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CRYSTAL AND MOLECULAR STRUCTURE OF PYRYLIUM SALTS. IV. CRYSTAL AND MOLECULAR STRUCTURE OF 2,6-DIPHENYL-4-(4-CARBOXYPHENYL)PYRYLIUM PERCHLORATE. INTERRELATIONS BETWEEN STRUCTURAL PARAMETERS DUE TO SUBSTITUENT EFFECTS

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The crystal and molecular structure of 2,6-diphenyl-4-(4-carboxyphenyl)pyrylium perchlorate was solved by x-ray diffraction, yielding structural parameters of high precision (estimated standard deviations for bond length $\leqslant 0{\cdot}5$ pm, for bond angles $\leqslant 0{\cdot}2^\circ$). Comparison with other 4-substituted derivatives of 2,6-diphenyl-4(4-carboxytphenylpyrylium) perchlorate shows regularities in the variations of structural parameters following classical views of substituent effects.

INTRODUCTION

In continuation of our structural studies of 2,6-diphenyl-4-(4-substituted)pyrylium salt derivatives,[1–3] we have examined 2,6-diphenyl-4-(4-carboxyphenyl) pyrylium perchlorate ($DCP^+ClO_4^-$) with regard to the structural similarity of $DCP^+ClO_4^-$ with the 2,6-diphenyl-4-(nitrophenyl)pyrylium moiety in the perchlorate salt,[2] the effect of the bulkiness of the moiety on the possibility of formation of a cyclic dimer via COOH hydrogen bonding[4] and substituent effects on the geometry of the pyrylium ring and its aromatic character.

EXPERIMENTAL

The melting point was obtained on a Boetius apparatus and is uncorrected. Elemental analyses (C, H) were performed on a Perkin-Elmer Type 240 Analyser. The ^1H NMR spectrum was recorded on a Bruker AC-300 spectrometer (300 MHz) using DMSO-d_6 as solvent. The IR spectrum was obtained on a Bruker IFS-88 spectrometer (KBr pellet). The mass spectrum was measured with a Varian MAT 711 spectrometer (field desorption, FD).

2,6-Diphenyl-4-(4-carboxyphenyl)pyrylium perchlorate. A solution of 4-carboxybenzaldehyde (5·0 g; 0·033 mol) and acetophenone (8·0 g; 0·066 mol) in toluene (20 ml) was treated with 70 per cent perchloric acid (8·0 ml). The mixture was stirred and heated at 100 °C for 1 h, during which period the initially formed yellow precipitate dissolved. Then ethanol (50 ml) was added and boiling was continued for a further 30 min. Subsequently the mixture was cooled and the orange solid was separated and washed with hot acetic acid, ethanol and diethyl ether.

Yield 1·8 g (11·9%); m.p. 312–315 °C. Analysis for $C_{24}H_{17}O_3.ClO_4$ (452·86): calculated, C 63·65, H 3·79; found, C 63·39, H 3·69% IR (cm^{-1}): 3077 (very broad, COOH), 1714 (C=O), 1619, 1512 (aromatic rings), 1115 (ClO_4^-). ^1H NMR, δ (ppm): 3·56 (s, broad, combined signal from COOH and water in DMSO-d_6),

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7·83 (m, 6H, *meta-* and *para*-protons of aromatic rings at the 2- and 6-positions), 8·23 and 8·64 (2d, 4H, $J = 8\cdot5$ Hz, *AA'BB'* system, protons of the aromatic ring at the 4-position), 8·58 (m, 4H, *ortho*-protons of the aromatic rings at the 2- and 6-positions), 9·20 (s, 2H protons at the 3- and 5-positions at the pyrylium ring). MS, *m/z* (%): 353 (100; $M^+ - ClO_4$).

X-ray measurements. 2,6-Diphenyl-4-(4-carboxyphenyl)pyrylium perchlorate was recrystallized from nitromethane. Unit cell parameters were obtained from the least-squares refinement of 25 reflections in the range $8 \leqslant 2\theta \leqslant 16^\circ$. Intensities were collected on a CAD-4 diffractometer using Cu Kα radiation monochromatized by graphite up to $\theta = 75^\circ$, $\omega - 2\theta$ scan mode performed ($h \leqslant 13$, $k \leqslant 13$, $-22 \leqslant l \leqslant 22$); 4836 reflections were collected, 4284 were unique, ($R_{\text{int}} = 0\cdot023$), 4088 were classified as observed on the basis of the criterion $F_0 \geqslant 8\sigma(F_0)$. Intensities were corrected for Lorentz polarization factors and empirical absorption correction, as given by the program DIFABS.[5] The structure was solved by routine application of SHELXS[6] and SHELX76,[7] refined by full-martrix least squares. All non-hydrogen atoms were refined anisotropically; the phenyl hydrogens were included at calculated positions, C—H = 1·08 Å, and allowed to ride on their parent atoms; H atoms connected with the O-3 atome were located from a difference map and refined isotropically. Final values were $R = 0\cdot0634$, $wR = 0\cdot0771$, $w = 1[\sigma^2(F_0) + 0\cdot0001(F_0)^2]^{-1}$; 13 reflections per parameter; $(\Delta/\sigma)_{\max} = 0\cdot303$, residual density within maximum $+0\cdot45$, minimum $-0\cdot44$. The molecular illustration was drawn using PLUTO.[8] Atomic scattering factors were obtained from Ref. 9

RESULTS AND DISCUSSION

Table 1 gives crystal data for the title compound and Table 2 gives final atomic coordinates and temperature factors for non-hydrogen atoms. Figure 1 presents bond lengths and Figure 2 gives bond angles and selected values of dihedral angles between the best ring planes.

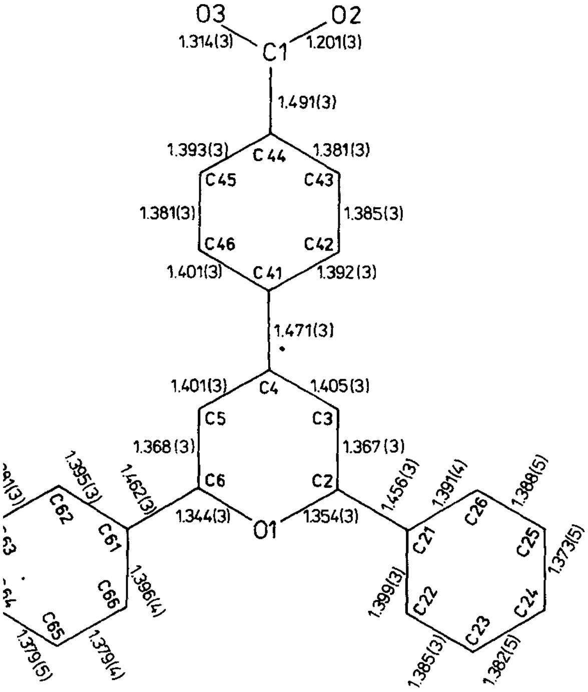
Table 1. Crystal data for 2,6-diphenyl-4-(4-carboxyphenyl)pyrylium perchlorate, $[C_{24}H_{17}O_3]^{+}ClO_4^-$ ($M_r = 452\cdot8$)

Monoclinic	$D_x = 1\cdot424$ mg cm^{-1}
$P2_1/c$	λ(Cu Kα) = 1·54178 Å
$a = 10\cdot812(1)$ Å	μ(Cu Kα) = 18·29 cm^{-1}
$b = 11\cdot062(1)$ Å	$F(000) = 936$
$c = 17\cdot822(1)$	$T = 295$ K
$\beta = 97\cdot89(1)^\circ$	$R = 0\cdot0634$
$V = 2111\cdot4$ Å^3	$wR = 0\cdot0771$
$Z = 4$	4088 reflections

Table 2. Atomic fractional coordinates ($\times 10^4$) (esd values in parentheses) with thermal parameters $B_{\text{eq}} = 8\pi^2 D_u^{1/3} (\sin\alpha^2 \sin\beta^2 \sin\gamma^2)^2$, where D_u is the determinant of the U_{ij} matrix

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
O-1	7502(1)	9968(1)	9984(1)	2·9
O-2	9015(2)	3699(2)	6886(1)	4·3
O-3	7512(2)	2821(2)	7417(1)	3·9
C-1	8286(2)	3713(2)	7337(1)	3·1
C-2	6845(2)	8973(2)	10128(1)	2·8
C-3	6986(2)	7925(2)	9742(1)	2·9
C-4	7805(2)	7885(2)	9195(1)	2·8
C-5	8467(2)	8939(2)	9071(1)	3·0
C-6	8305(2)	9969(2)	9471(1)	2·9
C-21	6020(2)	9171(2)	10697(1)	2·9
C-22	5877(2)	10325(2)	10994(1)	3·2
C-23	5068(3)	10504(3)	11523(1)	3·8
C-24	4403(3)	9543(3)	11761(2)	4·4
C-25	4542(3)	8410(3)	11470(2)	5·2
C-26	5346(3)	9209(2)	10939(2)	4·5
C-41	7938(2)	6785(2)	8749(1)	2·8
C-42	6985(2)	5930(2)	8643(1)	3·2
C-43	7095(2)	4926(2)	8193(1)	3·1
C-44	8151(2)	4757(2)	7849(1)	2·8
C-45	9119(2)	5596(2)	7963(1)	3·2
C-46	9023(2)	6595(2)	8416(1)	3·2
C-61	8919(2)	11132(2)	9398(1)	3·0
C-62	9881(2)	11221(2)	8953(1)	3·6
C-63	10469(3)	12315(2)	8882(1)	4·1
C-64	10110(3)	13325(2)	9258(2)	4·1
C-65	9162(3)	13243(2)	9700(2)	4·5
C-66	8563(3)	12157(2)	9772(2)	4·0
Cl	6649(1)	490(1)	6024(1)	3·4
O-4	7744(2)	849(3)	6526(2)	6·9
O-5	7038(3)	−177(3)	5443(2)	7·1
O-6	5994(3)	1549(2)	5780(2)	8·4
O-7	5854(3)	−231(3)	6412(2)	7·4
C-1	6953(10)	291(14)	6282(6)	6·8

The title compound shows similar patterns to other derivatives of 2,6-diphenylpyrylium salts, in particular a significant decrease of O-1—C-2—C-21 and O-1—C 6—C-61 bond angles [113·4(20) and 113·9(2)°, respectively]. This supports our earlier observations and interpretation[2] within the Walsh rule[10] framework that it is due to the highly electronegative oxygen atom in the pyrylium ring, further enhanced by the positive charge in the ring. The same may be said of the shortening of the C-6—C-61 and C-2—C-21 bond lengths [1·462(3) and 1·156(3) Å, respectively in comparison with the C-4—C-41 bond length of 1·471 Å. On examining the C-4—C-41 bond lengths and the dihedra angles between the pyrylium and phenyl rings attached to the pyrylium ring at position 4, one finds a regularity as shown in Figure 3, i.e. an increase in the electron accepting ability of the 4-substituent (from NMe_2 to NO_2) causes an increase in the C—C bond length and



Cl–O4	1.438 (3)
Cl–O5	1.383 (4)
Cl–O6	1.407 (3)
Cl–O7	1.420 (4)

Figure 1. Labelling of atoms and bond lengths in 2,6-diphenyl-4-(4-carboxyphenyl)pyrylium perchlorate

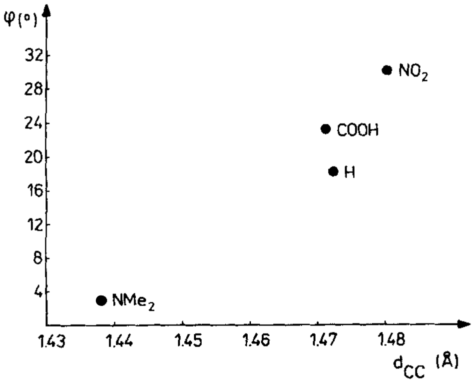
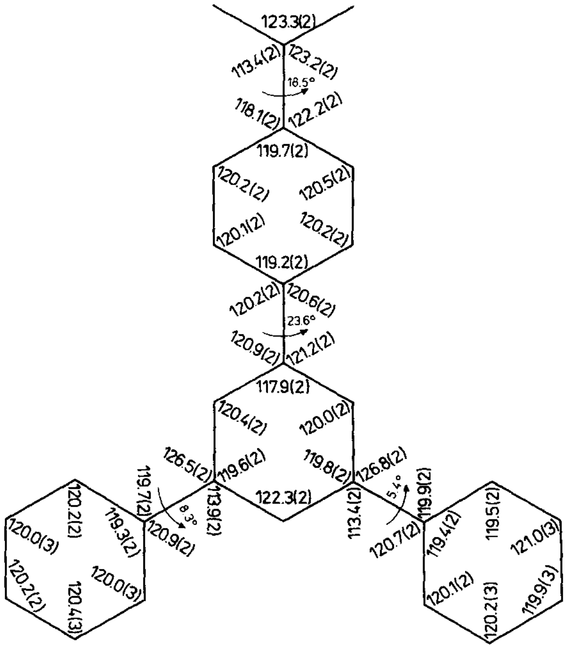


Figure 3. Dependence of the dihedral angle φ (between planes of pyrylium and 4-substituted phenyl rings) on the lengths of the linking bond C-4—C-41. Experimental data for derivatives: NME$_2$,[3] H,[11] COOH (this work), No$_2^2$



O4–Cl–O5	107.7 (2)	O5–Cl–O6	113.9(2)
O4–Cl–O6	107.4 (2)	O5–Cl–O7	109.4 (2)
O4–Cl–O7	110.7 (2)	O6–Cl–O7	107.8(2)

Figure 2. Bond angles and torsion angles in 2,6-diphenyl-4-(4-carboxyphenyl) pyrylium perchlorate

an increase in the angle φ. Evidently this is due to a decrease of the through-resonance effect, since the Py$^+$ring is a strong π-electron-accepting moiety. This was shown to be a very strong effect for the 2,6-diphenyl-4-(4-*N*,*N*-dimethylaminophenyl)pyrylium cation,[3] in which a very short C-bond was observed for the linkage between the two π-electron rings [1·438(7) Å].

The other consequence of the substituent effect on pyrylium ring geometry is a variation of the aromatic character of the ring. From the bond lengths a HOMA index of aromaticity[1] may be calculated. This is defined by the equation

$$\mathrm{HOMA} = 1 - 257{\cdot}7/n\sum_{i=1}^{n}(d_r - d_{\mathrm{opt}})^2 \qquad (1)$$

where d_r is the bond length in the system in question and d_{opt} is defined by the equation

$$d_{\mathrm{opt}} = (s + 2d)/3 \qquad (2)$$

which is based on the assumption that the force constants for stretching vibrations for a double bond are

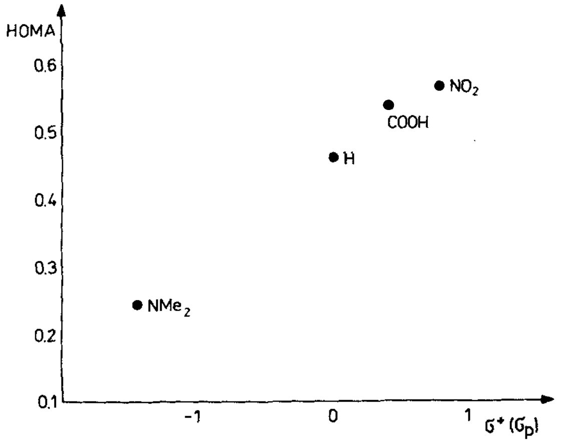


Figure 4. Dependence of aromaticity index HOMA for pyrylium ring on substituent constants σ_p^+ for electron-donating and σ_p for other substituents

twice those for a single bond. HOMA is a normalized index of aromaticity, i.e. equal to unity for an ideally aromatic system in which all bonds of length d_r have optimal lengths d_{opt}. Closest to this situation are benzene and pyridine, for which the HOMA values are in the range of 0·969–0·996 depending on the data used for calculation.

Application of the HOMA model[1] to the pyrylium ring geometry yields HOMA values which when plotted against σ_p^- for electron-donating and σ_p for other substituents give the graph shown in Figure 4; an increase in the electron-attracting power of the substituted benzene ring at the position of the pyrylium XPh—φ increases the aromatic character of the pyrylium ring. This is in line with our previous observation for the 4-*N*,N-dimethylaminophenyl derivative[3] that an electron-donating substituent causes a strong π-electron localization in the pyrylium ring.

Another problem is hydrogen bonding of the carboxylic group. Usually this group forms either cyclic dimers or chains.[4] In this case, owing to presence of the anions in the crystal lattice, the hydrogen bridge is between OH and the ClO_4^-. However, as shown from geometry parameters ($R_{O\cdots O} = 2\cdot73$ Å), it is a weak hydrogen bond. No disorder in the COOH group is observed and hence the geometry of this group may be discussed in more detail. The difference between the CCO(H) and CC=O bond angles is almost 10°, indicating a lack of disorder[12,13] Opposite to the short C=O bond we find a small bond angle of 113·4(2)°, whereas opposite to the C—OH bond the bond angle is 123·2(2)°. This is typical for a COOH group not affected by disorder.[4,12]

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