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**1-METHYL-2-((1E,3E)-4-PHENYLBUTA-1,3-DIENYL)PYRIDINIUM IODIDE:
SYNTHESIS, CHARACTERIZATION, AND X-RAY ANALYSIS****S. Chantrapromma¹, N. Boonnak², N. Kaewmanee¹, P. Ruanwas¹, H.-K. Fun^{3,4}**¹*Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla, Thailand*
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1-Methyl-2-((1E,3E)-4-phenylbuta-1,3-dienyl)pyridinium iodide (**1**) is synthesized and characterized by UV-Vis, FT-IR, ¹H and ¹³C NMR, and single crystal X-ray diffraction. Compound **1** crystallizes in an orthorhombic *Iba2* space group with the unit cell parameters $a = 12.8236(11)$ Å, $b = 20.1216(17)$ Å, $c = 11.2071(10)$ Å, $V = 2891.8(4)$ Å³ and $Z = 8$. X-ray diffraction indicates that the molecule of **1** displays *E,E* configurations with respect to the two middle C=C double bonds. The molecular structure of **1** is twisted and the dihedral angle between the pyridinium and phenyl rings is 15.0(2)°. In the crystal packing, cations form stacks in an anti-parallel V-shaped manner along the *a* axis through π — π interactions between pyridinium and phenyl rings.

Keywords: crystal structure, pyridinium, quaternary ammonium compound (QAC), π stacking, π — π interaction.

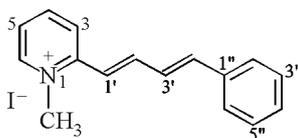
INTRODUCTION

Quaternary ammonium compounds (QACs) are generally known to be bioactive substances and are used mainly for environmental disinfection, disinfection of medical equipments, and disinfection in hospitals. However, due to the long-term usage of common QACs such as benzalkonium chloride and cetylpyridinium chloride, QACs resistant microorganisms have appeared. It was reported that some *Staphylococcus* spp. contain genes conveying resistance to this type of disinfectant [1–3]. Therefore, we have developed novel QACs which can overcome this *Staphylococcus*-resistant phenomenon by exhibiting strong anti-methicillin-resistant *Staphylococcus aureus* activity and reported this discovery in our previous work [4]. From this significant reason, title compound (**1**) was designed by extending the π -conjugated length as compared to the compounds in our previous work [4], and synthesized for a better antibacterial activity. Single crystal X-ray diffraction of **1** was performed in order to study the molecular structure and determine the interactions in the formation of the crystal.

EXPERIMENTAL

Synthesis of 1-methyl-2-((1E,3E)-4-phenylbuta-1,3-dienyl)pyridinium iodide (1**).** Compound **1** was prepared by mixing 1:1:1 solutions of 1,2-dimethylpyridinium iodide (2 g, 8.5 mmol), cinnamaldehyde (1.1 g, 8.5 mmol), and piperidine (0.84 ml, 8.5 mmol) in methanol (40 ml). The resulting solution was refluxed for 2 h in the nitrogen atmosphere. The yellow solid which formed was filtered, washed with diethyl ether, dried in vacuo and purified by recrystallization from methanol by slow

evaporation at room temperature to yield yellow block-shaped single crystals suitable for the X-ray diffraction analysis over a few weeks; melting point 245–247 °C (decompose).



(1)

UV-Vis, FT-IR, ^1H NMR and ^{13}C -NMR characterization. UV-Vis (CH_3OH) λ_{max} (nm): 260.3, 375.7; IR (KBr, cm^{-1}): $\nu(\text{CH}$ stretching) 2995 (m), $\nu(\text{C}=\text{C}$ alkene stretching) 1590 (s), $\nu(\text{C}=\text{C}$ aromatic stretching) 1565 (s), $\nu(\text{C}-\text{N}$ stretching) 1251; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ (ppm) 8.86 (d, $J = 6.3$ Hz, 1H, H-6), 8.45 (d, $J = 4.2$ Hz, Hz, 2H, H-3 & H-4), 7.85 (dt, $J = 6.3, 4.2$ Hz, 1H, H-5), 7.80 (dd, $J = 15.0, 10.5$ Hz, 1H, H-2'), 7.63 (dd, $J = 8.4, 1.2$ Hz, 2H, H-2'' & H-6''), 7.44 (br t, $J = 8.4$ Hz, 2H, H-3'' & H-5''), 7.39 (dd, $J = 15.0, 11.1$ Hz, 1H, H-3'), 7.39 (td, $J = 8.4, 1.5$ Hz, 1H, H-4''), 7.19 (d, $J = 15.0$ Hz, 1H, H-1'), 7.17 (d, $J = 15.0$ Hz, 1H, H-4'), 4.28 (s, 3H, CH_3 -1); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ (ppm) 152.5 (C-2), 146.4 (C-6), 144.5 (C-4), 143.9 (C-2'), 141.3 (C-4'), 136.3 (C-1''), 129.9 (C-3'), 129.5 (C-3'' & C-5''), 128.4 (C-4''), 127.8 (C-2'' & C-6''), 125.2 (C-5), 124.9 (C-3), 121.1 (C-1'), 46.3 (CH_3 -1).

Materials and measurements. All the chemicals and solvents were of analytical grade, purchase commercially, and used as received. Melting point was recorded in °C and measured using an electrothermal melting point apparatus. Infrared spectra were recorded using a FTS 165 FT-IR spectrophotometer. Ultraviolet-visible (UV-Vis) absorption spectra were recorded using a Shimadzu UV-2450 UV-Visible spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker FT-NMR Ultra ShieldTM spectrometer in a $\text{DMSO}-d_6$ solvent with TMS as the internal standard. Chemical shifts are reported in $\delta(\text{ppm})$ and coupling constants (J) are expressed in Hertz.

X-ray diffraction study. A yellow single crystal of **1** of the dimensions 0.19×0.17×0.12 mm was selected and data collection was performed on a Bruker Apex2 CCD diffractometer with graphite monochromated MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation at a detector distance of 5 cm using APEX2 [5] at 100.0(1) K with the Oxford Cryosystem Cobra low-temperature attachment. The collected data were reduced using the SAINT program [5], and the empirical absorption corrections were performed using the SADABS program [5]. The structures were solved by direct methods and refined by least-squares using the SHELXTL software package [6]. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions with $\text{C}-\text{H} = 0.95 \text{ \AA}$ for aromatic and CH , 0.98 \AA for CH_3 . The $U_{\text{iso}}(\text{H})$ values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. A rotating group model was used for the methyl group. The final refinement converged well. The crystal is racemic twinning. The BASF was refined to 0.226(1). Materials for publication were prepared using SHELXTL [6], PLATON [7], and Mercury [8]. The molecular formula of **1** is $\text{C}_{16}\text{H}_{16}\text{Ni}$, the formula weight is $M_r = 349.20$, the crystal system is orthorhombic, the space group is *Iba*2 with the unit cell parameters $a = 12.8236(11) \text{ \AA}$, $b = 20.1216(17) \text{ \AA}$, $c = 11.2071(10) \text{ \AA}$, $V = 2891.8(4) \text{ \AA}^3$, $Z = 8$ and $D_{\text{calc}} = 1.604 \text{ g/cm}^3$. Out of 3223 independent reflections, 2833 $I > 2\sigma(I)$ were used in the refinement. The final least-square cycle of the refinement by full-matrix least squares methods on F^2 gave $R_1 = 0.0325$, $wR_2 = 0.0598$ and $\text{GOOF} = 1.071$.

RESULTS AND DISCUSSION

Single crystal X-ray analysis. Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in orthorhombic *Iba*2 and consists of a $\text{C}_{18}\text{H}_{16}\text{N}^+$ cation and an Γ anion. The molecular structure and the atom labeling scheme of **1** is shown in Fig. 1.

The cation molecule exists in the *E,E* configurations with respect to the $\text{C}_6=\text{C}_7$ and $\text{C}_8=\text{C}_9$ double bonds. The bond lengths of 1.337(7) \AA and 1.350(6) \AA for $\text{C}_6=\text{C}_7$ and $\text{C}_8=\text{C}_9$ respectively is con-

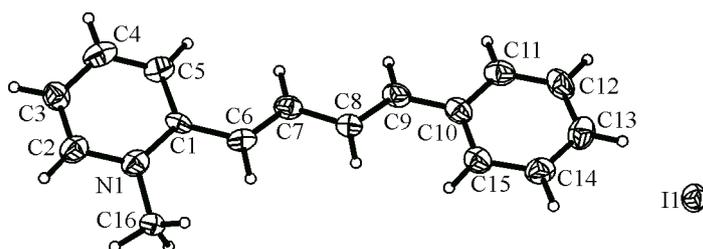


Fig. 1. Molecular structure of **1** showing the atom labeling scheme

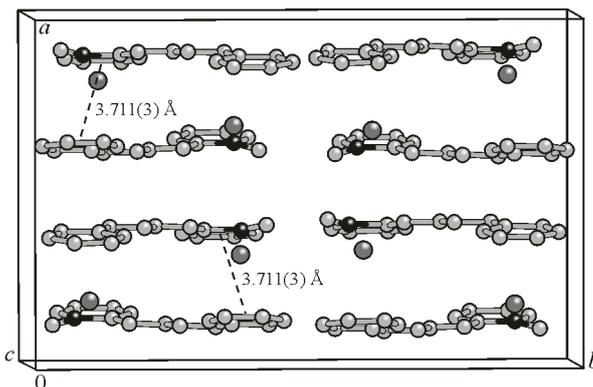


Fig. 2. View of the unit cell packing of **1** along the *c* axis, showing the stacking of the cations. H atoms were omitted for clarity

sistent with the double bond character. The C1—C6—C7—C8 and C7—C8—C9—C10 torsion angles are 174.7(5)° and 173.0(5)° indicate the *trans* configurations. The cation molecule is twisted with the dihedral angle between the pyridinium (C1—C5/N1) and the phenyl (C10—C15) rings being 15.0(2)°, which may result from the long π -conjugated bridge (C6—C9) and the C—C (C1—C6 and C9—C10) single bond rotation between the central bridge and pyridinium and phenyl rings. The middle buta-1,3-dienyl unit (C6—C9) is almost planar with the torsion angle C6—C7—C8—C9 = -178.7(5)°. The mean plane through this middle bridge makes the dihedral angles of 7.2(5)° and 7.9(5)° with the pyridinium and phenyl rings respectively. The methyl substituent is almost coplanar with the pyridinium ring with the C16—N1—C1—C5 torsion angle of 176.5(4)°. The cation bond lengths are in normal ranges [9] and are comparable with the closely related structure [10].

In the crystal packing (Fig. 2), the cations are stacked in an anti-parallel V-shaped manner along the *a* axis with significant π — π interactions between the pyridinium and phenyl rings, with the centroid-centroid distance of $Cg_1 \dots Cg_2^{ii} = 3.711(3)$ Å; Cg_1 and Cg_2 are the centroids of the C1—C5/N1 and C10—C15 rings respectively; symmetry code: (ii) $1/2-x, 1/2-y, 1/2+z$. The iodide ions are located interstitially amongst the cations. The compound is stabilized and consolidated by Coulomb interactions between the ions and π — π interactions.

CONCLUSIONS

In this study, 1-methyl-2-((1*E*,3*E*)-4-phenylbuta-1,3-dienyl)pyridinium iodide (**1**) was successfully synthesized and characterized by UV-Vis, FT-IR, ^1H and ^{13}C NMR, and single crystal X-ray diffraction. The X-ray diffraction study reveals that the molecule of **1** exists in the *E,E* configurations with respect to the two middle C=C double bonds and the molecule is slightly bent. In the solid state, the crystal structure is stabilized and consolidated by Coulomb interactions between the ions and π — π interactions.

Supplementary material. CIF file containing complete information on the studied structure was deposited with the Cambridge Crystallographic Data Center, CCDC No. 917917, and is freely avail-

lable upon request from the following website: www.ccdc.cam.ac.uk/data_request/cif or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk.

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