

**Structures of 1,4-Difluoro-1,1,4,4-tetranitro-2,3-butanediol Esters:  
1,2-Bis(fluorodinitromethyl)ethylene Diformate, C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>N<sub>4</sub>O<sub>12</sub>, (I), and  
4,5-Bis(fluorodinitromethyl)-1,3-dioxolan-2-one, C<sub>5</sub>H<sub>2</sub>F<sub>2</sub>N<sub>4</sub>O<sub>11</sub>, (II)**

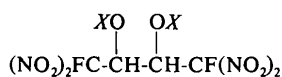
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**Abstract.** (I)  $M_r = 362.1$ , monoclinic,  $C2/c$ ,  $a = 15.055$  (1),  $b = 9.3782$  (7),  $c = 11.714$  (1) Å,  $\beta = 129.058$  (7)°,  $V = 1284.3$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.873$  g cm<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 18.55$  cm<sup>-1</sup>,  $F(000) = 728$ ,  $T = 298$  K,  $R = 0.047$  for 981  $I_s$   $3\sigma$  above background. A space-group ambiguity between  $C2$  and  $C2/c$  was decided in favor of the latter by diffractometer  $\psi$ -scan measurements. Statistical tests gave contrary results. (II)  $M_r = 332.1$ , monoclinic,  $P2_1/c$ ,  $a = 6.283$  (1),  $b = 9.819$  (1),  $c = 18.679$  (3) Å,  $\beta = 96.00$  (2)°,  $V = 1146.0$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.925$  g cm<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 19.39$  cm<sup>-1</sup>,  $F(000) = 664$ ,  $T = 298$  K,  $R = 0.055$  for 1509  $I_s$   $3\sigma$  above background. The formate ester (I) lies on a center of symmetry. The overall conformation is similar to that of 1,4-difluoro-1,1,4,4-tetranitro-2,3-butanediol and 1,4-difluoro-1,1,4,4-tetranitro-2,3-dinitrooxybutane. The conformation in the carbonate ester (II) is different. The O–C and C=O distances in the –O<sub>2</sub>CH group, compared with other esters, are distorted by the nearby CF(NO<sub>2</sub>)<sub>2</sub> group by an effect which could be described as ‘electron withdrawal inhibition of resonance’.

**Introduction.** The fluorodinitromethyl group is of interest as a substituent in energetic materials such as explosives and propellants. We are determining the structures of a number of high-crystal-density polynitro-group-containing organic compounds as a preliminary step in an investigation of the relationships between structure and crystal density in energetic substances. The structures of the formate (I) and cyclic carbonate (II) esters of 1,4-difluoro-1,1,4,4-tetranitro-2,3-butanediol are reported, and compared with the structures of the diol (III) (Dickinson & Holden, 1979) and nitrate ester (IV) (Ammon & Bhattacharjee, 1982).



(I)  $X = -\text{CHO}$       (II)  $X \cdots X = -\text{C}(=\text{O})-$

(III)  $X = -\text{H}$       (IV)  $X = -\text{NO}_2$

**Experimental.** Compounds obtained from Drs H. Adolph and W. Koppes, Naval Surface Weapons Center, Silver Spring, Maryland; formate ester recrystallized from acetone–hexane mixture (solvents dried over molecular sieves) as needles with triangular cross sections; carbonate ester obtained as needles with pentagonal cross sections by slow evaporation of a carbon tetrachloride solution. Picker FACS-I diffractometer, graphite monochromator. Formate ester (I):  $0.31 \times 0.12 \times 0.10$  mm crystal in glass capillary, cell parameters by least squares from 13 reflections manually centered at  $\pm 2\theta$  (average  $|2\theta_o - 2\theta_c| = 0.004^\circ$ ),  $\theta - 2\theta$  scan,  $2^\circ \text{ min}^{-1}$ , 10s backgrounds,  $2\theta$  scan width  $1.3^\circ + 0.29^\circ \tan \theta$ , 4 standards every 100 reflections, av. and max. deviations from mean standard intensities 0.7 and 2.7%, 1549 reflections measured,  $2\theta_{\text{max}} 127^\circ$ , 1056 unique reflections, 981  $3\sigma$  above background, max. and min.  $h, k, l$  17, 10, 10 and 0, 0, –13; MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); max. and av.  $\Delta/\sigma$  0.777 and 0.056 in final LS cycle; max. and min.  $\Delta\rho$  excursions in final difference map  $0.22$  and  $-0.25 \text{ e } \text{Å}^{-3}$ . Carbonate ester (II):  $0.57 \times 0.32 \times 0.25$  mm crystal, cell parameters by least squares from 13 reflections manually centered at  $\pm 2\theta$  (average  $|2\theta_o - 2\theta_c| = 0.008^\circ$ ),  $\theta - 2\theta$  scan,  $2^\circ \text{ min}^{-1}$ , 10s backgrounds,  $2\theta$  scan width  $1.74^\circ + 0.285^\circ \tan \theta$ , 4 standards every 100 reflections, crystal decomposed slowly on exposure to atmosphere, av. and max. deviations from mean standard intensities 4.4 and 17.4% before scaling, 1.9 and 6.3% after scaling, 2341 reflections measured,  $2\theta_{\text{max}} 127^\circ$ , 1692 unique reflections, 1509  $3\sigma$  above background; max. and min.  $h, k, l$  17, 11, 21 and 0, 0, –21; structure solved with direct-methods program PHASE in XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); max. and av.  $\Delta/\sigma$  0.128 and 0.025 in final LS cycle; max. and min.  $\Delta\rho$  excursions in final difference map  $0.37$  and  $-0.41 \text{ e } \text{Å}^{-3}$ .

Both structures refined by full-matrix least squares, minimizing  $\sum w(F_o - F_c)^2$ ,  $w = [1/\sigma(F)]^2$ , reflections with  $I_c < 3\sigma(I)$  omitted; anisotropic temperature factors for C, O, N and F, individual isotropic terms for H; C, N, O and F scattering factors from Cromer & Mann

(1968), H from Stewart, Davidson & Simpson (1965);  $R$ ,  $wR$  and  $S$  for (I) 0.047, 0.067, 8.44 and for (II) 0.055, 0.092, 2.40; all calculations on a Univac 1100/82 computer at the University's Computer Science Center; majority of crystallographic calculations done with XRAY76 system (Stewart *et al.*, 1976).

**Discussion.** We have assumed in this structure report that the space group of the formate ester is  $C2/c$ , with the  $C(1)-C(1')$  bond across a center of symmetry. The original assignment was  $C2$ , on the basis of several violations of the  $h0l$ ,  $l$  odd, systematic absences required by  $C2/c$ . For example, the values of  $I$  and  $\sigma(I)$  for several of the largest  $h0l$  violators were  $201 = 1412(59)$ ,  $401 = 3847(77)$ ,  $10,0,1 = 1353(53)$  and  $607 = 1607(49)$ . Consequently, the structure was solved and refined in  $C2$ , but later refined in  $C2/c$  when the symmetry of the  $C2$  molecule became clear. A preference for the  $C2$  structure was indicated by the Hamilton (1965)  $R$ -factor ratio test: the observed ratio  $R(C2/c \text{ model})/R(C2 \text{ model}) = 1.228$  compared with the theoretical  $\mathcal{R}_{160,851,0.001}$  value of 1.127 suggested that the hypothesis that the  $C2/c$  structure was correct could be rejected at the 99.9% confidence level. A more detailed test was made with the Prince (1982) method, which essentially involves a structure factor by structure factor comparison of two models. The test attempts to correlate the differences in the predictions of the models ( $I_{c1}$ ,  $I_{c2}$ ) with the differences between the observed values ( $I_o$ ) and the arithmetic means of the predictions, by determining the slope ( $\lambda$ ) of the line for  $Z_i = I_{oi} - \frac{1}{2}(I_{c1i} + I_{c2i})$  vs  $X_i = (I_{c1i} - I_{c2i})$  (*i.e.*  $Z = \lambda X$ ; a positive slope favoring model 1 and a negative value model 2), and comparing  $\lambda$  with its estimated variance. The comparison was set up with the  $C2$  structure as model 1, and the regression line calculated with 784 pairs of intensities [ $I_{c1}$  and  $I_{c2} > 3\sigma(I_o)$ ] yielded a slope of +0.00033 and estimated variance of 0.00015 for the 99.9% confidence interval. These calculations indicate that the  $C2$  structure is a significantly better model for the data, in good agreement with the Hamilton  $R$ -factor method.

A final experimental check of the  $h0l$  systematic-absence violations was accomplished by a series of diffractometer  $\psi$ -scan measurements. The original crystal of (I) had been lost by the time it became clear that additional experimental information on the  $h0l$  systematic absences was required. A new crystal was mounted, but the orientation was such that a full  $180^\circ$  rotation was possible for only the 401. The relative intensity [ $I$ ,  $\sigma(I)$ ] of the reflection was 44(29) at  $\psi = 0^\circ$ , and  $\psi$  rotation revealed several maxima, the largest of which was 5615(81) at  $\psi = 1.2^\circ$ . Thus, it would appear that the 401 is indeed unobserved (absent), and we have assumed that the other  $h0l$  violators would show a similar behavior on  $\psi$  rotation. The space group is,

therefore,  $C2/c$ , in contradiction of the indications obtained from the Hamilton and Prince tests.

Atomic coordinates and temperature factors are listed in Table 1\* while bond lengths and angles are given in Tables 2 and 3. *ORTEP* drawings (Johnson, 1971) of the two molecules are given in Fig. 1.

(I), (III) and (IV) have similar conformations and each straddles a center of symmetry midway between  $C(1)$  and  $C(1')$ . The  $-O-C-CF(NO_2)_2$  fragments in the three structures were compared with Nyburg's (1974) best-molecular-fit program, giving r.m.s. deviations of 0.089 Å for (I) vs (III), 0.123 Å for (I) vs (IV) and 0.182 Å for (III) vs (IV). Variations in the torsion angles associated with the fluorodinitromethyl groups account for the major differences in the structures, *viz* the torsion angles  $C(1)-C(2)-N(1)-O(1)$  and  $C(2)-C(1)-N(2)-O(4)$  are  $36.3$  (3) and  $-54.0$  (4)°,  $40.41$  (2) and  $-45.55$  (4) and  $20.7$  (5) and  $-59.9$  (5) in (I), (III) and (IV),

\* Lists of structure factors, anisotropic temperature factors, H coordinates and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38994 (16 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 temperature factors ( $\text{\AA}^2$ ) of (I) and (II)

$$U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} \rho_i^* \rho_j^* a_i a_j$$

The e.s.d. of the last significant digit is given in parentheses.

	x	y	z	$U_{eq}$
(I)				
C(1)	0.0249 (2)	0.4392 (3)	-0.0152 (3)	0.036 (4)
C(2)	0.0059 (3)	0.2960 (3)	0.0304 (3)	0.054 (6)
C(3)	0.1939 (3)	0.4674 (4)	0.0095 (4)	0.059 (3)
N(1)	0.0738 (2)	0.1747 (3)	0.0309 (3)	0.056 (5)
N(2)	-0.1196 (3)	0.2459 (3)	-0.0823 (4)	0.079 (5)
O(1)	0.0838 (2)	0.1765 (3)	-0.0625 (3)	0.136 (4)
O(2)	0.1081 (2)	0.0823 (3)	0.1233 (3)	0.108 (5)
O(3)	-0.1555 (2)	0.2394 (3)	-0.2075 (3)	0.051 (7)
O(4)	-0.1685 (3)	0.2172 (3)	-0.0345 (4)	0.156 (6)
O(5)	0.1460 (1)	0.4599 (2)	0.0776 (2)	0.039 (1)
O(6)	0.1444 (2)	0.4621 (3)	-0.1169 (3)	0.080 (2)
F(1)	0.0324 (2)	0.3007 (2)	0.1607 (2)	0.105 (3)
(II)				
C(1)	0.2106 (4)	0.1189 (3)	0.1096 (1)	0.034 (5)
C(2)	0.2008 (5)	0.2588 (3)	0.0746 (2)	0.044 (7)
C(3)	0.3092 (4)	0.1025 (3)	0.1888 (1)	0.041 (5)
C(4)	0.2891 (4)	0.2113 (3)	0.2449 (1)	0.036 (4)
C(5)	0.5587 (4)	0.0467 (3)	0.1147 (1)	0.033 (7)
N(1)	0.0324 (5)	0.3527 (3)	0.0989 (1)	0.070 (5)
N(2)	0.1367 (5)	0.2418 (3)	-0.0070 (1)	0.061 (6)
N(3)	0.0664 (4)	0.2113 (3)	0.2734 (1)	0.048 (4)
N(4)	0.4458 (4)	0.1791 (2)	0.3126 (1)	0.044 (3)
O(1)	-0.0931 (4)	0.3004 (3)	0.1365 (2)	0.086 (2)
O(2)	0.0372 (6)	0.4700 (3)	0.0793 (1)	0.157 (7)
O(3)	-0.0322 (4)	0.1853 (3)	-0.0227 (1)	0.057 (6)
O(4)	0.2602 (5)	0.2839 (3)	-0.0472 (1)	0.088 (4)
O(5)	-0.0285 (4)	0.1049 (3)	0.2708 (1)	0.064 (6)
O(6)	0.0124 (4)	0.3184 (2)	0.2971 (1)	0.079 (6)
O(7)	0.4377 (4)	0.0634 (2)	0.3339 (1)	0.065 (3)
O(8)	0.5574 (3)	0.2714 (2)	0.3368 (1)	0.039 (5)
O(9)	0.3655 (3)	0.0461 (2)	0.07304 (9)	0.039 (3)
O(10)	0.5338 (3)	0.0917 (2)	0.1814 (1)	0.037 (3)
O(11)	0.7203 (3)	0.0114 (2)	0.0944 (1)	0.054 (5)
F(1)	0.3870 (3)	0.3252 (2)	0.0824 (1)	0.049 (2)
F(2)	0.3279 (3)	0.3358 (1)	0.22441 (8)	0.046 (2)

respectively. No specific structural features could be singled out to account for the C—C—N—O torsion-angle variations in these compounds. Crystal packing undoubtedly is a factor.

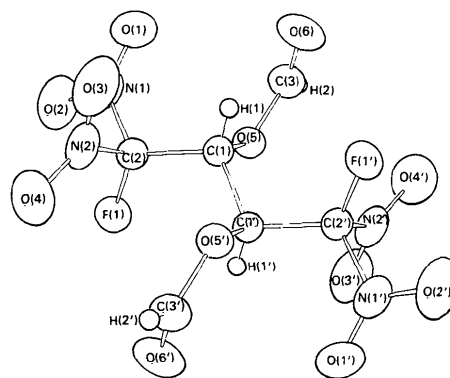
The r.m.s. deviation between the two C—CF(NO<sub>2</sub>)<sub>2</sub> moieties in the carbonate ester (II) is 0.163 Å, and the best fit between these fragments in (I) and (II) gives a r.m.s. deviation of 0.241 Å. The C—C—N—O torsion angles in the two halves of (II) are different as is evident from C(3)—C(4)—N(3)—O(5), C(3)—C(4)—

Table 2. Bond lengths (Å), angles (°) and torsion angles (°) of (I), with e.s.d.'s in parentheses

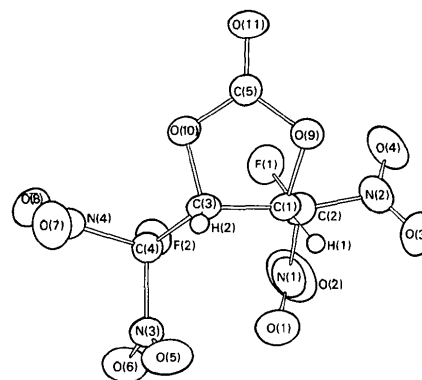
C(1)—C(2)	1.537 (5)	C(3)—O(5)	1.374 (6)
C(1)—O(5)	1.430 (3)	C(3)—O(6)	1.166 (5)
C(1)—C(1')	1.525 (5)	N(1)—O(1)	1.196 (6)
C(2)—N(1)	1.526 (5)	N(1)—O(2)	1.219 (4)
C(2)—N(2)	1.546 (4)	N(2)—O(3)	1.203 (6)
C(2)—F(1)	1.312 (5)	N(2)—O(4)	1.204 (8)
C(2)—C(1)—C(1')	110.3 (1)	O(5)—C(3)—O(6)	125.8 (3)
C(2)—C(1)—O(5)	106.4 (5)	C(2)—N(1)—O(1)	117.2 (3)
O(5)—C(1)—C(1')	107.4 (1)	C(2)—N(1)—O(2)	116.2 (4)
N(1)—C(2)—C(1)	112.5 (4)	O(1)—N(1)—O(2)	126.5 (4)
N(1)—C(2)—F(1)	107.9 (2)	C(2)—N(2)—O(3)	115.2 (4)
N(1)—C(2)—N(2)	103.4 (2)	C(2)—N(2)—O(4)	116.6 (4)
N(2)—C(2)—C(1)	111.3 (2)	O(3)—N(2)—O(4)	128.3 (3)
N(2)—C(2)—F(1)	108.4 (4)	C(1)—O(5)—C(3)	116.8 (2)
C(1)—C(2)—F(1)	112.8 (2)		
C(1')—C(1)—C(2)—N(1)	-168.8 (2)	C(1)—C(2)—N(1)—O(1)	-36.3 (3)
C(1')—C(1)—C(2)—N(2)	-75.8 (3)	C(1)—C(2)—N(2)—O(3)	54.0 (4)
C(1')—C(1)—C(2)—F(1)	-46.4 (3)	C(1)—O(5)—C(3)—O(6)	2.2 (7)
C(1')—C(1)—O(5)—C(3)	-124.1 (3)		

Table 3. Bond lengths (Å), angles (°) and torsion angles (°) of (II), with e.s.d.'s in parentheses

C(1)—C(2)	1.519 (4)	C(5)—O(9)	1.371 (3)
C(1)—C(3)	1.553 (3)	C(5)—O(10)	1.347 (3)
C(1)—O(9)	1.437 (3)	C(5)—O(11)	1.173 (3)
C(2)—N(1)	1.508 (4)	N(1)—O(1)	1.223 (4)
C(2)—N(2)	1.546 (4)	N(1)—O(2)	1.210 (4)
C(2)—F(1)	1.335 (3)	N(2)—O(3)	1.206 (4)
C(3)—C(4)	1.510 (4)	N(2)—O(4)	1.207 (4)
C(3)—O(10)	1.436 (3)	N(3)—O(5)	1.202 (4)
C(4)—N(3)	1.549 (4)	N(3)—O(6)	1.203 (4)
C(4)—N(4)	1.552 (3)	N(4)—O(7)	1.206 (3)
C(4)—F(2)	1.311 (3)	N(4)—O(8)	1.205 (3)
C(2)—C(1)—C(3)	119.8 (2)	O(9)—C(5)—O(10)	110.2 (2)
C(2)—C(1)—O(9)	104.2 (2)	O(9)—C(5)—O(11)	124.1 (2)
C(3)—C(1)—O(9)	100.3 (2)	O(10)—C(5)—O(11)	125.8 (2)
C(1)—C(2)—N(1)	115.0 (2)	C(2)—N(1)—O(1)	115.5 (3)
C(1)—C(2)—N(2)	108.7 (2)	C(2)—N(1)—O(2)	116.8 (3)
C(1)—C(2)—F(1)	113.6 (2)	O(1)—N(1)—O(2)	127.7 (3)
N(1)—C(2)—F(1)	107.6 (2)	C(2)—N(2)—O(3)	114.9 (3)
N(1)—C(2)—N(2)	104.1 (2)	C(2)—N(2)—O(4)	117.3 (3)
N(2)—C(2)—F(1)	107.2 (2)	O(3)—N(2)—O(4)	127.9 (3)
C(1)—C(3)—C(4)	122.3 (2)	C(4)—N(3)—O(5)	116.7 (2)
C(1)—C(3)—O(10)	102.2 (2)	C(4)—N(3)—O(6)	115.2 (2)
C(4)—C(3)—O(10)	105.9 (2)	O(5)—N(3)—O(6)	128.1 (3)
C(3)—C(4)—N(3)	112.5 (2)	C(4)—N(4)—O(7)	114.5 (2)
C(3)—C(4)—N(4)	109.2 (2)	C(4)—N(4)—O(8)	116.6 (2)
C(3)—C(4)—F(2)	115.2 (2)	O(7)—N(4)—O(8)	128.9 (2)
N(3)—C(4)—F(2)	107.6 (2)	C(1)—O(9)—C(5)	109.4 (2)
N(3)—C(4)—N(4)	103.8 (2)	C(3)—O(10)—C(5)	108.9 (2)
N(4)—C(4)—F(2)	107.8 (2)		
C(1)—C(3)—O(10)—C(5)	-24.0 (2)	C(3)—C(1)—C(2)—F(1)	50.1 (3)
C(3)—O(10)—C(5)—O(9)	9.1 (3)	C(1)—C(3)—C(4)—N(3)	78.1 (3)
O(10)—C(5)—O(9)—C(1)	11.6 (3)	C(1)—C(3)—C(4)—N(4)	-167.2 (2)
C(5)—O(9)—C(1)—C(3)	-25.0 (2)	C(1)—C(3)—C(4)—F(2)	-45.7 (3)
O(9)—C(1)—C(3)—O(10)	28.8 (2)	C(1)—C(2)—N(1)—O(1)	-8.8 (4)
C(2)—C(1)—C(3)—C(4)	33.8 (4)	C(1)—C(2)—N(1)—O(2)	58.3 (3)
C(3)—C(1)—C(2)—N(1)	-74.5 (3)	C(3)—C(1)—N(3)—O(5)	26.7 (3)
C(3)—C(1)—C(2)—N(2)	169.3 (2)	C(3)—C(4)—N(4)—O(7)	-48.9 (3)



(a)



(b)

Fig. 1.(a) ORTEP (Johnson, 1971) drawing of (I) with the C,N,O and F atoms depicted as 50% probability boundary ellipses. H atoms are shown as 0.1 Å radius circles. (b) ORTEP drawing of (II) with the C,N,O and F atoms depicted as 50% probability boundary ellipses. H atoms are shown as 0.1 Å radius circles.

N(4)—O(7) [26.7 (3) and -48.9 (3)°] and C(1)—C(2)—N(1)—O(1), C(1)—C(2)—N(2)—O(3) [-8.8 (4) and 58.3 (3)°], the former showing a better agreement with the formate ester than the latter.

The fluorodinitromethyl lengths and angles in (I)—(IV) are similar, with the largest deviations occurring in C(2)—N(1) {1.526 (5), [1.508 (4), 1.549 (4)], 1.535 (5), 1.561 (5) Å}. The CH—OX distances of 1.430 (3) in (I), 1.436 (3) and 1.437 (3) in (II), and 1.422 (4) Å in (IV), compared to the 1.400 (4) Å in diol (III), reflect a bond-lengthening effect by substitution of oxygen in (I), (II) and (IV).

There are only a few crystal structures of formate esters in the literature. The Cambridge Crystallographic Data Center (1982) files contained three formate ester entries, but coordinate data were available for only one, viz 4-oxo-3-azatricyclo[7.3.1.0<sup>3,8</sup>]tridec-11-yl formate (AZFXTD; Schagen, Overbeek, van der Putten & Schenk, 1978). The —O—C=O distances of 1.326 (5) and 1.188 (6) Å in AZFXTD are similar to those reported in acetate esters, such as the 1.341 (4)

and 1.186 (5) Å in methyl 2,3,4-tri-*O*-acetyl- $\beta$ -D-lyxopyranoside (James & Stevens, 1981). These distances differ from the 1.374 (6) and 1.166 (5) Å values in formate ester (I) in a way which suggests that of the two principal ester canonical forms,  $-\text{O}-\text{C}=\text{O} \leftrightarrow -\text{O}^+=\text{C}-\text{O}^-$ , the dipolar contribution is disfavored in (I) compared to other esters. One might expect that the energy of the dipolar form in (I) would be raised by the adjacent electron-withdrawing  $\text{CF}(\text{NO}_2)_2$  group, resulting in a smaller contribution to the resonance hybrid. This effect should lengthen the  $\text{O}-\text{C}$  bond and shorten the  $\text{C}=\text{O}$  bond. A similar phenomenon is present in nitrate ester (IV), in terms of the long  $-\text{O}-\text{N}$  bond in the  $-\text{O}-\text{NO}_2$  group.

The  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  stretching frequencies in the infrared spectra of (I) and (II) (Koppes, 1983) are consistent with ester and carbonate functionalities that contain smaller dipolar resonance form contributions than usual. The  $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{C}-\text{O}}$  values of 1773 and 1090  $\text{cm}^{-1}$  in (I), compared to 1720 and 1180  $\text{cm}^{-1}$  in ethyl formate (Sadtler Standard Spectra, 1973), correspond to a stronger  $\text{C}=\text{O}$  and weaker  $\text{C}-\text{O}$ . Bellamy (1964) has suggested that the  $\nu_{\text{C}=\text{O}}$  of 1776  $\text{cm}^{-1}$  in vinyl acetate is due to a decreased contribution of the dipolar resonance form. In carbonate ester (II), the  $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{C}-\text{O}}$  of 1874 and 1146  $\text{cm}^{-1}$ , compared to 1800 and 1160  $\text{cm}^{-1}$  in ethylene carbonate (Sadtler Standard Spectra, 1966), show the same trend.

The deviations of the five ring atoms in (II) from their LS plane are C(5) 0.011 (2), O(9) -0.070 (9), O(10) 0.070 (1), C(1) 0.207 (2), C(3) -0.187 (3) Å (LS plane program of Ito, 1982). The carbonate ( $-\text{O}_2\text{C}=\text{O}$ ) is planar, and the remaining two ring carbon atoms are displaced by equal, but opposite, amounts from the  $\text{CO}_3$  plane. Since the two  $\text{CF}(\text{NO}_2)_2$  substituents are *cis*, the ring twist is necessary to provide a staggered conformation about C(1)-C(3). Bond lengths and angles of the ring compare well with similar parameters in five other ethylene carbonates found in the literature, the largest deviations being in the  $\text{C}-\text{O}$  distances.

The intermolecular contacts in (I) are dominated by  $\text{O}\cdots\text{O}$  and  $\text{F}\cdots\text{O}$  interactions, while in (II) there is a larger number of  $\text{O}\cdots\text{O}$  interactions and about equal numbers of  $\text{F}\cdots\text{O}$  and  $\text{N}\cdots\text{O}$  contacts. The shortest

$\text{O}\cdots\text{O}$ ,  $\text{F}\cdots\text{O}$  and  $\text{N}\cdots\text{O}$  contacts are 3.008 (5) [O(3) $\cdots$ O(6) ( $-x, y, -\frac{1}{2}-z$ )], 3.007 (3) [F(1) $\cdots$ O(6) ( $x, 1-y, \frac{1}{2}+z$ )], 2.794 (4) Å [N(2) $\cdots$ O(5) ( $-x, 1-y, -z$ )] in (I) and 2.991 (4) [O(7) $\cdots$ O(4) ( $x, \frac{1}{2}-y, \frac{1}{2}+z$ )], 2.947 (3) [F(2) $\cdots$ O(7) ( $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ )] and 2.999 (4) Å [O(4) $\cdots$ N(4) ( $x, \frac{1}{2}-y, -\frac{1}{2}+z$ )] in (II), respectively.

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#### References

- AMMON, H. L. & BHATTACHARJEE, S. K. (1982). *Acta Cryst.* **B38**, 2718-2721.
- BELLAMY, L. J. (1964). *The Infrared Spectra of Complex Molecules*, p. 182. New York: John Wiley.
- CAMBRIDGE CRYSTALLOGRAPHIC DATA CENTER (1982). January update. Univ. Chemical Laboratory, Lensfield Road, Cambridge, England. *Molecular Structures and Dimensions*, Vol. 13. Dordrecht:Reidel.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- DICKINSON, C. & HOLDEN, J. R. (1979). *Acta Cryst.* **B35**, 487-489.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502-510.
- ITO, T. (1982). *Acta Cryst.* **A38**, 869-870.
- JAMES, V. J. & STEVENS, J. D. (1981). *Cryst. Struct. Commun.* **10**, 719-722.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOPPE, W. (1983). Unpublished.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- NYBURG, S. C. (1974). *Acta Cryst.* **B30**, 251-253.
- PRINCE, E. (1982). *Acta Cryst.* **B38**, 1099-1100.
- Sadtler Standard Spectra (1966). IR spectrum no. 375. Sadtler Research Laboratories, Philadelphia, PA.
- Sadtler Standard Spectra (1973). IR spectrum no. 29717. Sadtler Research Laboratories, Philadelphia, PA.
- SCHAGEN, J. D., OVERBEEK, A. R., VAN DER PUTTEN, N. & SCHENK, H. (1978). *Cryst. Struct. Commun.* **7**, 707-710.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. S. & FLACK, H. (1976). The XRAY system - version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland 20742.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.