

$\text{H}_5\text{P}_2\text{O}_8 \cdot \text{H}_2\text{PO}_4^-$ (Bagieu-Beucher, Durif & Guitel, 1989) is noteworthy due to its anionic aggregate. The anion should be written $\text{H}_7\text{P}_3\text{O}_{12}^{3-}$. These three materials which show various steps in the aggregation of H_2PO_4^- anions and H_3PO_4 molecules allow us to imagine the possible formation of clathrate structures with monophosphoric acid.

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Structures of 2,3,5,6-Tetrahalogeno-3',4'-diphenylspiro[2,5-cyclohexadiene-1,2'-oxetan]-4-one, $\text{C}_{20}\text{H}_{12}\text{O}_2\text{X}_4$ ($\text{X} = \text{F}, \text{Cl}$ and Br)

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Abstract. Fluoro compound: $\text{C}_{20}\text{H}_{12}\text{F}_4\text{O}_2$, $M_r = 360.31$, $F(000) = 736$, (I): *cis* isomer, triclinic, $P\bar{1}$, $a = 10.938$ (1), $b = 16.336$ (2), $c = 9.925$ (2) Å, $\alpha = 93.82$ (1), $\beta = 103.92$ (1), $\gamma = 104.00$ (1)°, $V = 1655.5$ (5) Å³, $Z = 4$, $D_m = 1.43$, $D_x = 1.45$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 1.093$ mm⁻¹, $R = 0.057$ for 4740 observed reflections. (II): *trans* isomer, monoclinic, $P2_1/c$, $a = 7.895$ (2), $b = 13.708$ (4), $c = 15.456$ (3) Å, $\beta = 94.54$ (2)°, $V = 1667.5$ (7) Å³, $Z = 4$, $D_m = 1.42$, $D_x = 1.44$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.133$ mm⁻¹, $R = 0.058$ for 1655 observed reflections. Chloro compound: $\text{C}_{20}\text{H}_{12}\text{Cl}_4\text{O}_2$, $M_r = 426.13$, $F(000) = 432$, (III): *trans* isomer, triclinic, $P\bar{1}$, $a = 10.060$ (2), $b = 10.652$ (2), $c = 10.030$ (2) Å, $\alpha = 98.98$ (2), $\beta = 116.36$ (1), $\gamma = 76.76$ (1)°, $V = 935.6$ (3) Å³, $Z = 2$, $D_x = 1.51$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.644$ mm⁻¹, $R = 0.034$ for 3211 observed reflections. Bromo compound: $\text{C}_{20}\text{H}_{12}\text{Br}_4\text{O}_2$, $M_r = 603.93$, $F(000) = 576$, (IV): *trans* isomer, triclinic, $P\bar{1}$, $a =$

10.354 (2), $b = 10.885$ (2), $c = 10.149$ (2) Å, $\alpha = 98.91$ (2), $\beta = 114.55$ (2), $\gamma = 75.72$ (2)°, $V = 1006.5$ (4) Å³, $Z = 2$, $D_x = 1.99$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 8.480$ mm⁻¹, $R = 0.042$ for 2434 observed reflections. All measurements were made at 296 K. In the oxetane rings of all the compounds, the bond lengths of O—C(3') and C(1)—C(4') are longer than those of O—C(1) and C(3')—C(4'), respectively. The lengthening is caused by the strong electron-attracting ability of the halogen-substituted quinone moiety. The puckering angles [the dihedral angles between the C(1)—O—C(3') and C(1)—C(4')—C(3') planes] range from 10.2 to 18.7° in all the *trans* halogen-substituted spirooxetanes. One of the two crystallographically independent molecules in (I) has a planar oxetane ring and the other has a puckered form with a puckering angle of 6.8 (3)°.

Introduction. Only a few X-ray analyses have been made of substituted oxetane derivatives. In the struc-

Table 1. *Experimental conditions and refinement details*

| | (I) | (II) | (III) | (IV) |
|----------------------------------------------------------------|-----------------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| M.p. (K) | 410-411 | 397-398 | 423 (dec.) | 403 (dec.) |
| Crystal size (mm) | 0.30 × 0.40 × 0.40 | 0.40 × 0.30 × 0.30 | 0.30 × 0.20 × 0.30 | 0.20 × 0.30 × 0.40 |
| Diffractometer | Ni-filtered Cu K α | | Graphite-monochromated Mo K α | |
| Radiation | Rigaku AFC-5R | | | |
| Scan mode | ω -2 θ scan | ω -2 θ scan | ω -2 θ scan | ω -2 θ scan |
| Scan speed | 4 | 8 | 4 | 6 |
| in ω ($^{\circ}$ min ⁻¹) | | | | |
| Scan width ($^{\circ}$) | 1.2 + 0.15tan θ | 1.2 + 0.3tan θ | 1.4 + 0.3tan θ | 1.0 + 0.3tan θ |
| No. and 2 θ range ($^{\circ}$) | 20 | 17 | 20 | 20 |
| of reflections used for measuring lattice parameters | 44 < 2 θ < 46 | 18 < 2 θ < 20 | 23 < 2 θ < 27 | 18 < 2 θ < 22 |
| Max. ($\sin\theta$)/ λ (\AA^{-1}) | 0.58 | 0.70 | 0.65 | 0.65 |
| Range of h, k, l | -12-12, -18-18, 0-11 | 0-11, 0-19, -22-22 | 0-13, -14-14, -13-13 | 0-13, -14-14, -13-13 |
| Standard reflections and their average intensity variation (%) | 461, 511, 363 -5.9 | 051, 044, 143 -18.1 | 306, 343, 145 -7.6 | 501, 144, 043 -16.5 |
| Absorption correction (transmission factors) | Not applied | Empirical ψ scan 0.935-1.000 | Not applied | Empirical ψ scan 0.828-1.000 |
| No. of reflections measured | 5632 | 5414 | 4571 | 4869 |
| No. of unique reflections | 5284 | 4876 | 4324 | 4614 |
| R_{int} | 0.010 | 0.013 | 0.004 | 0.009 |
| No. of observed reflections | 4740 | 1655 | 3211 | 2434 |
| Criterion for observed reflections | $F_o > 2\sigma(F_o)$ | $F_o > 3\sigma(F_o)$ | $F_o > 2\sigma(F_o)$ | $F_o > 2\sigma(F_o)$ |
| No. of parameters | 565 | 283 | 283 | 283 |
| R (wR) | 0.057 (0.105) | 0.058 (0.075) | 0.034 (0.051) | 0.042 (0.049) |
| S | 0.73 | 2.05 | 1.42 | 1.29 |
| w | $1/[\sigma^2(F_o) + 0.0504F_o + 0.0062F_o^2]$ | $1/\sigma^2(F_o)$ | $1/\sigma^2(F_o)$ | $1/\sigma^2(F_o)$ |
| $(\Delta/\sigma)_{\text{max}}$ | 0.47 | 0.25 | 0.56 | 0.07 |
| $(\Delta\rho)_{\text{max, min}}$ ($e \text{\AA}^{-3}$) | 0.25, -0.23 | 0.32, -0.25 | 0.21, -0.28 | 0.56, -0.80 |

ture of unsubstituted oxetane (C₃H₆O) (Luger & Buschmann, 1984), the oxetane ring exists in a puckered form with a puckering angle of approximately 10°. On the other hand, an oxetane ring was estimated to be planar from microwave spectra (Chan, Zinn, Fernandez & Gwinn, 1960). Introduction of substituents into the oxetane ring is expected to bring about ring deformation by the substituent steric and electronic effects.

Two of the authors prepared 2,3,5,6-tetrachloro-*trans*-3',4'-diphenylspiro[2,5-cyclohexadiene-1,2'-oxetan]-4-one (III) by the reaction of phenyldiazomethane with tetrachloro-1,4-benzoquinone (Oshima & Nagai, 1980). Similarly, an extension of this reaction system to tetrafluoro- and tetrabromo-1,4-benzoquinones produced the corresponding *cis*-fluoro-substituted (I), *trans*-fluoro-substituted (II) and *trans*-bromo-substituted (IV) spirooxetanes (Oshima & Nagai, unpublished data), but did not produce *cis* isomers of the chloro and bromo compounds. These compounds, which have bulky diphenyl groups and strong electron-withdrawing quinone moieties, prompted the investigation of the crystal structures by means of X-ray analysis in order to gain a better understanding of the steric and electronic effects on the ring structure of oxetanes and to compare the structure data with those of the oxetane derivatives reported previously.

Experimental. The compounds were recrystallized from benzene-hexane solutions at room temperature. The experimental conditions and the refinement details are summarized in Table 1. A crystal of (II) was coated with an epoxy-resin layer because of decomposition by X-rays. Since the intensities of the three standard reflections monitored periodically showed a mean linear decay in intensity of -18.1% for (II) and -16.5% for (IV), correction for the decay was made. The decomposed products of (I) and (IV) were identified as *trans*-stilbene and the corresponding tetrahalogeno-1,4-benzoquinone by HPLC. Using a ψ scan with three reflections, an empirical absorption correction was applied for (II) and (IV) (transmission factors 0.935-1.000 and 0.828-1.000, respectively). Structures were solved by direct methods and refined on F by block-diagonal least squares for (I) and full-matrix least-squares methods for the other compounds (non-H atoms anisotropically). All the H atoms were located from difference Fourier syntheses and refined isotropically. The atomic scattering factors and the anomalous-scattering coefficients are taken from *International Tables for X-ray Crystallography* (1974). Calculations for (I) were carried out with *The Universal Crystallographic Computing System-Osaka* (1979), *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and

ORTEPII (Johnson, 1976) on an ACOS-S930 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University. Computation for (II), (III) and (IV) was made with the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1985) on a MicroVAXII computer at the Faculty of Science, Osaka University.

Discussion. There are two crystallographically independent molecules, (I)-(A) and (I)-(B), in the unit cell of the *cis*-fluoro compound (I). The final atomic parameters are given in Table 2.* The molecular structures with the atomic numbering scheme are shown in Fig. 1. Bond distances and angles are in Table 3. The corresponding values in the halogen-substituted spirooxetanes agree fairly well with each other. The average $X-C$ bond lengths for $X = F, Cl$ and Br are 1.331, 1.709 and 1.874 Å, respectively.

Table 4 lists the $C-O$ and $C-C$ bond lengths and puckering angles [the dihedral angles between the plane through the $C(1)$, $O(2)$ and $C(14)$ atoms and the plane through the $C(1)$, $C(7)$ and $C(14)$ atoms] of the oxetane rings, together with those of some oxetane derivatives. The $O(2)-C(14)$ and $C(1)-C(7)$ bond lengths of the present halogen-substituted spirooxetanes are appreciably longer than those of $O(2)-C(1)$ and $C(7)-C(14)$, respectively. This lengthening of the former bonds is caused by the electron-withdrawing ability of the tetrahalogenated quinone moieties; the effect on the remote $O(2)-C(14)$ bond may be ascribed to the conjugative relay of charge by way of mobile lone-pair electrons of the ethereal oxygen [$O(2)$]. A similar effect is also observed in the $O-C$ bonds of 3,5-dinitrobenzoate of *threo*-3,3,4,4,α-pentamethyl-2-oxetanemethanol (Hospital, Leroy, Bats & Moulines, 1978) which has the electron-attractive dinitrobenzoate moiety. However, in oxetane, 2,2-bis(*p*-ethoxyphenyl)-3,3-dimethyloxetane (Holan, Kowala & Wunderlich, 1973), and dictyoxetane (Pullaiah, Surapaneni, Rao, Albizati, Sullivan, Faulkner, Cunneng & Clardy, 1985) which have no electron-attractive groups, the $O-C$ bonds in the four-membered ring are nearly equal in length, and so are the $C-C$ bonds in the ring. The puckering angles [$6.8(3)$ and $0.2(3)^\circ$] of the *cis* fluoride, (I)-(A) and (I)-(B), are smaller than that of the *trans* fluoride (II) [$18.6(4)^\circ$]; the oxetane ring of (I)-(B) is planar in contrast with that of the unsubstituted oxetane.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52391 (75 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic coordinates of non-H atoms and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^*$$

| | x | y | z | $B_{eq}(\text{Å}^2)$ |
|----------------|-------------|-------------|-------------|----------------------|
| (I)-(A) | | | | |
| F(1A) | 0.5579 (2) | 0.3739 (1) | 0.4389 (2) | 6.28 (5) |
| F(2A) | 0.4645 (2) | 0.2500 (1) | 0.2178 (2) | 7.36 (6) |
| F(3A) | 0.7924 (2) | 0.1173 (1) | 0.4141 (3) | 8.15 (8) |
| F(4A) | 0.8955 (2) | 0.2480 (1) | 0.6267 (2) | 7.83 (7) |
| O(1A) | 0.5829 (3) | 0.1230 (2) | 0.2105 (3) | 9.01 (10) |
| O(2A) | 0.7222 (2) | 0.3369 (1) | 0.6767 (2) | 5.55 (6) |
| C(1A) | 0.7409 (3) | 0.3231 (2) | 0.5395 (3) | 4.71 (7) |
| C(2A) | 0.6186 (2) | 0.3137 (2) | 0.4272 (3) | 4.83 (7) |
| C(3A) | 0.5713 (3) | 0.2523 (2) | 0.3188 (3) | 5.29 (8) |
| C(4A) | 0.6284 (3) | 0.1803 (2) | 0.3065 (3) | 5.96 (9) |
| C(5A) | 0.7416 (3) | 0.1834 (2) | 0.4204 (3) | 5.75 (9) |
| C(6A) | 0.7921 (3) | 0.2467 (2) | 0.5240 (3) | 5.32 (8) |
| C(7A) | 0.8479 (2) | 0.4113 (1) | 0.5666 (2) | 4.43 (7) |
| C(8A) | 0.8224 (2) | 0.4736 (1) | 0.4635 (2) | 4.50 (7) |
| C(9A) | 0.8238 (3) | 0.4516 (2) | 0.3279 (3) | 5.00 (8) |
| C(10A) | 0.7997 (3) | 0.5041 (2) | 0.2253 (3) | 5.56 (8) |
| C(11A) | 0.7771 (4) | 0.5801 (2) | 0.2605 (3) | 6.63 (11) |
| C(12A) | 0.7826 (5) | 0.6052 (2) | 0.3971 (4) | 8.65 (17) |
| C(13A) | 0.8048 (4) | 0.5524 (2) | 0.4986 (3) | 7.18 (13) |
| C(14A) | 0.8292 (3) | 0.4155 (2) | 0.7177 (3) | 5.05 (8) |
| C(15A) | 0.7913 (3) | 0.4869 (2) | 0.7851 (2) | 5.08 (8) |
| C(16A) | 0.8886 (3) | 0.5553 (2) | 0.8632 (3) | 6.00 (9) |
| C(17A) | 0.8594 (4) | 0.6251 (2) | 0.9225 (3) | 6.97 (12) |
| C(18A) | 0.7294 (4) | 0.6256 (2) | 0.9058 (3) | 6.95 (12) |
| C(19A) | 0.6318 (4) | 0.5569 (2) | 0.8319 (4) | 7.00 (12) |
| C(20A) | 0.6613 (3) | 0.4873 (2) | 0.7704 (3) | 6.29 (10) |
| (I)-(B) | | | | |
| F(1B) | 0.3556 (2) | -0.0592 (1) | 0.2698 (2) | 7.76 (7) |
| F(2B) | 0.1756 (2) | -0.1344 (2) | 0.0278 (2) | 8.62 (8) |
| F(3B) | 0.3994 (2) | -0.3464 (1) | -0.0047 (2) | 7.60 (6) |
| F(4B) | 0.5698 (2) | -0.2764 (1) | 0.2433 (2) | 6.28 (5) |
| O(1B) | 0.2020 (2) | -0.2735 (2) | -0.1080 (2) | 8.60 (9) |
| O(2B) | 0.5039 (2) | -0.1588 (1) | 0.4082 (2) | 5.42 (6) |
| C(1B) | 0.4840 (2) | -0.1569 (2) | 0.2611 (2) | 4.26 (6) |
| C(2B) | 0.3641 (2) | -0.1285 (2) | 0.1983 (3) | 5.18 (8) |
| C(3B) | 0.2765 (2) | -0.1650 (2) | 0.0815 (3) | 5.61 (8) |
| C(4B) | 0.2831 (3) | -0.2405 (2) | 0.0020 (3) | 5.66 (8) |
| C(5B) | 0.3937 (3) | -0.2745 (2) | 0.0635 (3) | 5.12 (8) |
| C(6B) | 0.4785 (2) | -0.2391 (2) | 0.1839 (3) | 4.47 (7) |
| C(7B) | 0.6143 (2) | -0.0839 (1) | 0.2849 (2) | 4.05 (6) |
| C(8B) | 0.7112 (2) | -0.0982 (1) | 0.2066 (2) | 3.96 (6) |
| C(9B) | 0.8047 (3) | -0.1420 (2) | 0.2492 (3) | 4.84 (7) |
| C(10B) | 0.8874 (3) | -0.1526 (2) | 0.1664 (3) | 6.11 (10) |
| C(11B) | 0.8761 (3) | -0.1214 (2) | 0.0402 (3) | 6.32 (10) |
| C(12B) | 0.7835 (3) | -0.0791 (2) | -0.0036 (3) | 6.69 (11) |
| C(13B) | 0.7029 (3) | -0.0660 (2) | 0.0805 (3) | 5.18 (8) |
| C(14B) | 0.6262 (2) | -0.0909 (2) | 0.4430 (2) | 4.61 (7) |
| C(15B) | 0.7374 (2) | -0.1152 (2) | 0.5377 (2) | 4.30 (6) |
| C(16B) | 0.7251 (3) | -0.1965 (2) | 0.5708 (3) | 5.26 (8) |
| C(17B) | 0.8315 (3) | -0.2176 (2) | 0.6571 (3) | 6.11 (10) |
| C(18B) | 0.9487 (3) | -0.1570 (2) | 0.7067 (3) | 6.17 (10) |
| C(19B) | 0.9603 (3) | -0.0752 (2) | 0.6772 (3) | 6.27 (9) |
| C(20B) | 0.8543 (3) | -0.0536 (2) | 0.5929 (3) | 5.39 (8) |
| (II) | | | | |
| F(1) | 0.2845 (3) | 0.7125 (2) | 0.2648 (2) | 5.6 (1) |
| F(2) | 0.5897 (3) | 0.6837 (2) | 0.3537 (2) | 6.4 (1) |
| F(3) | 0.4292 (4) | 0.3609 (2) | 0.4138 (2) | 7.8 (2) |
| F(4) | 0.1203 (4) | 0.3920 (2) | 0.3298 (2) | 6.5 (1) |
| O(1) | 0.6547 (4) | 0.5077 (3) | 0.4268 (2) | 7.0 (2) |
| O(2) | 0.0992 (3) | 0.5491 (2) | 0.2129 (2) | 4.7 (1) |
| C(1) | 0.1765 (5) | 0.5578 (3) | 0.3007 (2) | 3.9 (2) |
| C(2) | 0.3200 (5) | 0.6284 (3) | 0.3053 (3) | 4.2 (2) |
| C(3) | 0.4686 (5) | 0.6149 (3) | 0.3471 (3) | 4.5 (2) |
| C(4) | 0.5160 (6) | 0.5222 (4) | 0.3887 (3) | 5.2 (2) |
| C(5) | 0.3868 (6) | 0.4480 (3) | 0.3779 (3) | 5.1 (2) |
| C(6) | 0.2370 (6) | 0.4632 (3) | 0.3382 (3) | 4.7 (2) |
| C(7) | 0.0074 (6) | 0.5985 (3) | 0.3324 (3) | 4.2 (2) |
| C(8) | 0.0183 (5) | 0.6828 (3) | 0.3947 (3) | 4.1 (2) |
| C(9) | -0.0401 (6) | 0.7741 (3) | 0.3729 (3) | 5.1 (2) |
| C(10) | -0.0180 (8) | 0.8500 (4) | 0.4317 (4) | 6.5 (3) |
| C(11) | 0.0614 (7) | 0.8353 (5) | 0.5121 (4) | 6.2 (3) |
| C(12) | 0.1140 (7) | 0.7451 (5) | 0.5351 (3) | 6.2 (3) |
| C(13) | 0.0926 (7) | 0.6691 (4) | 0.4779 (3) | 5.6 (3) |
| C(14) | -0.0465 (5) | 0.6093 (3) | 0.2350 (3) | 4.2 (2) |
| C(15) | -0.2143 (5) | 0.5704 (3) | 0.1956 (3) | 4.3 (2) |

Table 2 (cont.)

| | x | y | z | $B_{eq}(Å^2)$ |
|-------|-------------|-------------|--------------|---------------|
| C(16) | -0.3188 (6) | 0.6292 (5) | 0.1437 (3) | 5.5 (3) |
| C(17) | -0.4710 (7) | 0.5953 (6) | 0.1058 (4) | 7.1 (3) |
| C(18) | -0.5189 (8) | 0.5026 (6) | 0.1191 (4) | 6.9 (3) |
| C(19) | -0.4158 (7) | 0.4421 (5) | 0.1700 (4) | 6.7 (3) |
| C(20) | -0.2629 (7) | 0.4754 (4) | 0.2089 (3) | 5.7 (3) |
| (III) | | | | |
| Cl(1) | 0.74128 (7) | 0.35098 (5) | 0.90661 (7) | 4.57 (3) |
| Cl(2) | 0.67553 (7) | 0.51159 (7) | 0.63940 (6) | 5.25 (3) |
| Cl(3) | 0.91847 (8) | 0.89470 (6) | 1.02512 (8) | 5.33 (3) |
| Cl(4) | 0.98220 (7) | 0.73712 (6) | 1.29394 (6) | 4.49 (3) |
| O(1) | 0.7496 (2) | 0.7674 (2) | 0.7404 (2) | 5.30 (8) |
| O(2) | 0.9390 (2) | 0.4665 (1) | 1.1963 (2) | 3.30 (5) |
| C(1) | 0.8316 (2) | 0.5590 (2) | 1.0921 (2) | 2.77 (7) |
| C(2) | 0.7791 (2) | 0.5035 (2) | 0.9344 (2) | 3.09 (8) |
| C(3) | 0.7521 (2) | 0.5711 (2) | 0.8209 (2) | 3.40 (8) |
| C(4) | 0.7849 (2) | 0.7019 (2) | 0.8436 (2) | 3.63 (8) |
| C(5) | 0.8640 (2) | 0.7488 (2) | 1.0002 (2) | 3.43 (8) |
| C(6) | 0.8892 (2) | 0.6820 (2) | 1.1132 (2) | 3.10 (8) |
| C(7) | 0.7154 (2) | 0.5645 (2) | 1.1608 (2) | 2.85 (7) |
| C(8) | 0.6358 (2) | 0.6923 (2) | 1.1991 (2) | 3.08 (8) |
| C(9) | 0.5415 (3) | 0.7741 (2) | 1.0854 (3) | 3.95 (9) |
| C(10) | 0.4586 (3) | 0.8888 (2) | 1.1144 (3) | 4.84 (12) |
| C(11) | 0.4679 (3) | 0.9221 (3) | 1.2549 (3) | 5.46 (13) |
| C(12) | 0.5614 (4) | 0.8429 (3) | 1.3686 (3) | 5.49 (13) |
| C(13) | 0.6461 (3) | 0.7279 (2) | 1.3410 (3) | 4.20 (9) |
| C(14) | 0.8466 (2) | 0.4802 (2) | 1.2790 (2) | 3.14 (8) |
| C(15) | 0.8229 (2) | 0.3535 (2) | 1.3036 (2) | 3.25 (8) |
| C(16) | 0.9288 (3) | 0.2427 (2) | 1.3139 (3) | 4.40 (10) |
| C(17) | 0.9044 (4) | 0.1270 (2) | 1.3394 (3) | 5.36 (13) |
| C(18) | 0.7777 (4) | 0.1221 (3) | 1.3553 (3) | 5.45 (13) |
| C(19) | 0.6730 (3) | 0.2318 (3) | 1.3464 (3) | 5.14 (12) |
| C(20) | 0.6952 (3) | 0.3481 (2) | 1.3204 (3) | 4.02 (9) |
| (IV) | | | | |
| Br(1) | 0.98015 (8) | 0.73803 (7) | 0.80181 (8) | 5.23 (4) |
| Br(2) | 0.90520 (9) | 0.90588 (7) | 0.52054 (10) | 6.30 (4) |
| Br(3) | 0.67388 (9) | 0.51186 (8) | 0.13139 (8) | 5.94 (4) |
| Br(4) | 0.74061 (8) | 0.34247 (7) | 0.40895 (8) | 5.17 (4) |
| O(1) | 0.7481 (6) | 0.7664 (5) | 0.2450 (6) | 6.3 (3) |
| O(2) | 0.9334 (4) | 0.4666 (4) | 0.6908 (4) | 3.8 (2) |
| C(1) | 0.8297 (6) | 0.5599 (5) | 0.5924 (6) | 3.2 (3) |
| C(2) | 0.8821 (6) | 0.6815 (6) | 0.6101 (7) | 3.9 (3) |
| C(3) | 0.8554 (7) | 0.7465 (6) | 0.4971 (8) | 4.3 (3) |
| C(4) | 0.7806 (7) | 0.7018 (7) | 0.3465 (8) | 4.4 (3) |
| C(5) | 0.7531 (6) | 0.5720 (6) | 0.3251 (7) | 4.1 (3) |
| C(6) | 0.7800 (6) | 0.5061 (6) | 0.4372 (7) | 3.7 (3) |
| C(7) | 0.7169 (7) | 0.5670 (6) | 0.6630 (7) | 3.6 (3) |
| C(8) | 0.6401 (6) | 0.6926 (6) | 0.7035 (7) | 3.9 (3) |
| C(9) | 0.5501 (7) | 0.7761 (7) | 0.5950 (8) | 4.5 (3) |
| C(10) | 0.4719 (9) | 0.8912 (7) | 0.6264 (11) | 5.9 (4) |
| C(11) | 0.4813 (12) | 0.9239 (10) | 0.7653 (12) | 7.0 (5) |
| C(12) | 0.5683 (12) | 0.8433 (9) | 0.8731 (12) | 7.2 (5) |
| C(13) | 0.6484 (9) | 0.7277 (8) | 0.8417 (9) | 5.4 (4) |
| C(14) | 0.8416 (7) | 0.4813 (6) | 0.7750 (7) | 3.7 (3) |
| C(15) | 0.8208 (7) | 0.3555 (6) | 0.7986 (6) | 4.0 (3) |
| C(16) | 0.6923 (8) | 0.3484 (7) | 0.8072 (7) | 4.7 (4) |
| C(17) | 0.6722 (10) | 0.2344 (8) | 0.8348 (9) | 6.0 (4) |
| C(18) | 0.7803 (12) | 0.1285 (8) | 0.8485 (9) | 6.4 (5) |
| C(19) | 0.9076 (13) | 0.1337 (9) | 0.8405 (10) | 6.5 (5) |
| C(20) | 0.9278 (10) | 0.2484 (7) | 0.8164 (8) | 5.2 (4) |

There is little difference between the torsion angles of $C(1)-C(7)-C(8)-C(9)/C(13)$ of all compounds except for that of (I)-(B) as shown in Table 5. The torsion angles of $C(7)-C(14)-C(15)-C(16)/C(20)$ in the *trans*-halogen-substituted spirooxetanes vary to reduce the steric repulsion between a phenyl group and a halogen atom, and those in the *cis*-fluoride are close to 90° owing to the steric hindrance between the phenyl groups.

The two crystallographically independent molecules (I)-(A) and (I)-(B) which have the same optically active configuration are packed in pairs and, in

these pairs, the distance between the ethereal oxygen [O(2)] and the best plane through C(2), C(3), C(4), C(5) and C(6) of the quinone moiety is about 3.15 \AA .

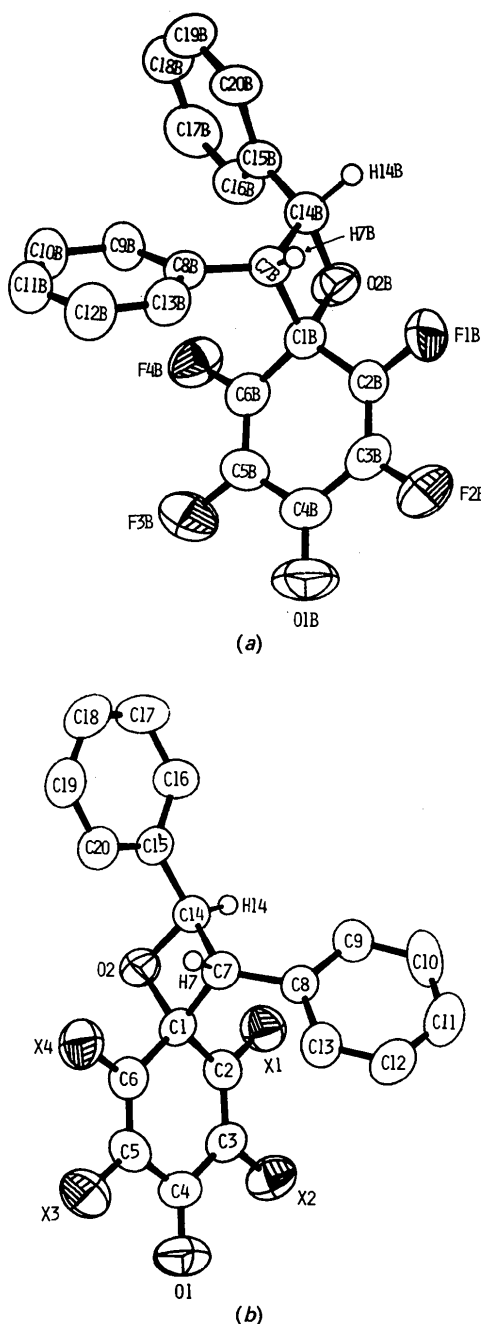


Fig. 1. Molecular structures with atomic numbering scheme. The thermal ellipsoids of the non-H atoms are drawn at 50% probability level. All the H atoms except H(7) and H(14) are omitted for clarity. (a) *cis* isomer [(I)-(B)]. The same atomic numbering scheme as (I)-(B) was used for (I)-(A), and the distinction between the atoms in (I)-(A) and those in (I)-(B) was made by the letters A and B. (b) *trans* isomers. X is the halogen atom, F, Cl or Br.

Table 3. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

| | (I)-(A) | (I)-(B) | (II) | (III) | (IV) |
|-------------------|-----------|-----------|-----------|-----------|------------|
| X(1)-C(2) | 1.327 (3) | 1.331 (4) | 1.331 (5) | 1.705 (2) | 1.868 (6) |
| X(2)-C(3) | 1.334 (4) | 1.332 (4) | 1.341 (5) | 1.711 (2) | 1.882 (6) |
| X(3)-C(5) | 1.333 (4) | 1.338 (4) | 1.346 (5) | 1.711 (2) | 1.869 (6) |
| X(4)-C(6) | 1.323 (4) | 1.332 (3) | 1.341 (5) | 1.709 (2) | 1.877 (6) |
| O(1)-C(4) | 1.214 (5) | 1.222 (4) | 1.218 (5) | 1.212 (2) | 1.220 (7) |
| O(2)-C(1) | 1.436 (4) | 1.427 (3) | 1.448 (4) | 1.436 (2) | 1.438 (6) |
| O(2)-C(14) | 1.469 (4) | 1.466 (3) | 1.478 (5) | 1.468 (2) | 1.489 (7) |
| C(1)-C(6) | 1.500 (4) | 1.482 (4) | 1.485 (6) | 1.500 (3) | 1.510 (8) |
| C(1)-C(2) | 1.489 (4) | 1.505 (4) | 1.487 (6) | 1.497 (3) | 1.509 (8) |
| C(1)-C(7) | 1.580 (4) | 1.577 (3) | 1.562 (6) | 1.586 (2) | 1.586 (8) |
| C(2)-C(3) | 1.330 (4) | 1.310 (4) | 1.307 (6) | 1.334 (3) | 1.336 (8) |
| C(3)-C(4) | 1.463 (4) | 1.445 (5) | 1.459 (6) | 1.466 (3) | 1.464 (9) |
| C(4)-C(5) | 1.451 (5) | 1.469 (4) | 1.441 (6) | 1.476 (3) | 1.474 (9) |
| C(5)-C(6) | 1.320 (5) | 1.318 (4) | 1.306 (6) | 1.329 (3) | 1.334 (8) |
| C(7)-C(8) | 1.516 (4) | 1.508 (3) | 1.502 (6) | 1.501 (3) | 1.494 (8) |
| C(7)-C(14) | 1.561 (4) | 1.557 (3) | 1.539 (6) | 1.534 (3) | 1.532 (9) |
| C(8)-C(9) | 1.375 (4) | 1.387 (4) | 1.367 (6) | 1.389 (3) | 1.395 (8) |
| C(8)-C(13) | 1.381 (5) | 1.381 (4) | 1.384 (6) | 1.379 (3) | 1.367 (9) |
| C(9)-C(10) | 1.392 (4) | 1.392 (5) | 1.382 (7) | 1.382 (3) | 1.385 (10) |
| C(10)-C(11) | 1.363 (5) | 1.373 (5) | 1.362 (8) | 1.364 (4) | 1.368 (12) |
| C(11)-C(12) | 1.373 (7) | 1.364 (5) | 1.344 (8) | 1.372 (4) | 1.366 (13) |
| C(12)-C(13) | 1.385 (7) | 1.393 (5) | 1.368 (7) | 1.388 (2) | 1.388 (11) |
| C(14)-C(15) | 1.499 (4) | 1.501 (4) | 1.511 (6) | 1.498 (3) | 1.505 (8) |
| C(15)-C(16) | 1.376 (5) | 1.373 (4) | 1.367 (6) | 1.380 (3) | 1.390 (9) |
| C(15)-C(20) | 1.396 (5) | 1.383 (4) | 1.378 (6) | 1.382 (3) | 1.372 (9) |
| C(16)-C(17) | 1.387 (5) | 1.400 (5) | 1.376 (8) | 1.391 (3) | 1.395 (9) |
| C(17)-C(18) | 1.393 (6) | 1.373 (5) | 1.345 (9) | 1.367 (4) | 1.372 (11) |
| C(18)-C(19) | 1.368 (6) | 1.369 (5) | 1.366 (8) | 1.367 (4) | 1.369 (12) |
| C(19)-C(20) | 1.396 (5) | 1.393 (5) | 1.383 (7) | 1.391 (3) | 1.388 (11) |
| C(1)-O(2)-C(14) | 93.2 (2) | 93.2 (2) | 90.9 (3) | 92.8 (1) | 92.0 (4) |
| O(2)-C(1)-C(6) | 111.0 (2) | 113.1 (2) | 113.1 (3) | 111.9 (1) | 111.6 (5) |
| O(2)-C(1)-C(2) | 111.9 (2) | 111.8 (2) | 111.3 (3) | 112.1 (2) | 113.1 (5) |
| O(2)-C(1)-C(7) | 91.2 (2) | 91.6 (2) | 90.9 (3) | 90.3 (1) | 91.0 (4) |
| C(6)-C(1)-C(2) | 110.0 (2) | 110.2 (2) | 109.3 (3) | 112.3 (1) | 111.9 (5) |
| C(6)-C(1)-C(7) | 114.5 (2) | 116.4 (2) | 116.5 (4) | 115.1 (2) | 113.1 (5) |
| C(2)-C(1)-C(7) | 117.0 (2) | 112.7 (2) | 114.8 (3) | 113.2 (1) | 114.6 (5) |
| C(3)-C(2)-X(1) | 120.1 (3) | 121.4 (3) | 120.2 (4) | 121.7 (2) | 122.4 (5) |
| C(3)-C(2)-C(1) | 124.9 (3) | 124.7 (3) | 125.6 (4) | 122.8 (2) | 122.4 (6) |
| X(1)-C(2)-C(1) | 115.0 (2) | 113.9 (3) | 114.1 (3) | 115.3 (1) | 115.2 (4) |
| C(2)-C(3)-X(2) | 121.8 (3) | 121.8 (3) | 123.0 (4) | 122.3 (2) | 122.2 (5) |
| C(2)-C(3)-C(4) | 122.3 (3) | 122.5 (3) | 122.1 (4) | 122.1 (2) | 122.7 (6) |
| X(2)-C(3)-C(4) | 115.8 (3) | 115.6 (3) | 115.0 (4) | 115.5 (1) | 115.1 (5) |
| O(1)-C(4)-C(5) | 122.7 (3) | 122.8 (3) | 122.8 (5) | 122.1 (2) | 122.2 (7) |
| O(1)-C(4)-C(3) | 122.7 (3) | 122.1 (3) | 123.0 (5) | 122.2 (2) | 121.8 (6) |
| C(5)-C(4)-C(3) | 114.6 (3) | 115.1 (3) | 114.2 (4) | 115.7 (2) | 115.9 (6) |
| C(6)-C(5)-X(3) | 121.5 (3) | 121.5 (3) | 121.4 (5) | 122.9 (2) | 123.7 (5) |
| C(6)-C(5)-C(4) | 122.8 (3) | 121.9 (3) | 123.2 (4) | 121.8 (2) | 121.4 (6) |
| X(3)-C(5)-C(4) | 115.7 (3) | 116.4 (3) | 115.3 (4) | 115.3 (1) | 114.9 (5) |
| C(5)-C(6)-X(4) | 121.9 (3) | 120.2 (3) | 121.3 (4) | 121.2 (2) | 121.2 (5) |
| C(5)-C(6)-C(1) | 125.0 (3) | 124.7 (3) | 125.1 (4) | 123.0 (2) | 123.5 (5) |
| X(4)-C(6)-C(1) | 113.1 (3) | 115.1 (2) | 113.7 (4) | 115.6 (1) | 115.1 (4) |
| C(8)-C(7)-C(14) | 126.2 (2) | 125.9 (2) | 123.4 (4) | 122.9 (2) | 122.9 (5) |
| C(8)-C(7)-C(1) | 116.2 (2) | 117.4 (2) | 117.9 (4) | 120.2 (2) | 120.5 (5) |
| C(14)-C(7)-C(1) | 84.4 (2) | 84.3 (2) | 84.5 (3) | 84.7 (1) | 84.9 (4) |
| C(9)-C(8)-C(13) | 118.2 (3) | 118.0 (2) | 117.6 (4) | 118.9 (2) | 118.0 (7) |
| C(9)-C(8)-C(7) | 117.4 (2) | 125.6 (2) | 123.1 (4) | 118.7 (2) | 118.9 (6) |
| C(13)-C(8)-C(7) | 124.4 (3) | 116.4 (2) | 119.4 (4) | 122.3 (2) | 123.0 (6) |
| C(8)-C(9)-C(10) | 121.6 (3) | 120.4 (3) | 120.3 (5) | 120.4 (2) | 121.0 (7) |
| C(11)-C(10)-C(9) | 119.4 (3) | 120.6 (3) | 120.9 (6) | 120.2 (2) | 119.9 (8) |
| C(12)-C(11)-C(10) | 119.7 (4) | 119.5 (4) | 119.2 (5) | 120.2 (2) | 120.0 (9) |
| C(11)-C(12)-C(13) | 120.8 (5) | 120.2 (4) | 120.7 (5) | 120.2 (3) | 120.0 (10) |
| C(12)-C(13)-C(8) | 120.2 (4) | 121.2 (3) | 121.3 (5) | 120.2 (2) | 121.0 (8) |
| O(2)-C(14)-C(15) | 112.7 (2) | 112.7 (2) | 112.6 (3) | 113.2 (2) | 112.3 (5) |
| O(2)-C(14)-C(7) | 90.7 (2) | 91.0 (2) | 90.7 (3) | 91.2 (1) | 91.2 (4) |
| C(15)-C(14)-C(7) | 123.6 (2) | 123.3 (2) | 121.7 (4) | 118.5 (2) | 119.5 (5) |
| C(16)-C(15)-C(20) | 118.7 (3) | 119.7 (3) | 118.9 (5) | 119.5 (2) | 119.1 (6) |
| C(16)-C(15)-C(14) | 118.7 (3) | 121.5 (2) | 119.8 (4) | 120.9 (2) | 119.4 (6) |
| C(20)-C(15)-C(14) | 122.6 (3) | 118.8 (2) | 121.3 (4) | 119.6 (2) | 121.4 (6) |
| C(15)-C(16)-C(17) | 121.2 (3) | 120.1 (3) | 121.1 (6) | 119.4 (2) | 120.7 (7) |
| C(18)-C(17)-C(16) | 119.8 (4) | 119.7 (3) | 120.0 (6) | 120.9 (3) | 118.4 (8) |
| C(17)-C(18)-C(19) | 119.6 (4) | 120.3 (3) | 120.0 (6) | 120.0 (2) | 121.6 (8) |
| C(18)-C(19)-C(20) | 120.6 (4) | 120.2 (3) | 120.7 (6) | 119.9 (3) | 119.4 (9) |
| C(15)-C(20)-C(19) | 120.1 (3) | 119.9 (3) | 119.4 (5) | 120.4 (2) | 120.6 (8) |

Among the intermolecular distances less than the van der Waals contacts, the distances between halogens are quite short as shown in the following: Cl(3)⋯Cl(3)(2-x, 2-y, 2-z), 3.279; Cl(2)⋯Cl(2)(1-x, 1-y, 1-z), 3.430; Br(2)⋯Br(2)(2-x, 2-y,

1-z), 3.340 and Br(3)⋯Br(3)(1-x, 1-y, -z), 3.523 Å.

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Table 4. Bonding data in the oxetane rings for spirooxetanes and some derivatives

| Compound (1)-(IV) (average) | O(2)—C(1) 1.437 (3) Å | O(2)—C(14) 1.469 (3) Å | C(1)—C(7) 1.582 (3) Å | C(7)—C(14) 1.547 (4) Å | Puckering angle 0.4 (2)–18.2 (4)° | Reference a |
|------------------------------------------------------------------------------|--------------------------|---------------------------|--------------------------|---------------------------|--------------------------------------|----------------|
| Oxetane (90 K) | 1.460 (1) | | 1.534 (2) | | 10.7 (1) | b |
| Oxetane (140 K) | 1.443 (2) | | 1.517 (2) | | 8.7 (2) | b |
| 3,5-Dinitrobenzoate of <i>threo</i> -3,3,4,4,α-pentamethyl-2-oxetanemethanol | 1.437 (3) | 1.445 (3) | 1.558 (3) | 1.550 (3) | 22.9 (2) | c |
| 2,2-Bis(<i>p</i> -ethoxyphenyl)-3,3-dimethyloxetane | 1.47 | 1.48 | — | — | 16.0* | d |
| Dictyoxetane | 1.50 (1) | 1.48 (1) | 1.55 (1) | 1.57 (2) | 9.0 | e |

References: (a) this work; (b) Luger *et al.* (1984); (c) Hospital *et al.* (1978); (d) Holan *et al.* (1973); (e) Pullaiah *et al.* (1985).

* Dihedral angle between the O—C—C planes.

Table 5. Selected torsion angles (°) with *e.s.d.*'s in parentheses

| | (I)-(A)* | (I)-(B) | (II)* | (III) | (IV) |
|------------------------------|-----------|-----------|----------|-----------|-----------|
| C(1)—C(7)—C(8)—C(9)/C(13) | 66.3 (3) | -84.4 (3) | 67.4 (6) | 61.9 (2) | 61.5 (8) |
| C(7)—C(14)—C(15)—C(16)/C(20) | -88.2 (4) | 80.7 (4) | 51.6 (6) | -47.9 (3) | -43.5 (8) |

* Molecules with the symmetry code $-x, -y, -z$.

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1-(1-Aziridinyl)-3-(2-nitro-1-imidazolyl)-2-propanol [RSU-1069] (I) and 1-(2-Methyl-1-aziridinyl)-3-(2-nitro-1-imidazolyl)-2-propanol [RSU-1131] (II)

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Abstract. RSU-1069 (I): C₈H₁₂N₄O₃, *M_r* = 212, monoclinic, *P*2₁/*c*, *a* = 9.127 (1), *b* = 9.763 (1), *c* = 11.581 (1) Å, β = 103.14 (1)°, *V* = 1004.9 (2) Å³, *Z* = 4, *D_x* = 1.401 Mg m⁻³, Cu *Kα*, λ = 1.54178 Å, μ = 0.830 mm⁻¹, *F*(000) = 448, *T* = 298 K, *R* = 0.064 for

1469 unique observed reflections (*F* > 6σ*F*). RSU-1131 (II): C₉H₁₄N₄O₃, *M_r* = 226, triclinic, *P*1̄, *a* = 7.111 (2), *b* = 9.305 (1), *c* = 10.395 (2) Å, α = 62.00 (1), β = 67.80 (1), γ = 79.66 (1)°, *V* = 562.3 (2) Å³, *Z* = 2, *D_x* = 1.334 Mg m⁻³, Cu *Kα*, λ = 1.54178 Å, μ = 0.769 mm⁻¹, *F*(000) = 240, *T* = 298 K, *R* = 0.051 for 1827 unique observed reflections (*F* > 6σ*F*). The title compounds are 2-nitroimidazoles with current application as hypoxia-

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