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Structures of the Tetrafluoroborate Salts of Triphenylcarbenium Ions with One and with Two 4-Methoxy Substituents: Stable Carbocations

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Abstract. *p*-Methoxyphenyldiphenylcarbenium tetrafluoroborate (1): $[C_{20}H_{17}O][BF_4]$, $M_r = 360.2$, monoclinic, $P2_1/n$, $a = 7.962$ (1), $b = 15.463$ (2), $c = 14.567$ (1) Å, $\beta = 95.54$ (1)°, $V = 1785.1$ Å³, $Z = 4$, $D_x = 1.340$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 1.0$ cm⁻¹, $F(000) = 744$, $T = 295$ K, $R = 0.063$ for 2356 unique observed reflections. Di(*p*-methoxyphenyl)phenylcarbenium tetrafluoroborate (2): $[C_{21}H_{19}O_2][BF_4]$, $M_r = 390.2$, monoclinic, $P2_1/n$, $a = 7.942$ (2), $b = 16.773$ (4), $c = 14.447$ (2) Å, $\beta = 90.54$ (2)°, $V = 1924.4$ Å³, $Z = 4$, $D_x = 1.347$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 9.2$ cm⁻¹, $F(000) = 808$, $T = 295$ K, $R = 0.114$ for 1259 unique observed reflections. Both cations have a propeller structure, with the aryl rings twisted out of the plane of the carbenium-ion centre. The angle of twist is smaller for the 4-methoxyphenyl groups [26.6 (2), 27.8 (5) and 29.6 (5)°] than for the phenyl groups [31.3 (2), 38.6 (2) and 37.3 (5)°] as a consequence of greater conjugation.

Introduction. Previous crystal structure analyses of triarylcarbenium ions $[Ar_3C]^+$ have been almost entirely restricted to substances in which the aryl groups are identical, the one exception being the 4,4'-biphenylbis(diphenylmethyl) ion (McKechnie & Paul, 1971), in which two triphenylcarbenium ions are joined together through a *para*-biphenyl link between a phenyl group of each one. All the cations adopt a propeller shape, the tendency of at least one aryl group to be coplanar

with the carbenium centre being opposed by steric interactions between neighbouring *ortho* H atoms. The aryl rings are twisted about 30° out of the central carbenium plane in each case, for unsubstituted triphenylcarbenium ions with a variety of counterions (Gomes de Mesquita, MacGillavry & Eriks, 1965; Krebs & Paulat, 1979; Fenske, Kujanek & Dehnicke, 1983; Cook, Dahl & Dickerhoof, 1972) and for tris(4-aminophenyl)carbenium perchlorate (Koh & Eriks, 1971). A similar angle of twist has been estimated for the tris(4-methoxyphenyl)carbenium ion in a structure subject to considerable disorder (Andersen & Klewe, 1965).

We report here the crystal structures of 4-(methoxyphenyl)diphenylcarbenium tetrafluoroborate [4-methoxytritylium tetrafluoroborate, (1)] and bis(4-methoxyphenyl)phenylcarbenium tetrafluoroborate [4,4'-dimethoxytritylium tetrafluoroborate, (2)]. We have recently shown that these salts are very useful reagents for the protection of alcohols including nucleosides and sugars (Bleasdale, Ellwood & Golding, 1990). It was of interest to determine the precise structures of the salts and, in particular, the relative degrees of interaction of the 4-methoxyphenyl and phenyl groups with the carbenium centre, for comparison with the triphenyl and tris(4-methoxyphenyl) end members of the series. This will assist the correlation of structure with reactivity, and the design of new 'fine-tuned' protecting groups for amino, hydroxy and thiol functions.

Experimental. The red-orange, air-stable salt (2) was prepared as previously described by Bleasdale, Ell-

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for (1)

	$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	2505 (3)	3366 (2)	-1309 (2)	58 (1)
C(2)	2362 (3)	4167 (2)	-843 (2)	57 (1)
C(3)	3048 (3)	4296 (2)	79 (2)	59 (1)
C(4)	2897 (3)	5067 (2)	530 (2)	60 (1)
C(5)	1999 (3)	5744 (2)	68 (2)	61 (1)
C(6)	1295 (3)	5643 (2)	-846 (2)	62 (1)
C(7)	1483 (3)	4880 (2)	-1292 (2)	60 (1)
C(8)	2710 (3)	2553 (2)	-806 (2)	62 (1)
C(9)	1985 (4)	2425 (2)	23 (2)	73 (1)
C(10)	2185 (5)	1642 (2)	478 (3)	88 (1)
C(11)	3085 (5)	980 (2)	119 (3)	94 (1)
C(12)	3801 (5)	1094 (2)	-691 (3)	86 (1)
C(13)	3626 (4)	1872 (2)	-1162 (2)	71 (1)
C(14)	2451 (3)	3354 (2)	-2308 (2)	60 (1)
C(15)	3251 (4)	4014 (2)	-2771 (2)	68 (1)
C(16)	3262 (5)	3988 (2)	-3723 (2)	82 (1)
C(17)	2442 (5)	3327 (3)	-4220 (3)	92 (1)
C(18)	1633 (5)	2687 (3)	-3777 (3)	89 (1)
C(19)	1639 (4)	2684 (2)	-2829 (2)	73 (1)
O(1)	1734 (3)	6510 (1)	453 (2)	74 (1)
C(20)	2348 (5)	6658 (2)	1404 (3)	86 (1)
B	2067 (6)	9123 (3)	2155 (3)	81 (1)
F(1)	689 (4)	9130 (2)	2637 (2)	142 (2)
F(2)	1678 (6)	8841 (2)	1295 (2)	156 (2)
F(3)	2735 (6)	9918 (2)	2204 (2)	172 (2)
F(4)	3151 (6)	8560 (3)	2619 (3)	174 (2)

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for (2)

	$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	2625 (11)	3626 (6)	1633 (6)	63 (3)
C(2)	2356 (11)	4371 (5)	1137 (6)	59 (3)
C(3)	3016 (12)	4409 (5)	244 (6)	63 (4)
C(4)	2767 (12)	5100 (6)	-241 (7)	67 (4)
C(5)	1890 (13)	5729 (6)	100 (7)	68 (4)
C(6)	1204 (13)	5650 (6)	987 (7)	73 (4)
C(7)	1431 (11)	4992 (5)	1507 (6)	62 (3)
C(8)	2870 (12)	2885 (5)	1208 (6)	58 (3)
C(9)	2154 (11)	2714 (6)	313 (6)	65 (3)
C(10)	2410 (13)	2005 (6)	-127 (7)	76 (4)
C(11)	3467 (13)	1452 (5)	313 (7)	73 (4)
C(12)	4160 (14)	1583 (5)	1174 (7)	81 (4)
C(13)	3852 (13)	2259 (6)	1619 (7)	73 (4)
C(14)	2658 (11)	3660 (7)	2685 (6)	78 (4)
C(15)	3412 (13)	4291 (8)	3127 (7)	91 (5)
C(16)	3518 (18)	4317 (13)	4078 (9)	132 (8)
C(17)	2892 (10)	3677 (14)	4590 (10)	159 (9)
C(18)	2131 (19)	3080 (11)	4160 (8)	147 (8)
C(19)	1998 (15)	3018 (7)	3202 (8)	100 (5)
O(1)	1568 (9)	6422 (4)	-335 (5)	93 (3)
C(20)	2148 (16)	6518 (8)	-1262 (9)	118 (6)
O(2)	3827 (10)	751 (4)	-63 (5)	96 (3)
C(21)	3366 (17)	598 (7)	-997 (9)	115 (6)
B	-3491 (23)	6297 (11)	2393 (11)	108 (7)
F(1)	-4610 (11)	6188 (7)	1715 (6)	182 (5)
F(2)	-4050 (16)	6496 (9)	3154 (6)	226 (7)
F(3)	-2241 (17)	6775 (9)	2099 (9)	227 (7)
F(4)	-2610 (22)	5614 (7)	2440 (8)	233 (8)

wood & Golding (1990). Crystals suitable for X-ray analysis were obtained by vapour diffusion of diethyl ether into a solution in acetonitrile; repeated attempts gave only crystals of poor quality. The yellow-brown salt (1) was prepared from 4-methoxytrityl alcohol essentially by the method described for obtaining tritylium tetrafluoroborate from trityl alcohol (Dauben, Honnen & Harmon, 1960): the alcohol (2.9 g, 10 mmol) in acetic anhydride (20 cm³) was treated with tetrafluoroboric acid (40% w/v in water, 3.5 cm³) at such a rate that the temperature did not rise above 298 K. A dark brown solution was obtained, to which dry diethyl ether was added, causing the product to precipitate as yellow-brown crystals (3.3 g, 90%). Recrystallization by vapour diffusion of diethyl ether into a solution in acetonitrile gave suitable crystals for X-ray analysis: m.p. 478–481 K; ¹H NMR (CDCl₃) δ 4.1 (s, 3H), 7.0–7.75 (m, 14H). Found: C 66.58, H 4.79%. C₂₀H₁₇OBF₄ requires C 66.70, H 4.76%.

For (1) [for (2) in square brackets where different]: crystal size 0.48 × 0.52 × 0.68 mm [0.12 × 0.20 × 0.54 mm], Stoe-Siemens diffractometer, unit-cell parameters from 2 θ values of 32 reflections (20–25° [25–40°]) measured at $\pm\omega$. Data collection in ω/θ scan mode with on-line profile fitting (Clegg, 1981), 2 θ_{max} 50° [110°], index ranges $h -9 \rightarrow 9$, $k 0 \rightarrow 18$, $l 0 \rightarrow 17$ and $h -9 \rightarrow 9$, $k -3 \rightarrow 0$, $l -17 \rightarrow 0$ [three complete equivalent sets of data, and a partial fourth set, with maximum indices of 8, 17 and 15]; no significant variation in intensities of three standard reflections, no absorption corrections; 4149 [7535]

Table 3. Bond lengths (\AA) and angles ($^\circ$) for (1)

C(1)–C(2)	1.422 (4)	C(1)–C(8)	1.456 (4)
C(1)–C(14)	1.452 (4)	C(2)–C(3)	1.414 (4)
C(2)–C(7)	1.430 (4)	C(3)–C(4)	1.372 (4)
C(4)–C(5)	1.402 (4)	C(5)–C(6)	1.403 (4)
C(5)–O(1)	1.335 (3)	C(6)–C(7)	1.363 (4)
C(8)–C(9)	1.402 (5)	C(8)–C(13)	1.409 (4)
C(9)–C(10)	1.383 (5)	C(10)–C(11)	1.381 (6)
C(11)–C(12)	1.370 (7)	C(12)–C(13)	1.385 (5)
C(14)–C(15)	1.410 (4)	C(14)–C(19)	1.404 (4)
C(15)–C(16)	1.387 (5)	C(16)–C(17)	1.381 (6)
C(17)–C(18)	1.374 (6)	C(18)–C(19)	1.381 (5)
O(1)–C(20)	1.443 (4)	B–F(1)	1.359 (6)
B–F(2)	1.334 (5)	B–F(3)	1.339 (6)
B–F(4)	1.359 (6)		
C(2)–C(1)–C(8)	121.4 (3)	C(2)–C(1)–C(14)	119.6 (2)
C(8)–C(1)–C(14)	119.0 (2)	C(1)–C(2)–C(3)	122.3 (2)
C(1)–C(2)–C(7)	120.7 (2)	C(3)–C(2)–C(7)	116.9 (2)
C(2)–C(3)–C(4)	122.3 (2)	C(3)–C(4)–C(5)	118.9 (2)
C(4)–C(5)–C(6)	120.7 (2)	C(4)–C(5)–O(1)	123.7 (3)
C(6)–C(5)–O(1)	115.6 (2)	C(5)–C(6)–C(7)	119.8 (2)
C(2)–C(7)–C(6)	121.4 (3)	C(1)–C(8)–C(9)	121.4 (3)
C(1)–C(8)–C(13)	119.8 (3)	C(9)–C(8)–C(13)	118.8 (3)
C(8)–C(9)–C(10)	119.9 (3)	C(9)–C(10)–C(11)	120.5 (4)
C(10)–C(11)–C(12)	120.3 (4)	C(11)–C(12)–C(13)	120.6 (3)
C(8)–C(13)–C(12)	119.8 (3)	C(1)–C(14)–C(15)	120.0 (2)
C(1)–C(14)–C(19)	121.2 (3)	C(15)–C(14)–C(19)	118.8 (3)
C(14)–C(15)–C(16)	120.3 (3)	C(15)–C(16)–C(17)	119.8 (3)
C(16)–C(17)–C(18)	120.4 (4)	C(17)–C(18)–C(19)	121.0 (4)
C(14)–C(19)–C(18)	119.7 (3)	C(5)–O(1)–C(20)	119.4 (2)
F(1)–B–F(2)	111.2 (4)	F(1)–B–F(3)	107.5 (4)
F(2)–B–F(3)	113.9 (4)	F(1)–B–F(4)	104.7 (4)
F(2)–B–F(4)	109.7 (4)	F(3)–B–F(4)	109.4 (4)

reflections measured, 3150 [2420] unique, 2356 [1259] with $F > 4\sigma_c(F)$ (σ_c from counting statistics only), $R_{int} = 0.012$ [0.038].

Table 4. Bond lengths (Å) and angles (°) for (2)

C(1)—C(2)	1.457 (13)	C(1)—C(8)	1.400 (13)
C(1)—C(14)	1.520 (13)	C(2)—C(3)	1.398 (13)
C(2)—C(7)	1.384 (12)	C(3)—C(4)	1.368 (13)
C(4)—C(5)	1.360 (14)	C(5)—C(6)	1.403 (15)
C(5)—O(1)	1.344 (12)	C(6)—C(7)	1.347 (13)
C(8)—C(9)	1.438 (12)	C(8)—C(13)	1.433 (13)
C(9)—C(10)	1.365 (13)	C(10)—C(11)	1.399 (14)
C(11)—C(12)	1.373 (14)	C(11)—O(2)	1.329 (11)
C(12)—C(13)	1.327 (13)	C(14)—C(15)	1.371 (16)
C(14)—C(19)	1.414 (16)	C(15)—C(16)	1.377 (16)
C(16)—C(17)	1.398 (27)	C(17)—C(18)	1.322 (26)
C(18)—C(19)	1.391 (17)	O(1)—C(20)	1.430 (15)
O(2)—C(21)	1.418 (15)	B—F(1)	1.329 (19)
B—F(2)	1.235 (19)	B—F(3)	1.349 (23)
B—F(4)	1.344 (23)		
C(2)—C(1)—C(8)	124.5 (8)	C(2)—C(1)—C(14)	117.4 (8)
C(8)—C(1)—C(14)	118.1 (8)	C(1)—C(2)—C(3)	116.0 (8)
C(1)—C(2)—C(7)	122.1 (8)	C(3)—C(2)—C(7)	121.8 (8)
C(2)—C(3)—C(4)	117.3 (8)	C(3)—C(4)—C(5)	122.9 (9)
C(4)—C(5)—C(6)	117.6 (9)	C(4)—C(5)—O(1)	126.6 (9)
C(6)—C(5)—O(1)	115.8 (9)	C(5)—C(6)—C(7)	122.4 (9)
C(2)—C(7)—C(6)	118.0 (9)	C(1)—C(8)—C(9)	121.1 (8)
C(1)—C(8)—C(13)	123.1 (8)	C(9)—C(8)—C(13)	115.8 (8)
C(8)—C(9)—C(10)	122.2 (9)	C(9)—C(10)—C(11)	117.2 (9)
C(10)—C(11)—C(12)	122.7 (9)	C(10)—C(11)—O(2)	122.1 (9)
C(12)—C(11)—O(2)	115.2 (9)	C(11)—C(12)—C(13)	120.0 (9)
C(8)—C(13)—C(12)	121.8 (9)	C(1)—C(14)—C(15)	119.8 (9)
C(1)—C(14)—C(19)	119.8 (9)	C(15)—C(14)—C(19)	120.3 (9)
C(14)—C(15)—C(16)	120.8 (13)	C(15)—C(16)—C(17)	119.0 (16)
C(16)—C(17)—C(18)	119.8 (13)	C(17)—C(18)—C(19)	123.6 (15)
C(14)—C(19)—C(18)	116.4 (12)	C(5)—O(1)—C(20)	118.3 (8)
C(11)—O(2)—C(21)	119.7 (8)	F(1)—B—F(2)	116.7 (16)
F(1)—B—F(3)	109.8 (13)	F(2)—B—F(3)	113.0 (16)
F(1)—B—F(4)	105.4 (14)	F(2)—B—F(4)	112.1 (15)
F(3)—B—F(4)	98.0 (15)		

Structure solution by direct methods, blocked-cascade least-squares refinement on F , weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 9 - 21G - 2G^2 - 22H + 13H^2 + 56GH$ [$\sigma_c^2(F) = 3 + 224G - 26G^2 + 8H + 3H^2 - 359GH$] ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$; Wang & Robertson, 1985), anisotropic thermal parameters for all non-H atoms, H atoms constrained: C—H 0.96 Å, H—C—H 109.5°, aromatic H atoms on ring angle external bisectors, $U(H) = 1.2U_{eq}(C)$, extinction parameter $x = 1.21(1) \times 10^{-6}$; $F_c = F_o/(1 + xF_c^2/\sin^2\theta)^{0.25}$ [extinctions effects negligible]. $R = 0.063$ [0.114], $wR = 0.071$ [0.106], $S = 0.99$ [1.10] for 239 [254] parameters, mean $\Delta/\sigma = 0.005$ [0.001], max. $\Delta/\sigma = 0.018$ [0.003], $(\Delta\rho)_{max} = 0.49$ [0.38] $(\Delta\rho)_{min} = -0.31$ [-0.29] e Å⁻³. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149); *SHELXTL* (Sheldrick, 1985) and local computer programs were used.

Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 1 and 2, bond lengths and angles in Tables 3 and 4.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53269 (31pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structures of the two cations are shown in Figs. 1 and 2. Like previously determined triarylcarbenium ions, they have a propeller shape, with the aryl rings all twisted in the same sense out of the plane of the central carbenium-ion centre. The carbenium unit is planar within the limits of experimental error: C(1) lies 0.001 (3) Å from the plane of C(2), C(8) and C(14) for (1), and 0.004 (9) Å from this plane for (2). The dihedral angles between this central unit and the aryl rings for each structure are: phenyl groups, 31.3 (2) and 38.6 (2)° in (1), 37.3 (5)° in (2); 4-methoxyphenyl groups, 26.6 (2)° in (1), 27.8 (5) and 29.6 (5)° in (2). The O and C atoms of the methoxy substituents lie close to the plane of the aryl ring to which they are attached in each case: dihedral angles between the rings and the C—O—C units are 2.4 (2)° for (1), 2.6 (5) and 8.8 (5)° for (2). Thus there is a clear tendency for 4-methoxy-substituted phenyl rings to be more nearly coplanar with the carbenium centre in these mixed systems. This is because the methoxy group offers greater stabilization of the carbenium centre than does an H

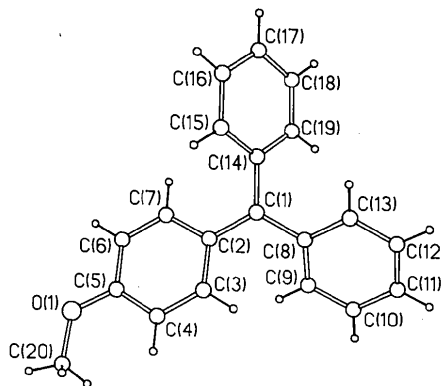


Fig. 1. The structure of the cation of (1) projected on the plane of the carbenium ion centre.

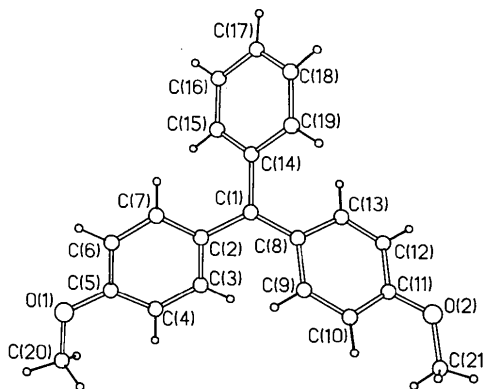


Fig. 2. The structure of the cation of (2) projected on the plane of the carbenium ion centre.

atom. The average twist is similar to that found in the triphenylcarbenium cation (Gomes de Mesquita, MacGillavry & Eriks, 1965; Krebs & Paulat, 1979) and in derivatives with identical substitution on all three rings (Koh & Eriks, 1971; Andersen & Klewe, 1965).

The unit-cell dimensions of the structures reported here are quite similar, and they have a common space group. The addition of an extra 4-methoxy substituent in (2) makes very little difference to the packing of the ions in the two structures.

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2,6-Dimethoxy-3-nitrobenzoic Acid. A Hydrogen-Bonded Chain Structure

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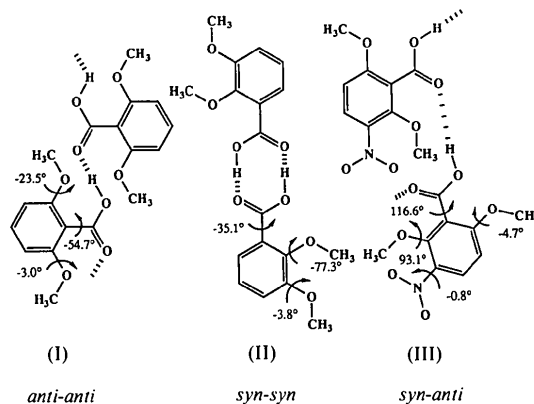
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Abstract. 2,6-Dimethoxy-3-nitrobenzoic acid, $C_9H_9NO_6$, $M_r = 227.18$, orthorhombic, *Pccn*, $a = 14.837$ (2), $b = 18.096$ (2), $c = 7.501$ (2) Å, $V = 2014$ (1) Å³, $Z = 8$, $D_x = 1.498$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.1203$ cm⁻¹, $F(000) = 944$, $T = 300$ K, $R_F = 0.061$, $wR = 0.049$ for 1301 observed reflections with $I > \sigma(I)$. Hydrogen-bonded chains rather than the typical hydrogen-bonded dimer are formed. Glide-related molecules ($x, \frac{1}{2} - y, -\frac{1}{2} + z$) are linked together in extended chains [$O \cdots O = 2.668$ (2), $H \cdots O = 1.86$ (4), $O - H = 0.84$ (3) Å, $O - H \cdots O = 160$ (3)°]. The carboxyl group is in the *syn* conformation, but the lone pair of electrons acting as the hydrogen-bond acceptor is in an *anti* orientation.

Introduction. As part of an ongoing project directed at designing hydrogen-bonded chains of molecules, we sought to determine whether derivatives of 2,6-dimethoxybenzoic acid (I) would retain the unusual chain pattern manifested in the structure of (I) (Bryan & White, 1982*b*). No other

2,6-dimethoxybenzoic acid crystal structures were found in the literature, although another isomer, 2,3-dimethoxybenzoic acid (II), was found, which crystallizes in the normal acid dimer pattern, (Bryan & White, 1982*a*). In this paper, the crystal structure of 2,6-dimethoxy-3-nitrobenzoic acid (III) is reported and is shown to exist as a hydrogen-bonded chain. The carboxyl group in (III) is found to exist in the *syn* conformation, unlike the carboxyl group in (I), which exists in the *anti* conformation.



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