Crystal and Molecular Structure of Pyrylium Salts. Part 1. Crystal and Molecular Structure of 2,6-Diphenyl-4-(2-phenylpropan-2-yl)pyrylium Perchlorate and Aromaticity of the Pyrylium Ring

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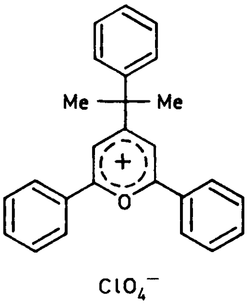
The crystal structure of 2,6-diphenyl-4-(2-phenylpropan-2-yl)pyrylium perchlorate has been solved by direct methods and refined to $R = 0.069$. The aromatic character of the pyrylium ring has been described in terms of the HOMA parameter indicating its properties as intermediate between typical aromatic and non-aromatic systems. Relatively good dependence between HOMA and Bird's I_6 indices of aromaticity has been found.

The crystal and molecular structure of pyrylium salts has been determined for a few cases only.[1-4] The structure of 2,6-diphenyl-4-(2-phenylpropan-2-yl)pyrylium perchlorate (**1**), hereafter abbreviated as PPPy$^+$ClO$_4^-$, is the first of a series of pyrylium salts to be studied in our laboratory. The purpose of these studies is to estimate the dependence of pyrylium geometry on the nature of substituents. In the present paper aromaticity of a pyrylium ring is determined by use of the HOMA index[5,6] and compared with other systems of known aromaticity.



(1)

Table 1. Crystallographic data.

$[C_{26}H_{23}O]^+ClO_4^-$ $M = 450.92$
Monoclinic
$a = 8.217(1)$ Å
$b = 29.033(3)$ Å
$c = 9.962(1)$ Å
$\beta = 108.05(1)°$
$V = 2\,259.7(4)$ Å^3
Room temperature
$\lambda(\text{Cu-}K_\alpha) = 1.541\,78$ Å
$\mu(\text{Cu-}K_\alpha) = 16.85$ cm^{-1}
$F(000) = 944$
$P2_1/n$
$Z = 4$
$D_x = 1.33$ Mg m^{-3}

Experimental

Yellow needles of the salt (**1**) were crystallized from nitromethane. Unit-cell parameters were obtained from least-squares treatment of setting angles of 15 reflections measured on a Syntex P2$_1$ diffractometer using Cu-K_α radiation with a graphite monochromator. Profiles of 2 926 unique reflections with $2\theta \leq 115°$ were measured using the θ–2θ scan technique. Intensities of two standard reflections ($\bar{1}42$ and $\bar{2}\bar{2}0$) were monitored for every 100 reflections and showed no significant variation during data collection. Background and integrated intensities were evaluated by the profile analysis method[7] with a PRARA program.[8] 2 272 Reflections were considered as observed on the grounds of the $|F_o| \geq 3.92\sigma(F_o)$ criterion. The structure was solved by direct methods using a MULTAN 80 program[9] and was refined with SHELX 76.[10] Anisotropic refinement of non-hydrogen atoms followed by difference syntheses led to the location of all hydrogen atoms. Positional parameters and isotropic temperature factors of all hydrogen atoms were included in the refinement. The maximum electron density on the final difference Fourier map was 0.45 e Å^{-3} (near ClO$_4^-$) and the largest hole was -0.32 e Å^{-3}. The final refinement converged to a conventional $R = 0.069$ and $wR = 0.083$ for 2 272 observed reflections. The weights were $w = 1.0/[\sigma^2(F_o) + gF_o^2]$ with $g = 0.000\,15$. The empirical isotropic extinction parameter x was used to correct F_c according to $F_c' = F_c(1 - xF_c^2/\sin\theta)$, x converged at $1.7(2) \times 10^{-6}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[11] Additional calculations were performed with programs GEOME,[12] PLANE,[13] and THMB 6.[14] Crystallographic data are collected in Table 1. Table 2 gives final fractional co-ordinates for non-H atoms, and Table 3(*a*) and (*b*) record bond lengths and bond angles, respectively.

Results and Discussion

Aromaticity of Pyrylium Ring in PPPy Cation.—A pyrylium ring is iso-π-electronic with benzene and pyridine and hence it is expected to be aromatic. Since the ring in PPPy cation is almost planar, with maximum deviation from the best plane less than 0.010 Å, one of the criteria of aromaticity is fulfilled. From structural data (geometry) another criterion may be applied to check the aromatic character of the ring, namely the HOMA index of aromaticity.[5,6] Its definition is given by equation (1)

Table 2. Final fractional co-ordinates.

Atom	*x*	*y*	*z*
O(1)	0.254 1(4)	0.436 92(9)	−0.006 8(3)
C(2)	0.194 2(5)	0.436 6(1)	0.104 2(4)
C(3)	0.155 5(6)	0.395 3(1)	0.153 8(5)
C(4)	0.174 3(6)	0.354 0(1)	0.088 1(4)
C(5)	0.235 0(6)	0.357 1(2)	−0.027 3(5)
C(6)	0.273 3(6)	0.398 3(1)	−0.075 6(4)
C(11)	0.180 2(5)	0.482 6(1)	0.158 2(4)
C(12)	0.122 8(6)	0.488 4(2)	0.276 1(5)
C(13)	0.106 1(7)	0.531 6(2)	0.326 0(6)
C(14)	0.144 1(7)	0.569 6(2)	0.258 5(6)
C(15)	0.200 3(7)	0.564 7(2)	0.141 6(7)
C(16)	0.221 0(6)	0.521 4(2)	0.093 5(5)
C(21)	0.333 2(6)	0.406 7(2)	−0.195 4(5)
C(22)	0.392 6(7)	0.370 2(2)	−0.260 1(6)
C(23)	0.439 9(8)	0.378 9(3)	−0.379 5(7)
C(24)	0.430 5(7)	0.422 2(3)	−0.434 5(6)
C(25)	0.376 5(7)	0.457 4(2)	−0.371 8(6)
C(26)	0.327 7(7)	0.449 9(2)	−0.253 4(5)
C(7)	0.126 7(6)	0.307 2(1)	0.134 0(5)
C(8)	−0.054 6(8)	0.297 2(3)	0.032 7(9)
C(9)	0.120(1)	0.307 9(2)	0.286 6(7)
C(31)	0.259 3(6)	0.271 2(1)	0.123 7(5)
C(32)	0.431 2(8)	0.280 2(2)	0.184 8(6)
C(33)	0.551(1)	0.246 8(3)	0.176 5(8)
C(34)	0.503(1)	0.206 3(3)	0.111 1(7)
C(35)	0.334(1)	0.197 2(2)	0.052 7(7)
C(36)	0.214(1)	0.229 6(2)	0.058 0(7)
Cl	0.695 9(2)	0.403 26(4)	0.251 6(1)
O(2)	0.699 0(9)	0.370 9(3)	0.150 3(8)
O(3)	0.857 9(7)	0.407 9(2)	0.350 7(7)
O(4)	0.583 4(8)	0.386 1(2)	0.319 3(7)
O(5)	0.633(1)	0.442 0(2)	0.187(1)

Table 3.

(*a*) Bond lengths/Å

O(1)–C(2)	1.343(5)	C(3)–H(31)	0.81(4)
C(2)–C(3)	1.372(6)	C(5)–H(51)	1.01(5)
C(3)–C(4)	1.395(6)	C(12)–H(121)	0.98(5)
C(4)–C(5)	1.391(6)	C(13)–H(131)	0.97(5)
C(5)–C(6)	1.362(6)	C(14)–H(141)	1.01(4)
C(6)–O(1)	1.349(5)	C(15)–H(151)	0.90(5)
C(2)–C(11)	1.459(6)	C(16)–H(161)	0.90(6)
C(11)–C(12)	1.405(7)	C(22)–H(221)	0.95(4)
C(12)–C(13)	1.371(7)	C(23)–H(231)	0.74(6)
C(13)–C(14)	1.378(8)	C(24)–H(241)	1.08(7)
C(14)–C(15)	1.387(9)	C(25)–H(251)	0.95(7)
C(15)–C(16)	1.377(7)	C(26)–H(261)	0.82(4)
C(11)–C(16)	1.388(7)	C(8)–H(81)	0.95(6)
C(6)–C(21)	1.446(6)	C(8)–H(82)	0.98(5)
C(21)–C(22)	1.402(7)	C(8)–H(83)	0.95(6)
C(22)–C(23)	1.384(8)	C(9)–H(91)	1.00(6)
C(23)–C(24)	1.365(10)	C(9)–H(92)	1.00(6)
C(24)–C(25)	1.343(9)	C(9)–H(93)	0.91(6)
C(25)–C(26)	1.376(7)	C(32)–H(321)	0.98(5)
C(21)–C(26)	1.377(7)	C(33)–H(331)	0.88(5)
C(4)–C(7)	1.523(6)	C(34)–H(341)	0.98(7)
C(7)–C(8)	1.546(8)	C(35)–H(351)	1.09(7)
C(7)–C(9)	1.537(7)	C(36)–H(361)	0.70(4)
C(7)–C(31)	1.535(7)		
C(31)–C(32)	1.379(7)		
C(32)–C(33)	1.404(9)		
C(33)–C(34)	1.342(10)	Cl–O(2)	1.386(6)
C(34)–C(35)	1.353(10)	Cl–O(3)	1.397(5)
C(35)–C(36)	1.377(9)	Cl–O(4)	1.394(5)
C(31)–C(36)	1.370(7)	Cl–O(5)	1.322(7)

(*b*) Bond angles/°

C(2)–O(1)–C(6)	122.9(3)	C(4)–C(7)–C(8)	104.9(4)
O(1)–C(2)–C(3)	119.2(4)	C(4)–C(7)–C(9)	112.1(4)
C(2)–C(3)–C(4)	120.6(5)	C(4)–C(7)–C(31)	109.5(4)
C(3)–C(4)–C(5)	116.9(4)	C(8)–C(7)–C(9)	109.1(5)
C(4)–C(5)–C(6)	122.0(4)	C(8)–C(7)–C(31)	112.9(4)
C(5)–C(6)–O(1)	118.3(4)	C(9)–C(7)–C(31)	108.5(4)
O(1)–C(2)–C(11)	112.8(4)	C(32)–C(31)–C(36)	117.9(6)
C(3)–C(2)–C(11)	128.0(4)	C(31)–C(32)–C(33)	119.1(6)
O(1)–C(6)–C(21)	113.8(4)	C(32)–C(33)–C(34)	121.8(7)
C(5)–C(6)–C(21)	127.9(4)	C(33)–C(34)–C(35)	119.2(7)
C(3)–C(4)–C(7)	123.3(4)	C(34)–C(35)–C(36)	120.2(7)
C(5)–C(4)–C(7)	119.7(4)	C(31)–C(36)–C(35)	121.9(7)
C(12)–C(11)–C(16)	118.9(4)	C(7)–C(31)–C(32)	119.6(4)
C(11)–C(12)–C(13)	120.6(5)	C(7)–C(31)–C(36)	122.6(5)
C(12)–C(13)–C(14)	119.5(6)		
C(13)–C(14)–C(15)	120.8(5)	O(2)–Cl–O(3)	110.6(4)
C(14)–C(15)–C(16)	119.6(6)	O(2)–Cl–O(4)	105.9(4)
C(11)–C(16)–C(15)	120.4(6)	O(2)–Cl–O(5)	108.3(7)
C(2)–C(11)–C(12)	120.2(4)	O(3)–Cl–O(4)	108.8(4)
C(2)–C(11)–C(16)	120.9(4)	O(3)–Cl–O(5)	114.0(6)
C(22)–C(21)–C(26)	117.8(5)	O(4)–Cl–O(5)	108.8(6)
C(21)–C(22)–C(23)	119.2(6)		
C(23)–C(24)–C(25)	121.1(6)		
C(23)–C(24)–C(25)	120.0(6)		
C(24)–C(25)–C(26)	120.3(6)		
C(21)–C(26)–C(25)	121.5(6)		
C(6)–C(21)–C(22)	120.6(4)		
C(6)–C(21)–C(26)	121.6(4)		

$$\mathrm{HOMA} = 1 - \frac{a}{n}\sum_{r=1}^{n}(d_r - d_{\mathrm{opt}})^2 \qquad (1)$$

where d_r stands for bond length in the system in question whereas d_{opt} is defined by equation (2)[5] where s and d stand for

$$d_{\mathrm{opt}} + \frac{s + wd}{1 + w} \qquad (2)$$

lengths of pure single and pure double bonds, respectively, and w is the ratio of stretching force constants for double and single bonds $w = k(\mathrm{C{=}C})/k(\mathrm{C{-}C})$. This ratio for various bonds (CC, CN, CO)[6] is *ca.* 2 and hence equation (2) may be simplifed to equation (3).

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

HOMA is a normalized index of aromaticity, *i.e.* it is equal to 1.0 for benzene in which all d_r bonds would have optimal or close to optimal lengths d_{opt}, and equal to 0.0 for a Kekulé structure with a localized π-electron structure. From these conditions d_{opt}(C–C) = 1.397 Å and the constant $a = 98.89$ Å^{-2} were calculated accepting that $w = 2$, s(CC) = 1.524 Å, and d(CC) = 1.334 Å. *i.e.* C–C bond lengths in ethane and ethene,[15] respectively. Almost at the same time as this model was devised Hess and Schaad[16-18] substantiated (based on a vast collection of data and the ideas of Dewar[19] and Breslow[20]) that the reference structure in calculations of resonance energy should have a π-electron structure similar to that in acyclic polyenes. In this paper we accept fully this view and hence both d_{opt} and a parameters in equation (1) are now recalculated by use of d = 1.349 Å and s = 1.467 Å, *i.e.* double and single C–C bond lengths in buta-1,3-diene.[21] The new values are d_{opt} = 1.388 Å and a = 257.7 Å^{-2}. It is worth mentionining that the d_{opt} value is not very different from C–C bond lengths in benzene: *X*-ray determination with correction for libration 1.392 Å,[22] electron diffraction (ED) determination 1.399 Å,[23] and microwave (MW) determination 1.397 Å.[24] For our purpose the extended version of HOMA has to be used,[6] *i.e.* the formula which takes into account the systems with heteroatoms X and Y, equation (4) where $n = n_1 + n_2 + n_3 + n_4 + n_5 + n_6$, and $n_1, n_2, n_3, n_4, n_5, n_6$ are the numbers of bonds of type CC, CX, CY, XX, YY, and XY in the π-electron system in question. In Table 4 are given reference bond lengths for most common bonds in organic systems. Table 5 and Figure 3 present a few examples of typical π-electron systems with values of HOMA and the I_6 aromaticity index suggested recently by Bird.[25,26] A relatively good agreement between the values of HOMA and I_6 should be noted. The HOMA values for a pyrylium ring of PPPy$^+$ ClO$_4^-$ as well as for that taken from ref. 1 differ significantly from HOMAs for typically aromatic systems. This means that the pyrylium ring should not be considered as an aromatic system but rather as an intermediate one between aromatic and non-aromatic. This is clearly seen from Figure 3. Apart from the aromaticity of the rings in PPPy$^+$ an interesting finding is that

Table 4. Reference bond lengths and d_{opt}.

Type of bond	Single (Å)	Double (Å)	d_{opt} (Å)
CC	1.467[a]	1.349[a]	1.388
CN	1.474[b]	1.274[c]	1.341
CO	1.428[d]	1.209[e]	1.282
CS	1.820[f]	1.610[f]	1.680

[a] C–C and C=C taken from ED data for buta-1,3-diene.[21] [b] C–N taken from MW data for CH_3NH_2 (P. Pulay and F. Torok, *J. Mol. Struct.*, 1975, **29**, 239). [c] C=N taken from ED data for CH_2=CH–CH=NH (R. E. Penn, *J. Mol. Spectrosc.*, 1976, **69**, 373). [d] C–O taken from ED data for methanol (K. Kimma and M. Kubo, *J. Chem. Phys.*, 1959, **30**, 151). [e] C=O taken from ED data for acrolein (K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, 1969, **4**, 41). [f] C–S and C=S taken from J. Karolak-Wojciechowska, *Phosphorus Sulfur*, 1985, **25**, 229.

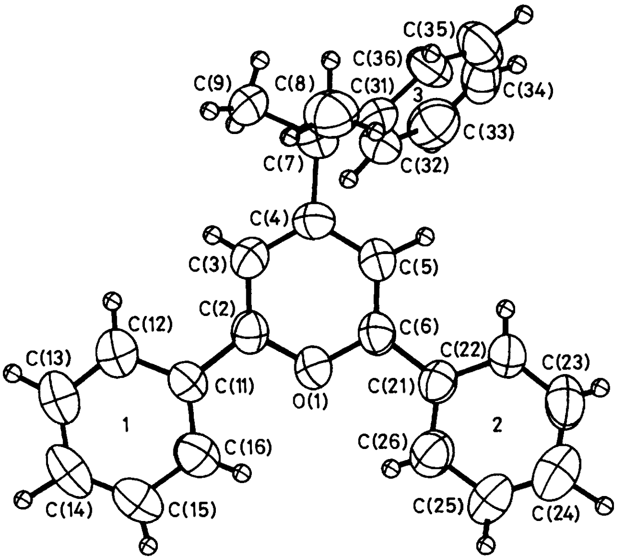


Figure 1. Non-hydrogen atoms and ring-labelling scheme of PPPy$^+$ClO$_4^-$.

Table 5. Aromaticity indices: HOMA and I_6.

Compound	HOMA	I_6
Benzene	0.996[a] 0.979[b] 0.969[c]	100
Pyridine	0.995	8.57
Pyridinium methiodide	0.825	66.7
Pyridine *N*-oxide	0.958	74.4
Pyridinium dicyanomethylide	0.927	70.1
Pyridinium *N*-nitroimine	0.968	76.0
Pyrimidine	0.998	84.3
Pyrazine	0.980	88.8
1,3,5-triazine	0.992	100
Pyran-2-one	−0.341	32.9
Pyran-4-one	−0.146	37.2
Pyran-4-thione	0.326	47.9
2,4,6-triphenylpyrylium cation	0.481	50.5
This work	0.605	53.6

[a] *X*-Ray. [b] MW. [c] ED.

Table 6. Interionic constants (Å) less than the sum of respective van der Waals radii taken from ref. 27.

C(2) ··· C(15)^{ii}	3.404(7)
C(6) ··· C(14)^{ii}	3.475(7)
C(11) ··· C(16)^{ii}	3.471(7)
C(13) ··· C(26)^{ii}	3.452(8)
C(14) ··· C(24)^{iii}	3.399(8)
C(15) ··· C(24)^{iii}	3.518(8)
C(26) ··· O(5)^{iii}	3.202(10)

Indices denote symmetry codes other than *i*: *i*, *x*, *y*, *z*; *ii*, −*x*, 1 − *y*, −*z*; *iii*, 1 − *x*, 1 − *y*, *z*.

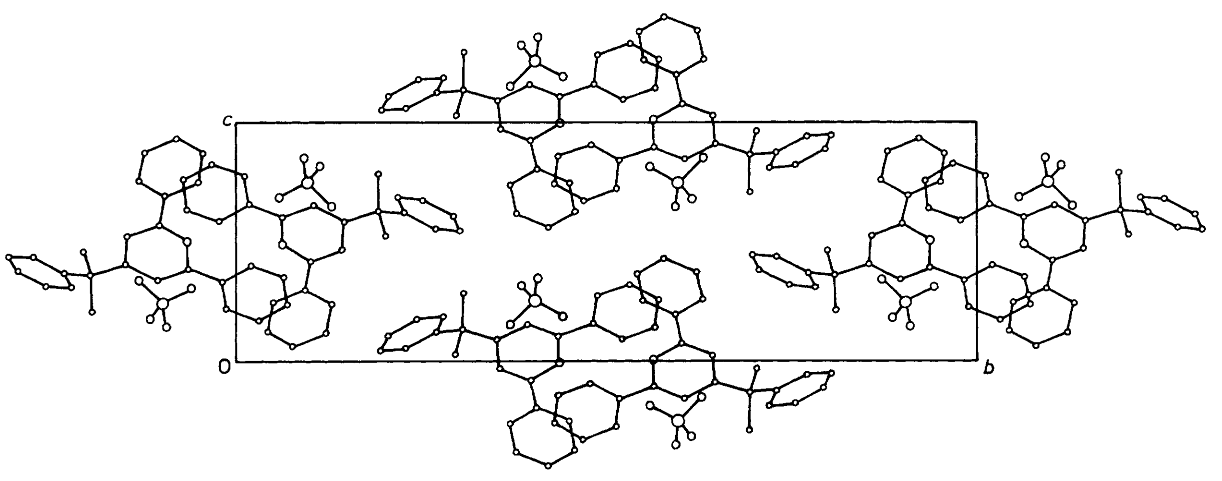


Figure 2. Projection along the *x* axis.

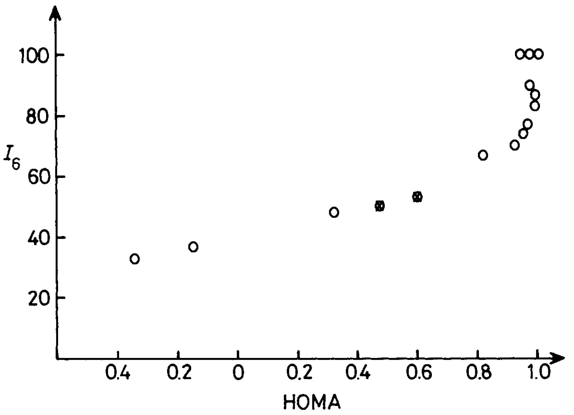


Figure 3. Dependence between the I_6 and the HOMA indices.

the angles O(1)–C(2)–C(11) and O(1)–C(6)–C(21) [112.8(4)° and 113.8(4)°, respectively] are relatively small. This seems to be caused by two effects: (i) rather strong steric interactions between H(221) and H(51) as well as H(121) and H(31) for which exocyclic C(21)–C(6)–C(5) and C(11)–C(2)–C(3) angles are abnormally large [127.9(4)° and 128.0(4)°, respectively], (ii) possible attractive interactions between H(261) and H(161) with oxygen. The interatomic distances between these hydrogen atoms and oxygen are 2.44 and 2.38 Å, in comparison with the sum of the van der Waals radii 2.50 Å.[27]

$$\text{HOMA} = 1 - \frac{257.7}{n}\left[\sum_{i=1}^{n_1}[d^{CC}_{opt} - d^{CC}_i)^2 + \sum_{i=1}^{n_2}(d^{CX}_{opt} - d^{CX}_i)^2 + \sum_{i=1}^{n_3}(d^{CY}_{opt} - d^{CY}_i)^2 + \sum_{i=1}^{n_4}(d^{XX}_{opt} - d^{XX}_i)^2 + \sum_{i=1}^{n_5}(d^{YY}_{opt} - d^{XX}_i)^2 + \sum_{i=1}^{n_6}(d^{XY}_{opt} - \mathrm{d}^{XY}_i)^2\right] \quad (4)$$

When the deformations of angles in the benzene rings are analysed by use of equation (5) for ADP (angular parameter of

$$\text{ADP} = \sum_{i=1}^{\sigma}|120 - \psi_i| \quad (5)$$

deformation) then one ends up with the values ADP = 3.8, 5.9, and 7.7° for rings 1, 2, and 3 (Figure 1), respectively. These values may be compared with the angles of twist between these rings relative to a pyrylium ring: 2.8(5), 14.8(5), and 72.2(5)°. In the same direction, the HOMA values are changed thus: 0.966, 0.870, 0.823.

Crystal Structure.—Figure 2 shows a projection of the structure along the x axis. Two chemical species A and B represent a pair of PPPy cations with slightly stronger interactions than that observed between these pairs. Within the pair, shorter contacts are observed than between the pairs. Interionic contacts are presented in Table 6. Each pair is accompanied by two very weakly interacting counter ions (ClO_4^-). These units build up the stack along the x axis.

Acknowledgements

This work was supported by project RP.II.10 from the Polish Ministry of Science and Higher Education.

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Received 22*nd March* 1988; *Paper* 8/01173G