Fig. 1. Perspective drawing of 4,4-dimethyl-2-oxomorpholinium bromide. Distances (Å) and angles (°) involving methyl groups: N—C(5), 1·504 (4); N—C(6), 1·502 (4); C(1)—N—C(5), 110·1 (3); C(1)—N—C(6), 109·2 (3); C(4)—N—C(5), 112·2 (3); C(4)—N—C(6), 108·9 (3); C(5)—N—C(6), 109·1 (3).

ranges* in absolute value from 64 to 89°, with a mean of 77·5°. The conformation about the ester moiety is quite different. In the lactone, C(3)—O(1)—C(2)—O(2) is 176·2 (4)° whereas the corresponding torsion angle in the acyclic ester ranges from −5·4 to 5·2°. The torsion angle C(2)—O(1)—C(3)—C(4) is 26·5 (5)° in the title compound, whereas in acetylcholine it has two ranges of absolute values, 78–94 and 154–180°, depending on the counterion.

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* See Datta, Mondal & Pauling (1980) for a summary of all acetylcholine structures solved through 1980, and Jensen (1982) for the tartrate salts.

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Structure of a Difuran and a Dipyran

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Abstract. 2,3,6,7-Tetrahydro-2,2,4,6,6,8-hexamethylbenzo[1,2-b:4,5-b']difuran (I), $C_{16}H_{22}O_2$, $M_r = 246·3$, monoclinic, $P2_1/c$, $a = 5·330$ (1), $b = 10·263$ (1), $c = 12·384$ (1) Å, $\beta = 95·74$ (1)°, $V = 674$ Å^3, $Z = 2$, $D_m = 1·21$, $D_x = 1·214$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 0·43$ cm^{-1}, $F(000) = 268$, $T = 290$ K, final $R = 0·047$ for 1594 observed reflections.

3,4,8,9-Tetrahydro-2,2,5,7,7,10-hexamethylbenzo[1,2-b:4,5-b']dipyran (II), $C_{18}H_{26}O_2$, $M_r = 274·39$, monoclinic, $P2_1/c$, $a = 8·046$ (2), $b = 9·369$ (3), $c = 10·392$ (2) Å, $\beta = 90·45$ (2)°, $V = 783·4$ Å^3, $Z = 2$, $D_m = 1·10$, $D_x = 1·164$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1·5418$ Å, $\mu = 5·40$ cm^{-1}, $F(000) = 300$, $T = 290$ K, final $R = 0·063$ for 924 observed reflections. Both molecules have symmetry $\bar{1}$ and bond lengths and angles close to expected values. The geometry around the O atom in (I) is consistent with the observation that this molecule forms free radicals more readily than (II).

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Introduction. The difuran (I) and the dipyran (II) are analogues of α-tocopherol, vitamin E, (III). (III) is an efficient inhibitor of lipid autoxidation *in vivo*, a result of its ability to form a fairly stable free radical, (IIIR), when H is abstracted from the OH group. (I) and (II) form stable cation radicals, (IR) and (IIR), when an electron is abstracted. We wished to compare the furan- and pyran-ring geometries in (I) and (II) with details of the ring geometry of the cationic radicals, found by ESR (Smith, Sutcliffe, Wiesner, Lubitz & Kurreck, 1984).

(I)   (II)   (III)

$R = -CH_2\{CH_2-CH_2-CH(CH_3)-CH_2\}_3$ H
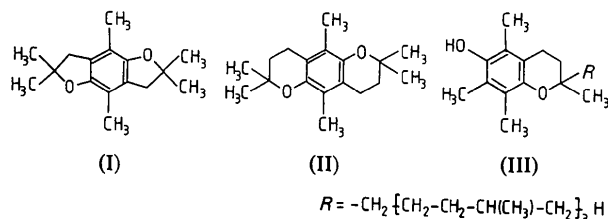
Experimental. (I) was prepared as described by Smith *et al.* (1984) and (II) by the method of Frampton, Skinner, Cambour & Bailey (1960). Crystals were obtained by allowing petroleum spirit (40–60°) to diffuse slowly into a chloroform solution of (I). Density measured by flotation. Enraf–Nonius CAD-4 diffractometer data (at Queen Mary College, London, SERC Service), $\theta_{max} = 30°$ for (I) and 70° for (II), empirical absorption corrections made for (I) (maximum and minimum transmission factors 1·0 and 0·95), 1965 and 1480 unique reflections of which 1594 and 924 have $F > 3\sigma(F)$ in (I) and (II) respectively. [$h = 0$ to 7, $k = 0$ to 14, $l = -17$ to 17 for (I), and $h = -9$ to 9, $k = 0$ to 11, $l = 0$ to 12 for (II); intensity-control reflections for (I) 1,0,$\overline{10}$, 351 and 3$\overline{53}$, e.s.d. 1%; intensity-control reflections for (II) 323, $\overline{1}34$ and $\overline{3}24$, e.s.d. 0·7%. Unit-cell dimensions refined using 25 reflections with $15 < \theta < 17°$ in (I) and $23 < \theta < 28°$ in (II).] Crystal dimensions, $1·0 \times 0·5 \times 0·5$ mm for (I), $0·4 \times 0·4 \times 0·3$ mm for (II). Structure analysis by direct methods, followed by Fourier maps, and then full-matrix least-squares refinement (using F) of positions and aniso-tropic thermal parameters for all non-H atoms. R 0·047, wR 0·057 (I); R 0·063, wR 0·068 (II); weights assigned: $[\sigma^2(F) + 0·0027F^2]^{-1}$ for (I) and $[\sigma^2(F) + 0·002F^2]^{-1}$ for (II). In both compounds H-atom positions refined with one isotropic vibration parameter for all; in (II) C—H bond lengths restrained at 1·00 (3) Å. Highest peaks in final difference map $0·4$ e Å^{-3} in (I) and $0·2$ e Å^{-3} in (II); maximum shift/e.s.d. in last cycle of least squares, 0·02 for (I) and 0·50 for (II). All calculations used the programs *SHELX*76 (Sheldrick, 1976), which includes scattering factors, *PLUTO* (Motherwell, 1976) and *CALC* (Gould, 1984).

Discussion. Table 1 gives atomic coordinates and Fig. 1 illustrates the molecules, and includes selected dimensions.* Both molecules have molecular symmetry $\overline{1}$ (or i) and bond lengths and angles close to expected values. They confirm that O and C(2) of the five-membered ring in (I) are much more nearly coplanar with the benzene ring (maximum atom displacement 0·16 Å, e.s.d. <0·005 Å) than are O and C(2) in the six-membered ring in (II) (maximum displacement 0·36 Å, e.s.d. <0·005 Å). Another vitamin E analogue, 'chroman-6-ol', has dimensions very similar to those of (II) (Burton, Le Page, Gabe & Ingold, 1980). In the radicals (IR) and (IIR) formed from these molecules, the π-orbital system must include the O atoms. The extent to which they are included in the parent

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* Lists of structure factors, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43087 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic thermal parameters*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

|	x	y	z	U_{eq}/U_{iso}(Å^2)
(a) The difuran (I)				
O(1)	0·9161 (2)	0·3949 (1)	0·2975 (1)	0·0349 (5)
C(2)	1·0588 (2)	0·4790 (1)	0·2291 (1)	0·0318 (5)
C(3)	1·2342 (2)	0·5624 (1)	0·3090 (1)	0·0333 (5)
C(4)	1·1249 (2)	0·5426 (1)	0·4149 (1)	0·0260 (5)
C(5)	0·9455 (2)	0·4439 (1)	0·4015 (1)	0·0258 (5)
C(6)	0·8119 (2)	0·3976 (1)	0·4849 (1)	0·0253 (5)
C(7)	0·6140 (2)	0·2936 (1)	0·4680 (1)	0·0339 (5)
C(8)	0·8666 (3)	0·5620 (2)	0·1619 (1)	0·0464 (5)
C(9)	1·2007 (3)	0·3898 (1)	0·1592 (1)	0·0482 (5)
H(31)	1·4130 (49)	0·5273 (20)	0·3174 (18)	
H(32)	1·2252 (41)	0·6559 (23)	0·2854 (18)	
H(71)	0·6123 (42)	0·2531 (23)	0·3934 (18)	
H(72)	0·4570 (46)	0·3228 (21)	0·4824 (19)	
H(73)	0·6581 (40)	0·2236 (21)	0·5127 (17)	
H(81)	0·7550 (46)	0·5052 (20)	0·1175 (18)	0·071 (2)
H(82)	0·9436 (48)	0·6219 (20)	0·1170 (21)	
H(83)	0·7700 (42)	0·6229 (21)	0·2079 (18)	
H(91)	1·3348 (46)	0·3347 (22)	0·2051 (18)	
H(92)	1·0892 (47)	0·3267 (18)	0·1201 (17)	
H(93)	1·2983 (42)	0·4435 (22)	0·1031 (18)	
(b) The dipyran (II)				
O(1)	0·7589 (3)	0·5160 (2)	0·6868 (2)	0·057 (1)
C(2)	0·7713 (4)	0·6236 (3)	0·7863 (3)	0·055 (1)
C(3)	0·9472 (4)	0·6221 (4)	0·8405 (3)	0·063 (2)
C(4)	1·0747 (4)	0·6536 (4)	0·7388 (3)	0·058 (2)
C(5)	1·1555 (3)	0·5655 (3)	0·5167 (3)	0·045 (2)
C(6)	1·0372 (3)	0·5758 (3)	0·6128 (2)	0·044 (2)
C(7)	0·8828 (3)	0·5115 (3)	0·5948 (2)	0·043 (2)
C(8)	1·3211 (4)	0·6385 (4)	0·5295 (3)	0·066 (2)
C(9)	0·7246 (5)	0·7682 (4)	0·7298 (4)	0·069 (2)
C(10)	0·6426 (5)	0·5773 (5)	0·8845 (4)	0·081 (3)
H(1)	1·4001 (40)	0·5692 (36)	0·5506 (31)	
H(2)	0·9669 (40)	0·5218 (36)	0·8705 (30)	
H(3)	1·0730 (40)	0·7635 (38)	0·7226 (31)	
H(4)	1·1924 (43)	0·6260 (37)	0·7649 (31)	
H(5)	0·8027 (43)	0·8040 (37)	0·6546 (31)	
H(6)	1·3118 (37)	0·7368 (34)	0·5702 (32)	
H(7)	0·5907 (43)	0·7638 (36)	0·7052 (32)	0·095 (3)
H(8)	0·5273 (38)	0·5506 (37)	0·8510 (32)	
H(9)	0·7325 (42)	0·8407 (31)	0·7900 (31)	
H(10)	0·9491 (44)	0·6937 (37)	0·9124 (33)	
H(11)	1·3726 (41)	0·6534 (35)	0·4431 (32)	
H(12)	0·6305 (42)	0·6607 (33)	0·9559 (32)	
H(13)	0·6786 (39)	0·4876 (33)	0·8910 (34)	

(a)

(b)
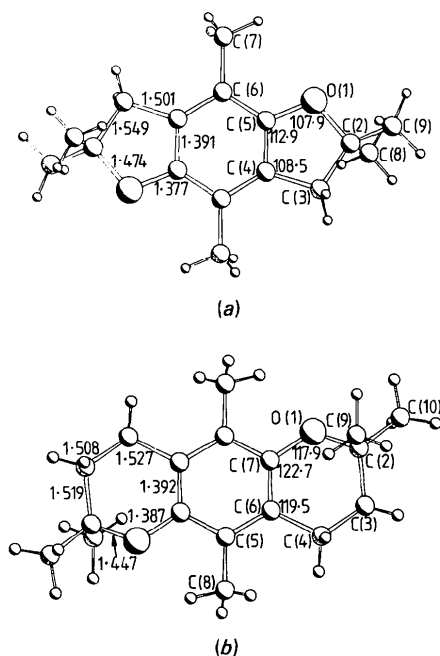
Fig. 1. (a) One molecule of (I) with selected bond lengths (Å, $\sigma = 0.002$ Å) and angles (°, $\sigma = 0.1°$). (b) One molecule of (II) with selected bond lengths (Å, $\sigma = 0.004$ Å) and angles (°, $\sigma = 0.2°$).

molecules must depend on the angle between the O p_z orbital and the normal to the benzene-ring plane, 8° in (I) and 18° in (II) (e.s.d.'s 0.1 and 0.3°); these angles are equivalent to the torsion angles C(4)—C(5)—O(1)—C(2) and C(6)—C(7)—O(1)—C(2) (0° would allow maximum overlap). It is entirely consistent, then, that (I) should form a radical more readily than (II).

ESR spectroscopy (Smith et al., 1984) allows the cation radicals to be compared; the benzylic proton hyperfine coupling constants give average values of

0.618 and 0.136 mT for the radicals (IR) and (IIR) respectively. These values show that much more spin density is present in the heterocyclic ring of the difuran cation radical (IR) due to the tendency towards maximum overlap. It has been shown (MacLean et al., 1985) that for some heterocyclic cations most bond lengths and angles are not greatly affected by the addition of a delocalized electron to give the (neutral) radical. ESR data for the cation radical (IIR) yielded separate values for the axial and equatorial proton coupling constants of 0.237 and 0.035 mT, respectively, and from these the angle between the axial C—H bond, C(3)—H(31), and the normal to the benzene-ring plane is calculated to be 6° (Morton, 1964). The crystallographic results give an angle of 25 (3)° for the parent compound (II), showing that there is a significant change in conformation on addition of a delocalized electron.

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Dipyridinium Bis(hydrogen oxalate)–Oxalic Acid

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Abstract. $2C_5H_6N^+.2C_2HO_4^-.C_2H_2O_4$, $M_r = 428.4$, monoclinic, $P2_1/n$, $a = 3.725$ (1), $b = 8.908$ (2), $c = 26.842$ (4) Å, $\beta = 92.94$ (2)°, $V = 889.5$ (6) Å³, $Z = 2$, $D_x = 1.599$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.31$ cm⁻¹, $F(000) = 444$, $T = 296$ K, $R = 0.049$ for 1179 observations (of 1838 unique data). The structure