C21	−1.1249 (10)	0.0592 (3)	0.2225 (3)	0.0443
C22	−0.9520 (9)	0.0859 (3)	0.2898 (3)	0.0433
C23	−0.9982 (8)	0.1483 (3)	0.3198 (3)	0.0372
C24	−0.8114 (8)	0.1743 (3)	0.3916 (3)	0.0384
C25	−0.8684 (8)	0.2385 (3)	0.4302 (3)	0.0361
C26	−0.7041 (8)	0.2608 (3)	0.5022 (3)	0.0412
C27	−0.7666 (8)	0.3202 (3)	0.5387 (3)	0.0400
C28	−0.9780 (8)	0.3578 (3)	0.5070 (3)	0.0377
C29	−1.1424 (8)	0.3363 (3)	0.4360 (3)	0.0361
C30	−1.0878 (8)	0.2750 (3)	0.3962 (3)	0.0338
C31	−1.2652 (8)	0.2511 (3)	0.3228 (3)	0.0346
C32	−1.2133 (8)	0.1869 (3)	0.2847 (3)	0.0366
C33	−1.3752 (8)	0.1600 (3)	0.2143 (3)	0.0393
C34	−1.3336 (9)	0.0964 (3)	0.1845 (3)	0.0446
C35	−0.9866 (8)	0.4188 (3)	0.5616 (3)	0.0414
C36	−0.7459 (9)	0.4094 (3)	0.6290 (3)	0.0466
C37	−0.6359 (10)	0.4879 (3)	0.5346 (4)	0.0563
C38	−0.9278 (9)	0.4830 (3)	0.5157 (3)	0.0471
C39	−1.2475 (15)	−0.0328 (3)	0.1320 (4)	0.0692
C40	−1.7350 (11)	0.1734 (4)	0.1046 (4)	0.0575

Table 2. *Selected bond lengths* ($\sigma \sim 0.006$ Å) *and angles* ($\sigma \sim 0.4°$)

C=O	1.218, 1.221 (not hydrogen bonded) 1.236, 1.236 (hydrogen bonded)
C—OH/OMe	1.339–1.354
C—OMe	1.420–1.438
C—C(=O)	1.462–1.487
C—C(aromatic)	1.367–1.418
C—C(5-ring)	1.496–1.555
C—O(5-ring)	1.357–1.382, 1.441–1.452
C—O—C(5-ring)	108.0–109.0
C—O—Me	116.7–119.2

Intramolecular hydrogen bonds (H atoms from difference map)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1···O2	0.99	1.65	2.547	147
O12—H12···O9	1.09	1.64	2.518	134

The structure was determined by direct methods. H atoms were placed in calculated positions, except those involved in the hydrogen bonds, which were positioned from difference syntheses. While the opposite configuration has marginally higher *R* factors (in the penultimate refinement round with a weighting scheme slightly different from that used in the final refinement cycles, $R = 0.0651$ *versus* 0.0649, $wR = 0.0736$ *versus* 0.0734), we hesitate to claim that we have established the absolute configuration. The data presented in this paper and Fig. 1 refer to the configuration with the lower pair of *R* values.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1990). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We thank Professor E. Bullock for crystals and the Natural Sciences and Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bullock, E., Kirkaldy, D., Roberts, J. C. & Underwood, J. G. (1963). *J. Chem. Soc.* pp. 829–835.

Molecular Structure Corporation (1985). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1990). *TEXRAY. TEXSAN Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1995). C**51**, 274–277

Hexaethyl (3,5-Di-*tert*-butyl-4-hydroxyphenyl)methanetrisphosphonate at 173 K

Matthias Ramm

Freie Universität Berlin, Institut für Kristallographie, Takustrasse 6, D-14195 Berlin, Germany

Burkhard Costisella and Hans Gross

Institut für Angewandte Chemie Adlershof e.V,, Rudower Chaussee 5, D-12484 Berlin, Germany

(*Received* 22 *December* 1993; *accepted* 11 *August* 1994)

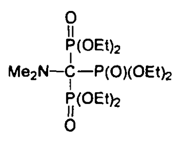
Abstract

In contrast to the liquid phase, in the solid state three ^{31}P NMR signals were found for the title compound, $C_{27}H_{51}O_{10}P_3$. The nonequivalence of the signals can be attributed to a hydrogen bond. The molecules bonded *via* hydrogen bonds form chains.

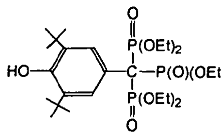
Comment

The hexaester (1) (Kuchar, Pasternak & Kirsanov, 1972) was the first *gem*-trisphosphonate structure to be solved unambiguously. The structures of the arylmethanetrisphosphonate ester (2) (Gross, Ozegowski, & Costisella, 1990) and the unsubstituted methanetrisphosphonate (3) (Gross, Costisella, Keitel & Ozegowski, 1993) were determined by ^{13}C NMR in solution. The methine C atoms of (2) and (3) showed quadruplets due to the coupling with the three equivalent P nuclei. The ^{31}P NMR spectra in $CHCl_3$ are very simple. Only one signal is observable for the equivalent P nuclei. In contrast, the ^{31}P solid-state NMR spectrum of (2) revealed three comparable signals. Two signals appear in the ^{31}P solid-state NMR spectrum of (4) (Costisella & Ramm, 1994). In the present paper we report the X-ray structure analysis of (2).

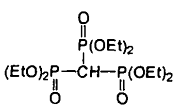
Acta Crystallographica Section C
ISSN 0108-2701 ©1995



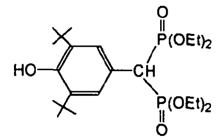
(1)



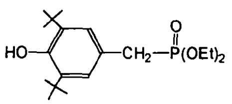
(2)



(3)



(4)



(5)

The object of this investigation was to explain the non-equivalence of the ^{31}P solid-state NMR signals. The NMR signals will be compared with those of tetraethyl (3,5-di-*tert*-butyl-4-hydroxyphenyl)methanebisphosphonate (4) and diethyl (3,5-di-*tert*-butyl-4-hydroxyphenyl)methanephosphonate (5). A previous X-ray structure analysis at room temperature (Ramm & Schulz, 1990) showed that the positions of the O—C_2H_5 groups could not be determined with accuracy due to high thermal motion. Therefore, the structure analysis was performed at 173 K.

A drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. The arrangement of the atoms around the P atoms is of special interest. Each P atom is coordinated by three O atoms and the C1 atom, forming a slightly distorted tetrahedron. The tetrahedral angles of the P atoms show the same systematic deviations from the ideal value. The three angles enclosing the P═O double bond are larger, the other three are smaller. This corresponds to the structure of α-substituted phosphoryl compounds (Kulpe & Seidel, 1979).

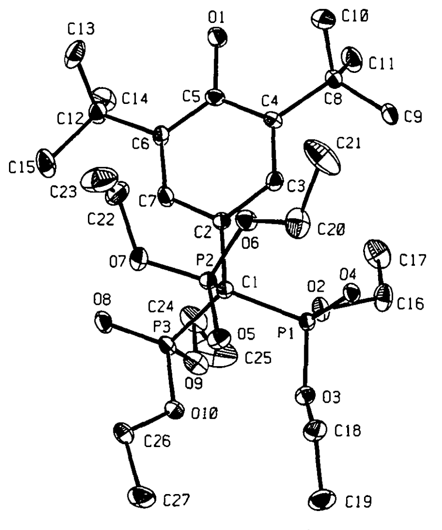


Fig. 1. *ORTEP* (Johnson, 1971) drawing of the molecular structure showing the crystallographic numbering scheme (50% probability displacement ellipsoids).

Table 3 gives the solution and solid-state ^{31}P NMR signals. The spectra of the solutions of (2), (4) and (5) show only one signal despite the different number of P atoms. The P atoms of (2) and (4) are magnetically equivalent due to the mobility of the molecule. In contrast, in the ^{31}P solid-state NMR spectra the number of signals corresponds to the number of P atoms.

Details of the packing of the molecules are shown in Fig. 2. The molecular arrangement is determined by an intermolecular hydrogen bond. The hydrogen bond formed between O1 and O5^i is characterized by O1$\cdots$O5^i = 2.725 (2), H1O$\cdots$O5^i = 2.09 (3) Å, O1—H1O$\cdots$O5^i = 143 (3)° [symmetry code: (i) x, $1.5 - y$, $0.5 + z$]. The molecules bonded *via* hydrogen bonds form chains.

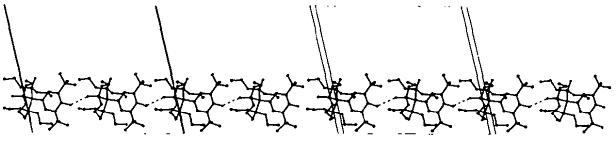


Fig. 2. *SCHAKAL*92 (Keller, 1992) drawing of one chain of molecules formed by hydrogen bonds (dashed lines represent hydrogen bonds).

The different solid-state NMR signals of (2) and (4) can be attributed to the different interactions of the phosphoryl O atoms of the diethylphosphono groups. As a result of the participation of O5 in the hydrogen bond, atom P2 is magnetically nonequivalent to the other P atoms. Therefore, three and two NMR signals appear for (2) and (4), respectively. The hydrogen bond of (4) was determined by X-ray structure analysis (Costisella & Ramm, 1994).

If recrystallized from ethyl acetate, (2) forms another monoclinic structure [space group $P2_1/c$, a = 10.202 (7), b = 36.65 (2), c = 9.341 (5) Å, β = 94.46 (5)°]. The molecular arrangement in this structure is also determined by an O1$\cdots$O5 hydrogen bond (Ramm & Schulz, 1990).

Experimental

Crystal data

$C_{27}H_{51}O_{10}P_3$
M_r = 628.52
Monoclinic
$P2_1/c$
a = 17.383 (3) Å
b = 9.538 (1) Å
c = 20.056 (3) Å
β = 102.60 (1)°
V = 3245.2 (8) Å^3
Z = 4
D_x = 1.287 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 36–40°
μ = 2.12 mm^{-1}
T = 173 K
Prism
0.27 × 0.24 × 0.23 mm
Colourless
Crystal source: crystallization from toluene

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.983$, $T_{\max} = 0.999$
6253 measured reflections
6087 independent reflections
4495 observed reflections $[F > 3.0\sigma(F)]$
$R_{\rm int} = 0.048$
$\theta_{\max} = 65°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 23$
2 standard reflections frequency: 60 min intensity decay: 7.5%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.050$
$S = 1.807$
4495 reflections
566 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.307$ e Å^{-3}
$\Delta\rho_{\min} = -0.118$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $2.6(5) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
P1	0.17149 (3)	0.44389 (6)	0.49817 (3)	0.0136 (1)
P2	0.28545 (3)	0.67443 (6)	0.48795 (3)	0.0145 (1)
P3	0.34802 (3)	0.40112 (6)	0.55606 (3)	0.0164 (1)
O1	0.21986 (9)	0.7929 (2)	0.78729 (8)	0.0262 (4)
O2	0.15128 (8)	0.3546 (2)	0.55768 (7)	0.0190 (4)
O3	0.19012 (9)	0.3273 (2)	0.44867 (7)	0.0179 (4)
O4	0.11155 (8)	0.5456 (2)	0.46537 (7)	0.0175 (4)
O5	0.28512 (9)	0.6286 (2)	0.41804 (7)	0.0205 (4)
O6	0.22661 (9)	0.7947 (2)	0.49486 (8)	0.0205 (4)
O7	0.36751 (9)	0.7334 (2)	0.52500 (8)	0.0226 (4)
O8	0.42251 (9)	0.4552 (2)	0.59640 (8)	0.0233 (4)
O9	0.31481 (9)	0.2673 (2)	0.58579 (8)	0.0232 (4)
O10	0.35323 (8)	0.3468 (2)	0.48339 (7)	0.0186 (4)
C1	0.2652 (1)	0.5296 (2)	0.5426 (1)	0.0136 (5)
C2	0.2546 (1)	0.5977 (2)	0.6109 (1)	0.0138 (5)
C3	0.1814 (1)	0.6476 (2)	0.6174 (1)	0.0154 (5)
C4	0.1700 (1)	0.7119 (2)	0.6767 (1)	0.0145 (5)
C5	0.2356 (1)	0.7287 (2)	0.7314 (1)	0.0166 (5)
C6	0.3107 (1)	0.6816 (2)	0.7262 (1)	0.0162 (6)
C7	0.3180 (1)	0.6177 (3)	0.6659 (1)	0.0181 (6)
C8	0.0872 (1)	0.7639 (2)	0.6815 (1)	0.0180 (6)
C9	0.0259 (1)	0.7321 (3)	0.6161 (1)	0.0215 (6)
C10	0.0879 (2)	0.9238 (3)	0.6911 (1)	0.0302 (7)
C11	0.0594 (1)	0.6912 (3)	0.7402 (1)	0.0280 (7)
C12	0.3842 (1)	0.6979 (3)	0.7850 (1)	0.0222 (6)
C13	0.4002 (1)	0.8533 (3)	0.8027 (1)	0.0297 (7)
C14	0.3730 (1)	0.6135 (3)	0.8474 (1)	0.0284 (7)
C15	0.4588 (1)	0.6395 (4)	0.7655 (1)	0.0392 (8)
C16	0.0711 (1)	0.3212 (3)	0.5619 (1)	0.0250 (7)
C17	0.0683 (2)	0.3108 (3)	0.6354 (1)	0.0315 (7)
C18	0.1862 (1)	0.3530 (3)	0.3765 (1)	0.0225 (6)
C19	0.1920 (2)	0.2134 (3)	0.3432 (1)	0.0306 (7)
C20	0.1653 (2)	0.8456 (3)	0.4378 (1)	0.0307 (7)
C21	0.1214 (2)	0.9566 (3)	0.4658 (2)	0.0486 (9)
C22	0.3805 (2)	0.8530 (3)	0.5708 (1)	0.0293 (7)
C23	0.4009 (2)	0.9778 (3)	0.5336 (2)	0.0486 (9)
C24	0.3076 (2)	0.2612 (3)	0.6568 (1)	0.0289 (7)
C25	0.2865 (2)	0.1157 (3)	0.6711 (2)	0.0483 (9)
C26	0.4220 (1)	0.3822 (3)	0.4553 (1)	0.0222 (6)
C27	0.4136 (2)	0.3099 (3)	0.3888 (1)	0.0321 (7)

Table 2. *Selected geometric parameters* (Å, °)

P1—O2	1.567 (2)	C2—C3	1.392 (3)
P1—O3	1.571 (2)	C2—C7	1.391 (3)
P1—O4	1.470 (2)	C3—C4	1.390 (3)
P1—C1	1.866 (2)	C4—C5	1.409 (3)
P2—O5	1.468 (2)	C4—C8	1.546 (3)
P2—O6	1.563 (2)	C5—C6	1.407 (3)
P2—O7	1.562 (2)	C6—C7	1.383 (3)
P2—C1	1.844 (2)	C6—C12	1.546 (3)
P3—O8	1.463 (2)	C8—C9	1.528 (3)
P3—O9	1.571 (2)	C8—C10	1.537 (3)
P3—O10	1.568 (2)	C8—C11	1.531 (3)
P3—C1	1.865 (2)	C12—C13	1.535 (4)
O1—C5	1.356 (3)	C12—C14	1.536 (3)
O2—C16	1.451 (3)	C12—C15	1.537 (4)
O3—C18	1.455 (3)	C16—C17	1.489 (3)
O6—C20	1.466 (3)	C18—C19	1.503 (4)
O7—C22	1.451 (3)	C20—C21	1.485 (4)
O9—C24	1.457 (3)	C22—C23	1.487 (4)
O10—C26	1.468 (3)	C24—C25	1.479 (4)
C1—C2	1.564 (3)	C26—C27	1.479 (4)
O2—P1—O3	102.00 (9)	C1—C2—C7	121.9 (2)
O2—P1—O4	116.41 (8)	C3—C2—C7	117.5 (2)
O2—P1—C1	101.07 (9)	C2—C3—C4	122.3 (2)
O3—P1—O4	114.09 (9)	C3—C4—C5	118.4 (2)
O3—P1—C1	109.45 (9)	C3—C4—C8	120.2 (2)
O4—P1—C1	112.58 (9)	C5—C4—C8	121.4 (2)
O5—P2—O6	115.92 (9)	O1—C5—C4	114.9 (2)
O5—P2—O7	112.00 (9)	O1—C5—C6	124.4 (2)
O5—P2—C1	112.51 (9)	C4—C5—C6	120.8 (2)
O6—P2—O7	103.95 (9)	C5—C6—C7	118.0 (2)
O6—P2—C1	106.47 (9)	C5—C6—C12	122.4 (2)
O7—P2—C1	105.07 (9)	C7—C6—C12	119.6 (2)
O8—P3—O9	115.52 (9)	C2—C7—C6	123.1 (2)
O8—P3—O10	114.02 (9)	C4—C8—C9	111.5 (2)
O8—P3—C1	114.2 (1)	C4—C8—C10	110.1 (2)
O9—P3—O10	100.65 (9)	C4—C8—C11	110.9 (2)
O9—P3—C1	104.64 (9)	C9—C8—C10	106.8 (2)
O10—P3—C1	106.36 (9)	C9—C8—C11	107.0 (2)
P1—O2—C16	122.8 (1)	C10—C8—C11	110.4 (2)
P1—O3—C18	122.6 (2)	C6—C12—C13	110.5 (2)
P2—O6—C20	123.5 (2)	C6—C12—C14	109.8 (2)
P2—O7—C22	125.7 (2)	C6—C12—C15	111.8 (2)
P3—O9—C24	121.4 (2)	C13—C12—C14	111.5 (2)
P3—O10—C26	119.9 (1)	C13—C12—C15	106.8 (2)
P1—C1—P2	107.7 (1)	C14—C12—C15	106.3 (2)
P1—C1—P3	110.3 (1)	O2—C16—C17	108.2 (2)
P1—C1—C2	110.1 (1)	O3—C18—C19	107.4 (2)
P2—C1—P3	109.7 (1)	O6—C20—C21	106.6 (2)
P2—C1—C2	106.5 (1)	O7—C22—C23	109.5 (2)
P3—C1—C2	112.3 (1)	O9—C24—C25	107.8 (2)
C1—C2—C3	120.6 (2)	O10—C26—C27	108.1 (2)

Table 3. ^{31}P *NMR signals of* (2), (4) *and* (5) (δ p.p.m.)

	(2)	(4)	(5)
Solution ($CHCl_3$)	16.97*	19.95*	27.30
Solid state	14.05	17.29†	23.80
	16.48	18.70	
	17.88		

* Gross, Keitel & Costisella (1991).
† Costisella & Ramm (1994).

Data were corrected for Lorentz and polarization factors, extinction and absorption. NMR–MAS spectra were recorded on a Bruker MSL 400 spectrometer (162.00 MHz; standard: adamantane external; rotation: 11 kHz) at room temperature.

Data collection: Enraf–Nonius CAD-4 diffractometer control software (Enraf–Nonius, 1988). Cell refinement: Enraf–Nonius CAD-4 diffractometer control software. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN LSFM*. Software used to prepare material for publication: *PLATON*92 (Spek, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Costisella, B. & Ramm, M. (1994). In preparation.
Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Gross, H., Costisella, B., Keitel, I. & Ozegowski, S. (1993). *Phosphorus Sulfur Silicon.* In the press.
Gross, H., Keitel, I. & Costisella, B. (1991). *Phosphorus Sulfur Silicon*, **62**, 35–45.
Gross, H., Ozegowski, S. & Costisella, B. (1990). *Phosphorus Sulfur Silicon*, **47**, 7–13.
Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
Keller, E. (1992). *SCHAKAL92. A Computer Program for the Graphic Representation of Molecular and Crystallographic Models.* Univ. of Freiburg, Germany.
Kuchar, V. P., Pasternak, V. I. & Kirsanov, A. V. (1972). *Zh. Obshch. Khim.* **42**, 1169–1171.
Kulpe, S. & Seidel, I. (1979). *Krist. Tech.* **14**, 1089–1096.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Ramm, M. & Schulz, B. (1990). Unpublished results.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1995). C**51**, 277–279

(*E*,*E*)-4-[3-(3,5-Dichloro-2-hydroxyphenylazo)-2-morpholino-2-butenoyl]morpholine

Matthias Ramm

Freie Universität Berlin, Institut für Kristallographie, Takustrasse 6, D-14195 Berlin, Germany

Hendrik Baumann and Klaus Kirschke

Institut für Angewandte Chemie, D-12484 Berlin, Germany

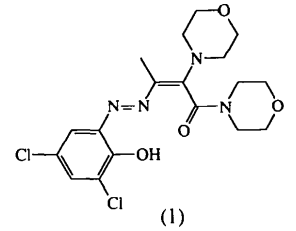
(*Received* 29 *November* 1993; *accepted* 11 *August* 1994)

Abstract

The title morpholide, $C_{18}H_{22}Cl_2N_4O_4$, shows an (*E*,*E*) configuration. An intramolecular hydrogen bond is formed between O4 and N3.

Comment

We synthesized (*E*,*E*)-4-[3-(3,5-dichloro-2-hydroxyphenylazo)-2-morpholino-2-butenoyl]morpholine (1) to investigate its catalytic and complexing properties. A satisfactory determination of the configuration of the C═C double bond was not possible by usual NMR techniques. Therefore, the compound was purified by column chromatography and an X-ray structure analysis performed.



(1)

A drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. The bond lengths indicate that N3—N4 and C1—C11 are double bonds. The molecule shows an (*E*,*E*) configuration. An intramolecular hydrogen bond is formed between O4 and N3 [O4···N3 2.593 (2), H4O···N3 1.810 (3) Å, O4—H4O···N3 150 (3)°]. The packing of the molecules in the unit cell is shown in Fig. 2. The molecular arrangement is determined by van der Waals interactions.

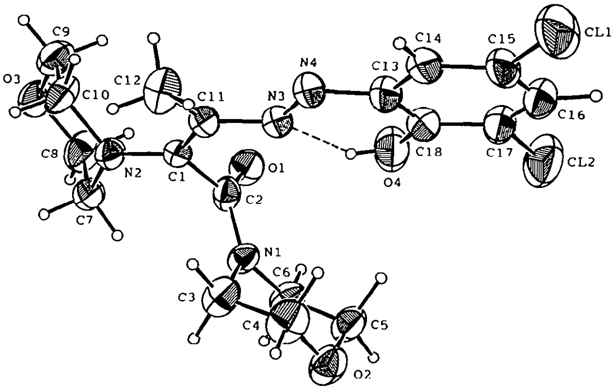


Fig. 1. *ORTEP* (Johnson, 1971) drawing of the molecular structure showing the crystallographic numbering scheme (50% probability displacement ellipsoids, hydrogen bond shown by dashed line).

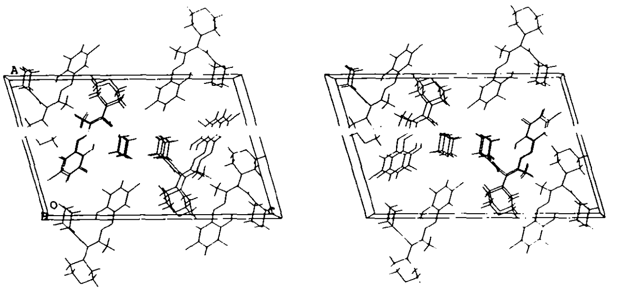


Fig. 2. *PLUTO* (Motherwell & Clegg, 1976) drawing of the molecular packing.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995