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Structure of 1,1′-Methylenebis(4,4′-dimethylaminopyridinium) Iodide

By S. Munavalli and E. J. Poziomek

US Army Chemical Research Development and Engineering Center, Research Directorate, Aberdeen Proving Ground, Maryland 21010, *USA*

and Cynthia S. Day

Crystalytics Company, Lincoln, Nebraska 68501, *USA*

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Abstract. $C_{15}H_{22}N_4I_2.H_2O$, $M_r = 530{\cdot}2$, monoclinic, $C2/c$, $a = 19{\cdot}064\ (5)$, $b = 9{\cdot}085\ (3)$, $c = 11{\cdot}471\ (4)$ Å, $\beta = 92{\cdot}81\ (2)^\circ$, $V = 1984\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}77\ \text{g cm}^{-3}$, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 31{\cdot}4\ \text{cm}^{-1}$, $F(000) = 1024$, $T = 293$ K, $R = 0{\cdot}040$, $wR = 0{\cdot}044$ for 3088 observed reflections. In spite of the anomalous NMR chemical shift of the methylene protons flanked by two positively charged N atoms and the absence of the characteristic downfield displacement of the NMR signal of the α protons due to quaternization of the ring N, X-ray crystallography results confirm that quaternization unequivocally takes place at the ring N.

Introduction. Since its introduction, high-resolution nuclear magnetic resonance (NMR) has become accepted as one of the most versatile analytical tools available to organic chemists. The NMR chemical shifts depend on the nature and position of the substituent and the molecular environment. As opposed to the benzene ring, the presence of the heteroatom in the pyridine ring causes subtle changes in the chemical environment of the aromatic protons. Thus the unshared pair of electrons of the ring N leads to differential shifts of the α, β and γ protons and thus three distinct signals for three types of protons are observed. The β protons are displaced upfield, the α protons appear farthest downfield and the γ protons somewhere in the middle (Spiesecke & Schneider, 1961). The presence of an exocyclic N introduces additional complications. NMR has been used to study the relative reactivity of the ring and the exocyclic nitrogens towards protonation and alkylation reactions (Essery & Schofield, 1961). Well defined changes occur in the NMR spectrum of the pyridines on quaternization. The presence of a positive charge on the N leads to lower screening for the neighboring protons. Consequently, the α protons can easily be distinguished by downfield displacement of their NMR signal. This characteristic feature is usually employed as a positive indication of the quaternization of the pyridine N (Smith & Schneider, 1961; Silverstein & Bassler, 1967; Sudmeier & Reilly, 1964).

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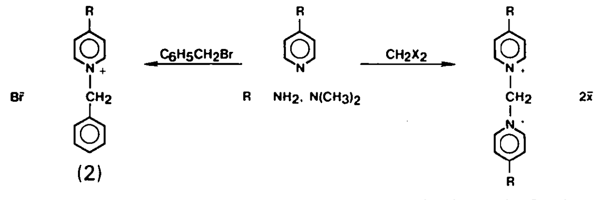
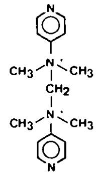
In connection with our work on the preparation and properties of the methylene bispyridinium compounds, the title compound was synthesized (Munavalli, Poziomek & Landis, 1986). The elemental analysis indicated the compound to be $C_{15}H_{22}N_4I_2$. Its molecular weight obtained through conventional mass spectra as well as through secondary-ion and fast-atom bombardment techniques was consistent with the above formula. However, the chemical shift of the methylene protons was not consistent with that expected from bisquaternization (1*a*). In fact, the chemical shift was dramatically displaced upfield by more than 1·2 p.p.m. in comparison with the unsubstituted compound (1*b*). Similar anomalies were also observed in the case of (1*c*) and (2). Even assuming the possibility of the solvent–solute interaction, this displacement of the methylene protons flanked by two positively charged adjacent nitrogens seemed highly unusual. Conspicuously absent from the NMR spectra of these compounds was the downfield displacement of the α protons on quaternization. This, much to our discomfort, led us to consider the possibility that the exocyclic N might have been bis-alkylated to give (3*a*), (3*b*) and (3*c*). To resolve this apparent anomaly, the structure of the title compound has now been unequivocally elucidated from its X-ray determination. The structure is indeed as represented by (1*a*).

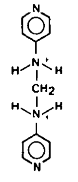


(2)

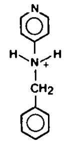
(1*a*) R = $N(CH_3)_2$
(1*b*) R = H
(1*c*) R = NH_2



(3*a*)

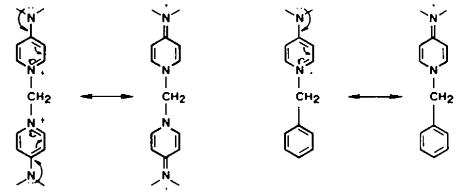


(3*b*)



(3*c*)

Recently, the absence of the downfield displacement of the NMR signal of the α protons on quaternization of the ring N has been attributed to the overall synergistic effects including the resonance contribution of the structures of the type (1*a*′) and (1*c*′) (Munavalli, Szafraniec, Beaudry & Poziomek, 1986). In these structures the ring N does not bear any formal charge. In view of these observations, judicious care must be exercised in using the chemical shift displacement of the α protons as the sole criterion for the quaternization of the pyridine ring.



(1*a*,*c*) (1*a*′,*c*′) (2) (2)

Experimental. Single crystals were obtained from an aqueous solution. Colorless rectangular parallelepiped; 3088 unique intensities were measured out to $2\theta <$ 71·0° using graphite-monochromated Mo $K\alpha$ radiation, cell dimensions were obtained by least-squares refinement from 15 computer-centered reflections having $2\theta > 30°$, crystal with dimensions 0·45 × 0·50 × 0·88 mm was oriented with its longest dimension nearly parallel to the φ axis of the diffractometer, the intensity data were corrected empirically for absorption effects using ψ scans with 2θ between 13·6 and 39·5° and then reduced to relative squared amplitudes $|F_o|^2$, by means of the standard Lorentz and polarization corrections.

Background counts were measured at settings 1·00° above and below the calculated value for each reflection. The ratio of the background counting time to net scanning time was 0·50, the range of relative factors being 0·67–1·00. The number of check reflections and frequency monitored were six and 300 respectively.

Standard deviations in the intensities were computed from $\sigma^2(I) = (C_t + k^2B)$ where C_t was the total scan count, k was the ratio of scan time to background time and B was the total background count. Least-squares minimization was of the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma_F^2$. The counterweight $\sigma_F = \{[\sigma(F_o)]^2 + (P/F_o)^2\}^{-1/2}$ where the 'ignorance factor' P had a value of 0·01. Final values of R and wR were 0·040 and 0·044 respectively for all 3088 reflections. During the final least-squares cycle the maximum shift of any parameter was 0·12σ, σ being the standard deviation of the parameter. The goodness of fit (GOF) was determined using GOF = $\{\sum w(|F_o| - |F_c|)^2/(\mathrm{NO}-\mathrm{NV})\}^{1/2}$ where NO is the number of observations and NV is the number of variables. Anomalous-dispersion corrections (Cromer & Waber, 1974) were made for the I atom. Three largest peaks (1·4→1·0 e Å^{-3}) in the final difference Fourier map were within 0·90 Å of the I^- anion. There were no other peaks above 0·42 e Å^{-3}.

The two terminal methyl groups of the cation (C7, C8 and their H atoms) were refined as rigid rotors with idealized sp^3-hybridized geometry and a C—H bond length of 0·96 Å. The initial orientation of each methyl group was determined from difference-Fourier peaks for the H atoms. The final orientation of each group was detected by three rotational parameters. The remaining H atoms were included in the structure-factor calculations as idealized atoms 'riding' on their respective atoms. The isotropic thermal parameter of each H atom was fixed at 1·2 times the equivalent isotropic thermal parameter of the C atom to which it is covalently bonded. The structure also contains a molecule of water of crystallization, which lies on a crystallographic twofold axis. The H atoms of the water molecule were not detected.

The structure was solved by heavy-atom Patterson techniques and refined using cascade block-diagonal least-squares techniques. The final scale factor was 2·081 (6) and the refined extinction-parameter value was found to be 0·00654 (Larson, 1967). All calculations were performed on a Data General Eclipse S-200 computer using versions of the Nicolet (Syntex) *E-XTL* or *SHELXTL* (Sheldrick, 1983) interactive crystallographic software package as modified at Crystalytic Company. The diffractometer used was a computer-controlled four-circle Nicolet Autodiffractometer.

The NMR spectra were run on a Varian EM-390 NMR spectrometer in D_2O at the probe temperature of 307 K. The chemical shifts were relative to the internal standard sodium 3-trimethylsilylpropionate (TSP). All signals were downfield from the reference.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10$) *for non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*
I	3765 (1)	2910 (1)	3675 (1)	39 (1)
N1	517 (1)	1656 (3)	1930 (3)	33 (1)
N2	1987 (1)	4112 (3)	287 (2)	33 (1)
C1	0†	740 (5)	2500†	41 (1)
C2	374 (2)	2191 (4)	851 (3)	40 (1)
C3	842 (2)	3006 (4)	283 (3)	38 (1)
C4	1511 (1)	3318 (3)	824 (2)	28 (1)
C5	1648 (2)	2710 (4)	1950 (3)	30 (1)
C6	1151 (2)	1916 (3)	2468 (3)	32 (1)
C7	1833 (2)	4785 (5)	−852 (3)	45 (1)
C8	2648 (2)	4529 (4)	883 (3)	41 (1)
O*w*	0†	5205 (6)	2500†	79 (2)

* This is one-third of the trace of the orthogonalized B_{ij} tensor.

† This is a symmetry-required value and is therefore listed without an estimated standard deviation.

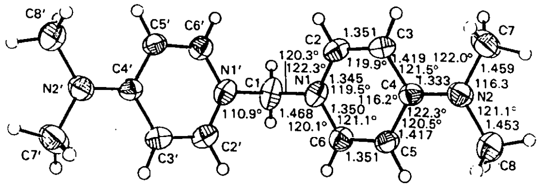


Fig. 1. Perspective drawing of the $(C_{15}H_{22}N_4)^{2+}$ cation in crystalline $(C_{15}H_{22}N_4)(I)_2.H_2O$. H atoms are arbitrarily represented by small spheres. Non-hydrogen atoms are represented by thermal-vibration ellipsoids drawn to encompass 50% of their electron density. Primed (′) atoms are related to non-primed atoms by the crystallographic twofold axis at 0, y, $\frac{1}{4}$. Bond lengths are in Å and angles in degrees; estimated errors in these values are about 0·004 Å and 0·3°, respectively.

Discussion. The downfield displacement of the NMR signal of the α protons on quaternization of the pyridine N is frequently used as a 'qualitative test' for the quaternization of the ring N. In the case of compounds (1*a*), (1*c*) and (2), no such displacement was seen. Besides, the chemical shift of the methylene protons flanked by two positively charged nitrogens [(1*a*) and (1*c*)] was dramatically displaced upfield by more than 1·2 p.p.m. This led us to consider alternative structures, namely (3*a*), (3*b*) and (3*c*), as potential candidates for these compounds. Since this possibility seemed remote and contradictory to the accepted concepts, the determination of the exact structure of the title compound seemed desirable. Thus, the X-ray structure analysis appeared interesting from theoretical as well as practical points of view. Final atomic coordinates are given in Table 1. Fig. 1 shows a perspective *ORTEP* drawing (Johnson, 1965) of the compound with bond lengths and angles. The positive charge present on the N atoms is not localized as implied by the structures (1*a*), (1*c*) and (2). Instead the positive charge is completely delocalized throughout the molecule. In other words, the exocyclic nitrogens [(1*a*) and (1*c*)] share the positive charge through the synergistic interaction as shown by the structures (1*a*′), (1*c*′) and (2′). These structures, therefore, do make a significant contribution to the overall structure. This is consistent with the enhanced resonance effects associated with π-electron donors and their stabilizing interactions (Essery & Schofield, 1963; Katritzky & Simmons, 1960; Becker, Miles & Bradley, 1965). The geometry-optimized *INDO* calculations have shown that the quinoid resonance hydbrids (1*a*′), (1*c*′) and (2′) do make a definite contribution to the overall structure of the compounds (Barbieri, Benassie, Grandi, Pagnoni & Taddei, 1979). These structures readily account for the absence of the downfield displacement of the signal of the α protons on quaternization of the pyridine N. This study definitely confirms the observation that alkylation and bis-alkylation of 4-amino- and 4-dimethylamino-pyridines takes place at the ring nitrogen. In view of the above considerations, care must be exercised in using the downfield displacement of the α protons as a positive indication of quaternization of the pyridine N.

Comparison of the C—C bond lengths and angles of pyridine (4), *N*-methylpyridinium iodide (5) and (1*a*) brings out some interesting observations. The molecular dimensions of (4) are extremely close to benzene. The bond angle opposite the ring N (that is C3—C4—C5) of (4) (Sommers, 1979) is almost the same as that of (5) (Lalancette, Furey, Costanzo, Hemmes & Jordan, 1978). In contrast, that of (1*a*) is almost 2·0° smaller. Also, the angle C5C6N of (5) differs from that of (1*a*) by more than 2·0°. Although the C—C bonds of (5) and (1*a*) are almost similar, the C4—C5 bonds vary (by about 0·04 Å). The N—C bond lengths of $N^+—CH_3$ and $N^+—CH_2—N^+$ are very close.

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Structure of 3-(4-Hydroxy-3-methoxyphenyl)-2-propenoic Acid (Ferulic Acid)

BY M. NETHAJI AND VASANTHA PATTABHI*

Department of Crystallography and Biophysics,† *University of Madras, Guindy Campus, Madras* 600 025, *India*

AND GAUTAM R. DESIRAJU*

School of Chemistry, University of Hyderabad, PO Central University, Hyderabad 500 134, *India*

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Abstract. $C_{10}H_{10}O_4$, $M_r = 194\cdot19$, monoclinic, $P2_1/n$, $a = 4\cdot6405\ (4)$, $b = 16\cdot824\ (5)$, $c = 12\cdot019\ (4)$ Å, $\beta = 90\cdot15\ (1)°$, $V = 938\cdot4\ (1)$ Å^3, $Z = 4$, D_m (by flotation) = 1·38, $D_x = 1\cdot38$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu(\text{Cu } K\alpha) = 0\cdot808$ mm^{-1}, $T = 295$ K, $F(000) = 408$, final $R = 0\cdot036$ for 1219 significant reflections where $I_o > 2\cdot5\sigma(I_o)$. The structure was solved by direct methods. The carbonyl oxygen is in the *syn* conformation with respect to the olefinic linkage. The phenyl ring makes an angle of 4·0 (1)° with the carboxyl group. Molecules are strongly O—H···O hydrogen bonded across inversion centres [O···O 2·629 (2) Å]. Additionally, there are unusual O—H···O—H bonds [O···O 2·889 (2) Å] between phenolic and carboxylic O—H groups of glide-related neighbours. The molecules are stabilized by an infinite zigzag chain of these intermolecular O—H···O and also C—H···O bonds. Molecules related by the short-axis translation are too far apart for solid-state photodimerization and the solid is thus photostable.

Introduction. Substituted *trans*-cinnamic acids are excellent choices for the study of organic solid-state photochemical processes (Schmidt, 1964; Desiraju, Kamala, Kumari & Sarma, 1984; Nakanishi & Hasegawa, 1985) and as model compounds for 'crystal engineering', that is the deliberate design and prediction of organic crystal structures (Sarma & Desiraju, 1986). These acids crystallize in one of three forms, the photoactive α and β modifications and the photostable γ modification. The distinguishing criterion for these forms is the value of the crystallographic short axis which is greater than 5·1 Å for the α, between 3·8 and 4·2 Å for the β and between 4·6 and 5·1 Å for the γ form. The title compound is part of a series of 3,4-dioxygenated cinnamic acids whose crystal structures and solid-state photochemistry have been studied systematically. Earlier reports have dealt with the 3,4-methylenedioxy and 3,4-dimethoxy acids (Desiraju,

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* To whom correspondence should be addressed.

† DCB contribution No. 710.

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