It is noticeable that all the chemically equivalent C—C and C—O bond lengths and angles are almost equal within the e.s.d.'s. This feature is similar to that in the furan ring of phthalic anhydride (Bates & Cutler, 1977), but different from that of a complexed TCPA molecule in naphthalene–TCPA (Wilkerson, Chodak & Strouse, 1975). The average C—Cl bond distance, 1.711 Å, is comparable to those of polychloroaromatic compounds in which the substituted Cl atoms occupy adjacent *ortho* positions to each other (Herbstein, 1979; Ito, Moriya, Kashino & Haisa, 1975; Brown & Strydom, 1974; Chu, Jeffrey & Sakurai, 1962).

Table 2 shows three least-squares planes about the TCPA molecule with the deviations of atoms from the planes. Each of the benzene and furan rings forms a fairly good plane. However, Cl atoms deviate much more than C atoms from the benzene plane. These deviations probably result from intramolecular steric repulsion, since strong intermolecular interactions do not exist about the Cl atoms: the shortest intermolecular Cl···Cl distances are 3.575 (1) Å for Cl(3ⁱ)···Cl(4ⁱⁱ) and 3.544 (2) Å for Cl(4ⁱ)···Cl(4ⁱⁱ) respectively [(i) x,y,z; (ii) $1 - x, 2 - y, 1 - z$].

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Complexe Moléculaire (2:1) d'Ethyl-13β Hydroxy-17β Dinor-18,19 17α-Pregnatriène-4,9,11 Yne-20 One-3 et de Toluène

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Abstract. $(C_{21}H_{24}O_2)_2 \cdot C_7H_8$, monoclinic, space group $P2_1$, $a = 7.513$ (4), $b = 21.150$ (8), $c = 12.745$ (6) Å, $\beta = 100.37$ (4)°, $Z = 4$. The structure was solved by direct methods. Full-matrix least-squares refinement with identical weights converged at $R = 0.084$, $R_w = 0.090$ for 3100 observed reflexions. The toluene