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Crystal Structure of 2,6-Di(2-thienyl)-4-phenylpyrylium Perchlorate: A Comparison with Theory

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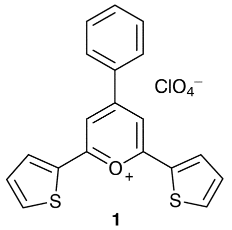
The crystal structure of the title compound is presented and the obtained parameters are compared with parameters from semiempirical (AM1 and PM3) and *ab initio* (B3LYP/6-311G) calculations.

The pyrylium ring is an electron-deficient aromatic system with very interesting photophysical properties.[1–8] One of us had previously synthesized several pyrylium salts substituted with heterocyclic groups (2-thienyl, 2-benzothiazolyl, and 2-benzimidazolyl) and described their electronic spectra.[9] Replacement of a phenyl substituent in these compounds by a better donor heterocyclic group such as 2-thienyl or 2-benzimidazolyl had the effect of shifting the longest-wavelength charge-transfer band of the pyrylium salts bathochromically. This was presumably the effect of an increase of the charge-transfer from the electron-rich substituent to the pyrylium ring. We now confirm this assumption by an X-ray diffraction analysis of one of these compounds, 2,6-di(2-thienyl)-4-phenylpyrylium perchlorate (**1**), comparing the obtained structure with other structures of pyrylium salts[10,11] and with theoretical parameters derived from semiempirical (AM1, PM3)[12] and *ab initio* (B3LYP/6-311G)[13] calculations.



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A crystal of **1** was mounted on a CAD4 diffractometer for data collection at room temperature with graphite monochromated MoKα radiation, $\lambda = 0.71073$ Å. Cell dimensions were based on the setting angles of 25 reflections with θ range from 8.72 to 13.36°. The intensities of 3426 reflections were estimated from $\omega/2\theta$ scans in the range $4.70 < 2\theta < 50°$, corrected for Lorentz-polarisation effects and for absorption (Psi-scan, maximum 0.9999, minimum 0.9353).[14] Averaging gave 3235 unique reflections ($R_{\text{int}} = 3.05\%$). Refinement was done on F^2 for all reflections, where 1883 were considered observed with $I \geqslant \sigma(I)$. The structure solved by direct methods with SHELXS-97[15] revealed all non-H atoms. All non-H atoms were refined anisotropically for 244 parameters on F^2 with $w = [\sigma^2(F_o^{\,2}) + (0.0694P)^2 + 3.84P]^{-1}$ where $P = [\text{Max}(F_o^{\,2}, 0) + 2F_c^{\,2}]/3$. The sp^2 H atoms rode on their parent C atoms with C–H = 0.93 Å and $U(\text{H}) = 1.2\ U_{\text{eq}}(\text{C})$. Scattering factors and anomalous dispersion corrections were those incorporated in the least-squares refinement program SHELXL-97.[16]

The crystal data for the title pyrylium perchlorate are given in Table 1 (see full text).

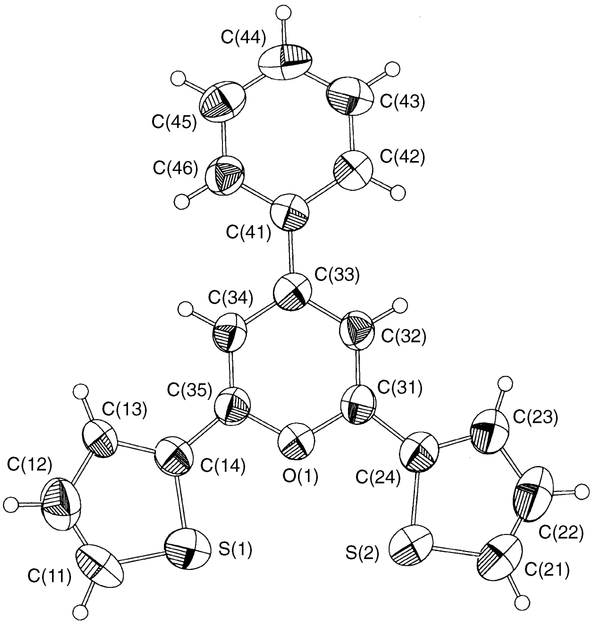

Fig. 1 A ZORTEP view of **1**

Fig. 1 shows a ZORTEP[17] view of the pyrylium salt. A least-squares plane calculation shows that the 4-phenyl substituent is not coplanar with the pyrilium ring, with a deviation from planarity of 8.8(3)°. The thienyl rings make angles of 4.7(4) and 4.6(4)° with the pyrilium ring. The perchlorate counterion is not fully symmetric, with the more elongated Cl–O(14) bond involved as an acceptor in a C–H···O bond.[18]

The positive charge on the pyrylium ring is distributed among the three aromatic substituents. The degree of charge transfer from the substituents is not the same for the phenyl and thienyl groups. The latter, more electron-rich group, is responsible for most of the charge-delocalization in the system. The evidence for this is provided by the different bond lengths between the pyrylium and the aromatic substituents. Shorter bond lengths (1.423 and 1.435 Å) were observed between the pyrylium and the thienyl groups than with the former and the phenyl substituent (1.473 Å). A shortened bond length of 1.438 Å between a pyrylium ring and a 4-dimethylaminophenyl substituent at the 4-position had been taken as an evidence of charge-transfer between the two rings.[19]

Theoretical calculations with this structure were performed with semiempirical (AM1 and PM3)[12] and a hybrid DFT method (B3LYP/6-311G).[13] The obtained results are listed in Table 2 (see full text), where some selected parameters, calculated with the three methods, may be com-

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pared with the experimental data. An inspection of the Table shows that none of the methods is entirely satisfactory in reproducing the experimental parameters. All three methods predicted full coplanarity between the substituents and the pyrylium ring, besides a higher degree of molecular symmetry than that observed experimentally. The B3LYP/6-311G method was quite successful in the calculation of pyrylium-substituent bond lengths, but departed from the experimental geometry when predicting the C–S bonds of the thienyl groups. Of the two semiempirical methods, the AM1 was clearly superior to the PM3 hamiltonian. The latter barely reproduced the greater degree of conjugation and charge-transfer between the central pyrylium and the thienyl groups, compared with the 4-phenyl substituent. According to the PM3 method, all three pyrylium-substituent bond lengths had nearly the same value (1.450 Å), much larger than the observed pyrylium–thienyl bond (1.423 Å).

Another way of measuring the degree of charge-transfer in the system is provided by the calculation of the charges on the oxygen and the sulfur atoms. All three methods agreed on assigning a positive charge on the S atoms, and a negative one on the pyrylium oxygen, but differed in the degree of charge transferred from the former to the latter. The largest positive charge on the sulfur atoms was obtained with the AM1 method. However, if the degree of charge-transfer is taken as the algebraic difference between the charges on both atoms, it was the B3LYP/6-311G method which predicted the greatest amount of charge-transfer between sulfur and oxygen.

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Techniques used: X-ray crystallography

References: 23

Tables 1–4: Atomic coordinates, bond lengths and angles and a comparison of experimental and calculated bond lengths for **1**

Fig. 2: Packing diagram

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