Difference-Density Distribution of a Prismane Derivative

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Abstract

Dimethyl propella[3]prismane dicarboxylate (dimethyl hexacyclo[9.5.0.0^{1,3}.0^{2,10}.0^{3,9}.0^{9,11}]hexadeca-2,10-dicarboxylate), $C_{20}H_{26}O_4$, $M_r = 330.4$, *Pnma*, $a = 15.129$ (1), $b = 14.853$ (1), $c = 7.768$ (1) Å, $V = 1745.7$ (5) Å^3, $Z = 4$, $D_x = 1.26$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71071 Å, $\mu = 0.0805$ mm^{-1}, $F(000) = 712$, $T = 95$ K. The steric strain of this polycyclic compound is indicated by bent bonds. From the difference electron-density distribution we determined a bending of 19° for the bonds in the plane of the three-membered ring and a bending of 7.5° in the planes of the four-membered rings.

Introduction

In the course of structural studies of cage compounds, we investigated the highly strained prismanes (Gleiter, Treptow, Oeser & Irngartinger, 1994; Wingert, Irngartinger, Kallfaß & Regitz, 1987; Irngartinger, Kallfaß, Litterst & Gleiter, 1987) and quadricyclanes (Irngartinger & Jahn, 1991; Irngartinger, Jahn, Rodewald, Kiers & Schenk, 1986).

The structure determinations of prismane derivatives suffer from deterioration on treating these compounds with X-rays (Wingert, Maas & Regitz, 1986; Maier *et al.*, 1986; Irngartinger, Kallfaß, Litterst & Gleiter, 1987; Srinivasan, Hu, Farona, Zarate & Youngs, 1987; Wingert, Irngartinger, Kallfaß & Regitz, 1987). In contrast to this instability, the propella[3]prismanes are stable against X-rays because of the protecting oligomethylene clamps. Therefore, we selected the propella[3]prismane (dimethyl hexacyclo[9.5.0.0^{1,3}.0^{2,10}.0^{3,9}.0^{9,11}]hexadeca-2,10-dicarboxylate) (I) for a difference-density determination.

(I)
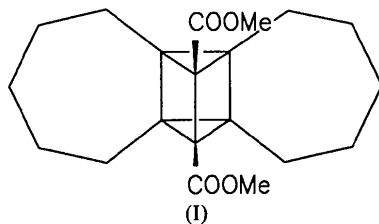
Discussion

The crystal compound (I) has *m* symmetry, with the mirror plane passing through the midpoints of the bonds C1—C1', C2—C2', C3—C3' and the atoms C6 and C9 (Fig. 1). In Fig. 2, the crystallographic mirror plane lies in the projection plane. The geo-
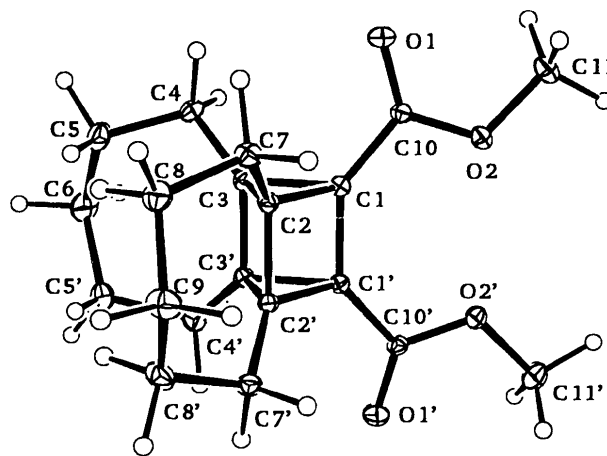
Fig. 1. Thermal ellipsoid plot of (I) with 50% probability (*ORTEP*II; Johnson, 1971).
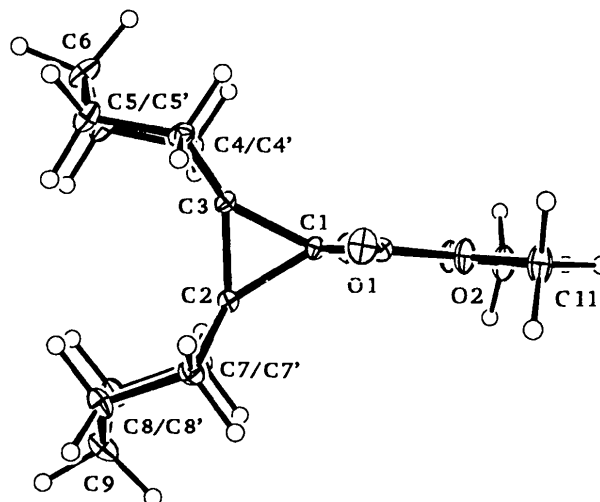
Fig. 2. Side view of (I).

metric parameters of the prismane frame determined at 243 K (Gleiter, Treptow, Oeser & Irngartinger, 1994) and at 95 K (Table 2) do not show significant differences, except the peripheral bond lengths of the substituents, which are shorter at low temperature because of smaller libration effects.

In addition to the protecting oligomethylene clamps, the prismane frame is substituted with two methylester groups. Because of their π-accepting properties, they shorten the distal bonds and lengthen the vicinal bonds of the cyclopropane subunits in (I), as also known for cyclopropane deriva-
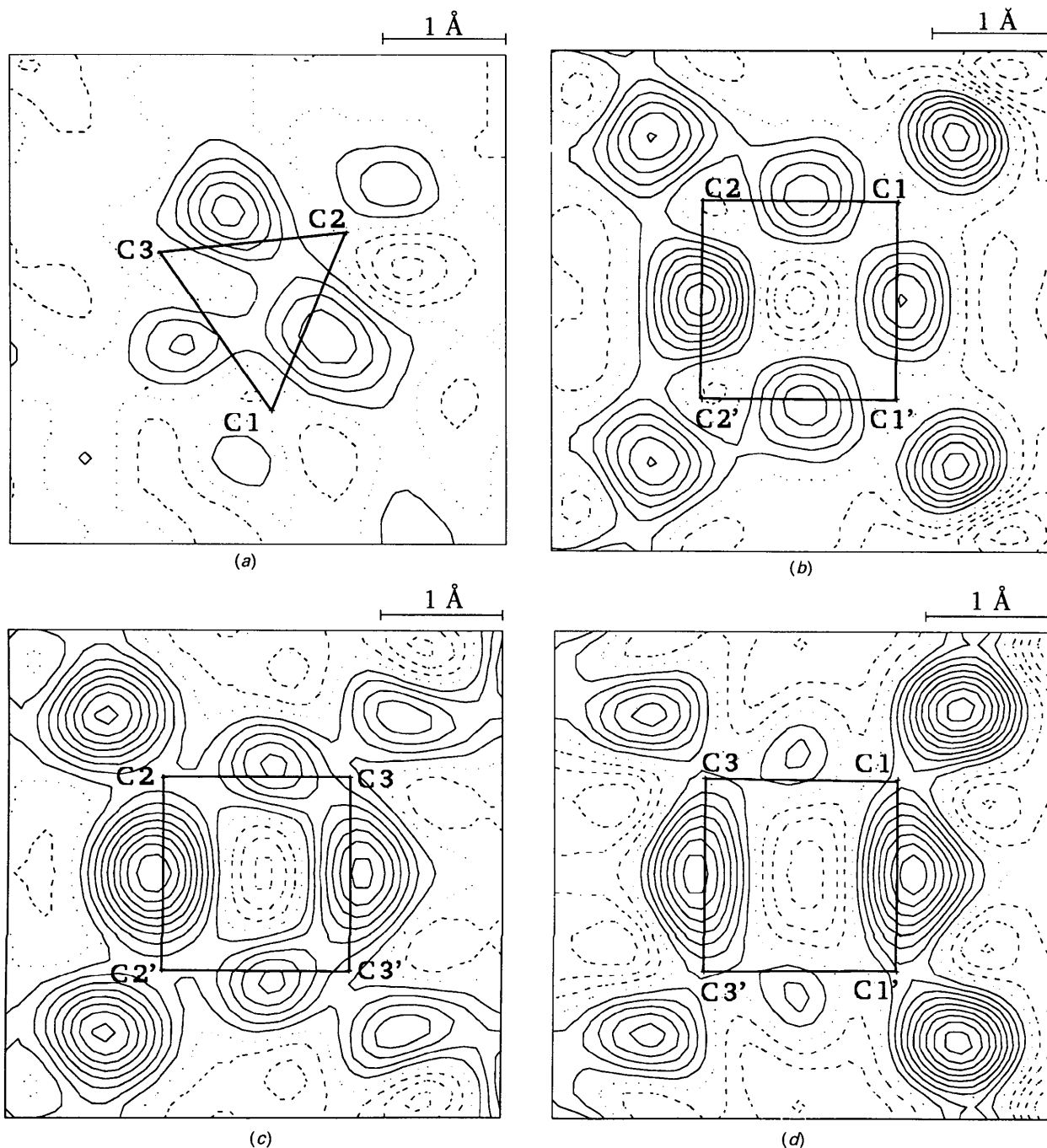

Fig. 3. Difference-density section 0.1 Å above the planes of the atoms: (a) C1, C2, C3; (b) C1, C2, C1', C2'; (c) C2, C3, C2', C3'; (d) C1, C3, C1', C3'. Contour interval is 0.05 e Å^{-3} (for all drawings).

tives (Allen, 1980). The average bond length of the three-membered ring is 1.539 (1) Å. Based on this value the shortening of the distal bond is 0.029 (1) Å, while the vicinal bonds are lengthened on average by 0.015 (1) Å. This electronic influence of the ester group on the three-membered ring subunit of pris-

mane (I) is 1.3 times larger than the corresponding effect in the less-strained cyclopropane derivatives. The deviation of only $-6.7\,(1)°$ (torsional angle O1—C10—C1—M23; M23 is the center of C2—C3) from the optimal *trans*-bisected orientation of the ester group is very small. In the prismane frame the
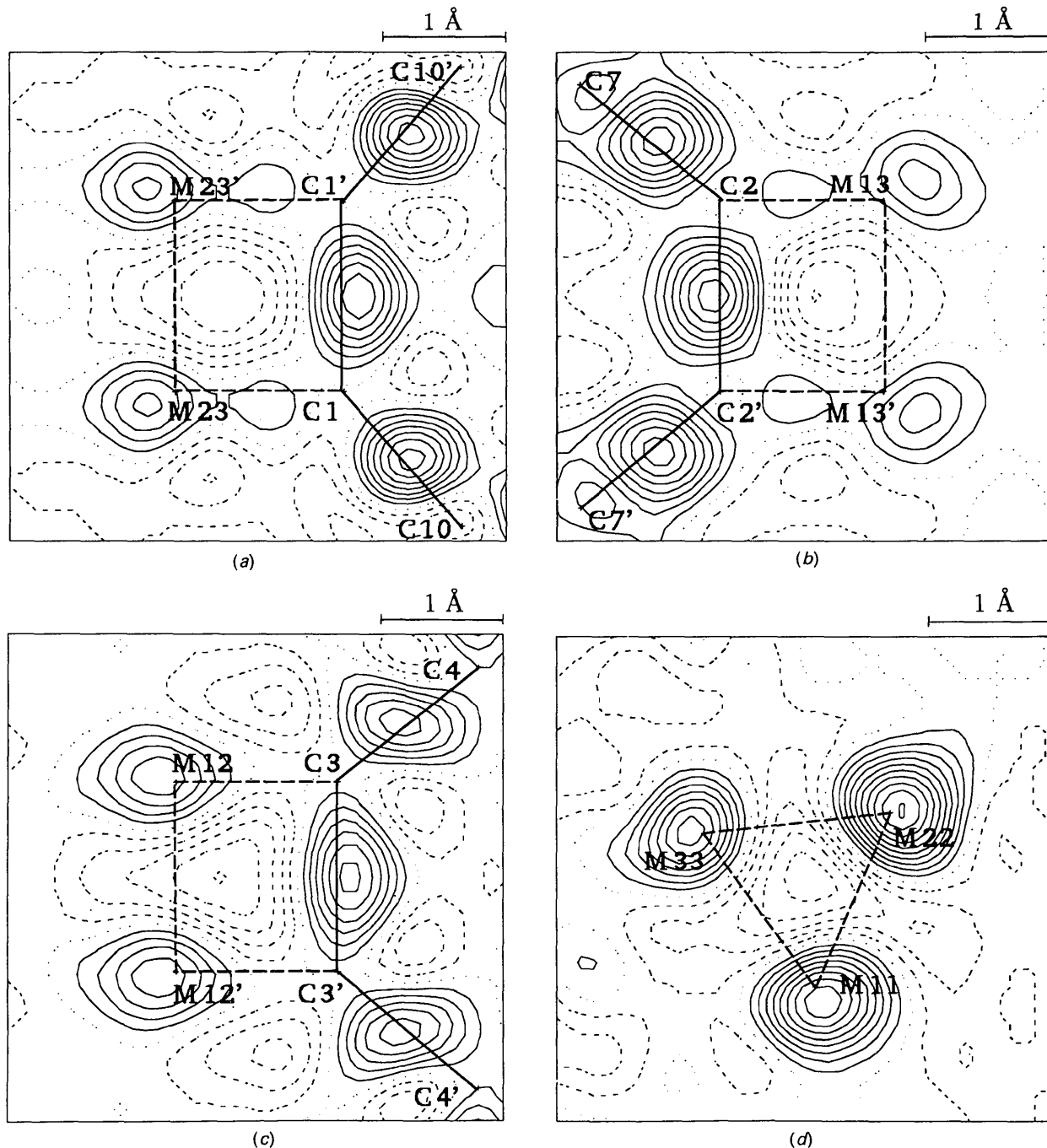

(a)

(b)

(c)

(d)

Fig. 4. Difference-density section through the planes: (a) C1, C1' and the midpoints of the opposite bonds C2—C3 (M23) and C2'—C3' (M23'); (b) C2, C2', M13, M13'; (c) C3, C3', M12, M12'; (d) difference-density section through the midpoints of the bonds C1—C1' (M11), C2—C2' (M22) and C3—C3' (M33).

angles between the planes of two four-membered rings are 60°, while those between the three- and four-membered rings amount to 90° (Table 2), as expected for a prism. Consequently, the bonds are bent (Fig. 3).

In monocyclic compounds the bonds are bent within the ring planes. In bicyclic ring systems the density maxima of the bridging bonds are no longer shifted within the ring planes, but within a plane bisecting the folding angle of both rings. As a consequence, the density maxima of the bridging bonds lie above the corresponding ring planes.

The density maxima of the bridging bonds common to two cyclobutyl subunits of compound (I) are shifted perpendicular to the bond axis within the plane bisecting the folding angle (Fig. 4d). This corresponds to a bending of 7.5°. The bridging bonds common to cyclopropyl and cyclobutyl subunits are bent to a higher degree of 19° (Fig. 4a–c). In these bonds there is a deviation from the bisecting plane corresponding to the different bending degree of the three- and four-membered rings. Therefore, the deviation of the density maximum from the three-membered ring plane is smaller than from the corresponding four-membered ring plane (Fig. 4a–c), because the bending contribution of the four-membered ring is smaller.

The electron densities of the bonds belonging only to four-membered rings (average 0.45 e Å^{-3}) are 1.9 times larger than the densities of those bonds which are common to a three- and a four-membered ring (average 0.24 e Å^{-3}). Obviously, the latter are more

Table 1. *Fractional atomic coordinates and equivalent displacement parameters of* (I)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (× 10^4 Å^2)
O1	0.85276 (4)	0.45559 (3)	0.07671 (8)	183 (2)
O2	0.77845 (4)	0.34814 (3)	−0.06996 (8)	168 (2)
C1	0.88660 (4)	0.30227 (4)	0.12707 (8)	107 (2)
C2	0.98841 (4)	0.30251 (4)	0.15784 (9)	106 (2)
C3	0.92661 (4)	0.30270 (4)	0.31045 (8)	110 (2)
C4	0.91722 (5)	0.36664 (4)	0.45769 (10)	153 (2)
C5	0.97760 (6)	0.33900 (5)	0.60775 (10)	198 (3)
C6	0.95268 (9)	1/4	0.69766 (15)	230 (4)
C7	1.05849 (4)	0.36690 (4)	0.10138 (10)	145 (2)
C8	1.14994 (5)	0.33881 (5)	0.16960 (12)	188 (3)
C9	1.18673 (7)	1/4	0.09709 (18)	208 (4)
C10	0.83847 (4)	0.37652 (4)	0.04535 (9)	116 (2)
C11	0.73306 (6)	0.41829 (5)	−0.16310 (13)	226 (3)

Table 2. *Geometric parameters* (Å, °) *of* (I)

O1—C10	1.219 (1)	C2—C3	1.510 (1)
O2—C10	1.343 (1)	C2—C7	1.494 (1)
O2—C11	1.443 (1)	C3—C3′	1.565 (1)
C1—C10	1.466 (1)	C3—C4	1.493 (1)
C1—C1′	1.553 (1)	C4—C5	1.537 (1)
C1—C2	1.559 (1)	C5—C6	1.542 (1)
C1—C3	1.548 (1)	C7—C8	1.539 (1)
C2—C2′	1.560 (1)	C8—C9	1.539 (1)
O1—C10—O2	123.75 (6)	C2—C2′—C7′	129.82 (5)
O1—C10—C1	123.38 (6)	C2—C3—C3′	89.89 (4)
O2—C10—C1	112.86 (5)	C2—C3—C4	131.41 (5)
C1—C1′—C2′	90.13 (4)	C2—C7—C8	111.30 (6)
C1—C1′—C3′	90.24 (5)	C3—C2—C1	60.56 (4)
C1—C1′—C10′	138.78 (6)	C3—C1—C10	126.13 (5)
C1—C2—C2′	89.87 (4)	C3—C2—C7	131.98 (6)
C1—C3—C2	61.28 (4)	C3—C3′—C4′	129.49 (6)
C1—C2—C7	131.13 (5)	C3—C4—C5	110.77 (6)
C1—C3—C3′	89.76 (4)	C4—C5—C6	115.29 (8)
C1—C3—C4	132.10 (5)	C5—C6—C5′	118.04 (9)
C2—C1—C3	58.16 (4)	C7—C8—C9	115.57 (7)
C2—C1—C10	123.75 (5)	C8—C9—C8′	118.05 (9)
C2—C2′—C3′	90.11 (5)	C10—O2—C11	115.45 (5)

weakened because of the higher strained cyclopropane subunits. Differences between equal bond types cannot be discussed by standard deviation reasoning (σ = 0.057 e Å^{-3}). The density sections of the substituents (Figs. 5 and 6) do not show any peculiarity, except for the fact that there is much noise in the lone-pair region of O1.

Data collection

An Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature device was used with a graphite-monochromator, Mo $K\alpha$ radiation and an ω–2θ scan. With the first set of intensities up to θ = 28°, the structural model of the measurement at 243 K (Gleiter, Treptow, Oeser & Irngartinger, 1994) was refined. The reflections which were expected to be observed (F_{calc} > 3.0) in the range 28–55° in θ were selected by computation and subsequently measured. Up to θ = 28°, three independent data sets (hkl twice, $\bar{h}kl$), and in the range 28 < θ < 55° two

$$\vdash\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!1\ \text{Å}\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!\dashv$$

Fig. 5. Difference-density section through the ester group.

data sets (*hkl* twice), were collected. Intensities were corrected for Lorentz and polarization effects. A numerical absorption correction (Coppens, Leiserowitz & Rabinovich, 1965) was applied. The refinement was performed using a full-matrix least squares technique on F^2 (C and O anisotropically refined, H atoms were located in difference maps and refined isotropically), according to the following scheme:

(*a*) Refinement of all atoms and the scale factor with low-order reflections up to $\sin\theta/\lambda = 0.66$ Å^{-1}. 1764 observed reflections [$F^2 \geq 3.0\sigma(F^2)$], 10.5 observations per variable, $R = 0.037$, $R_w = 0.046$, $S = 1.702$.

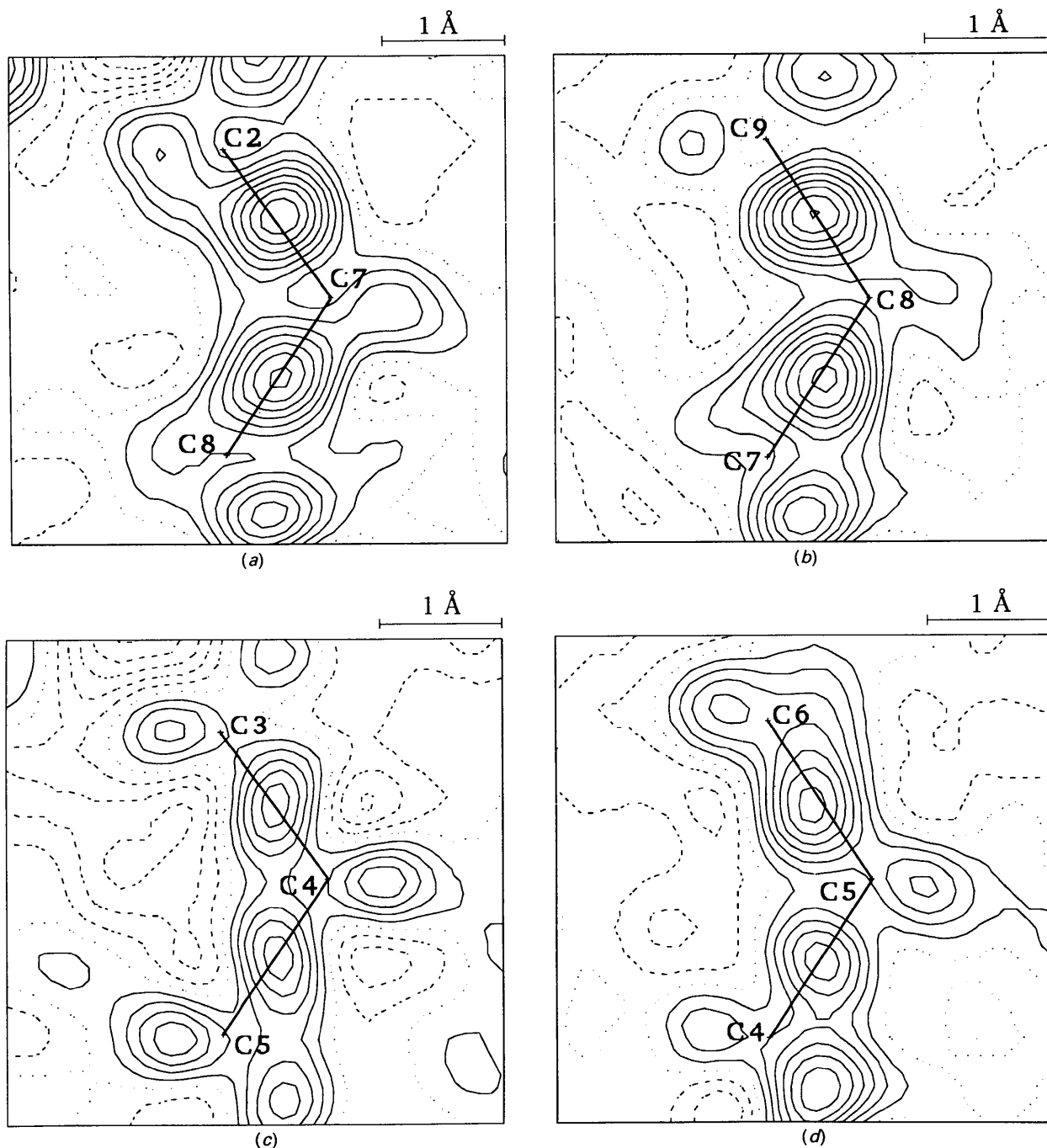Fig. 6. Difference-density section through the planes of: (*a*) C2, C7, C8; (*b*) C7, C8, C9; (*c*) C3, C4, C5; (*d*) C4, C5, C6.

Table 3. Crystal data, data collection and refinement parameters

Crystal data

Chemical formula	$C_{20}H_{26}O_4$
Molecular weight	330.4
Crystal system	Orthorhombic
Space group	Pnma
a (Å)	15.129 (1)
b (Å)	14.853 (1)
c (Å)	7.768 (1)
V (Å^3)	1745.7(5)
Z	4
D_x (Mg m^{-3})	1.26
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.7107
No. of reflections for cell parameters	75
θ range for cell parameters (°)	11–24
μ (mm^{-1})	0.0805
Temperature (K)	95
Crystal color	Colorless
Crystal form	Cubical
Crystal size (mm)	0.5 × 0.5 × 0.4

Data collection

Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans
Absorption correction	Analytical by integration from crystal shape
T_{min}	0.961
T_{max}	0.971
No. of measured reflections	10 896
No. of independent reflections	5174
No. of observed reflections	4736
Observation criterion	$[F > 3.0\sigma(F)]$
R_{int}	0.029
θ_{max} (°)	55
Range of h, k, l	$-19 \rightarrow h \rightarrow 34$
	$0 \rightarrow k \rightarrow 34$
	$0 \rightarrow l \rightarrow 17$
No. of standard reflections	4
Frequency of standard reflections (min)	60
Intensity variation (%)	11.0

Refinement

Refinement on	F^2
$R(F)$	0.037 (LO), 0.041 (HO)
$wR(F^2)$	0.046 (LO), 0.042 (HO)
S	1.702 (LO), 0.915 (HO)
No. of reflections used in refinement	1764 (LO), 2967 (HO)
No. of parameters used	168 (LO), 112 (HO)
H-atom refinement	All H-atom parameters refined
Weighting scheme	$w = 1/\sigma(F_o)^2 = 4F_o^2/\sigma(F_o^2)^2$
$(\Delta/\sigma)_{max}$	< 0.01
$\Delta\rho_{max}$ (e Å^{-3})	0.68
Source of atomic scattering factors	International Tables for X-ray Crystallography (1974, Vol. IV, Table 2.2B)

(b) Refinement of the C and O atoms and the scale factor with high-order reflections of the Bragg angle range $0.66 < \sin\theta/\lambda < 1.15$ Å^{-1}. The H atoms have been taken unchanged from (a). 2967 observed reflections, 26.5 observations per variable, $R = 0.041$, $R_w = 0.042$, $S = 0.915$.

(c) Refinement of the scale factor separately from reflections of $\sin\theta/\lambda = 0$–1.15 Å^{-1}. 4731 observed reflections, $R = 0.043$, $R_w = 0.051$, $S = 1.397$.

(d) Calculation of the structure factors (F_{calc}) within the range $\sin\theta/\lambda = 0$–0.66 Å^{-1} with the structural model of the high-order refinement (b) and scaling of the observed structure factors (F_{obs}) in the same range with the scale factor of (c). 1764 observed reflections, $R = 0.044$, $R_w = 0.056$, $S = 1.978$.

The difference densities were calculated with the structure factors F_{obs} and F_{calc} of (d). The atomic coordinates of the C atoms and the equivalent displacement parameters of the refinement (b) are given in Table 1. According to the rigid bond test (Hirshfeld, 1976), the difference between the thermal vibration contribution of two atoms along the bond connecting both atoms is for all cases below 0.001 Å^2 and has an average value of 0.0004 Å^2.

All calculations were carried out with the MolEN program package (Fair, 1990). Further crystal and refinement data of compound (I) are given in Table 3.*

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