$$\Xi = 10^8\chi_{\text{obsd}}/(10^8 + f) - 100\delta$$

where χ_{obsd} is the tin shift measured, δ is the chemical shift of the compound whose frequency is used to lock the spectrometer relative to tetramethylsilane (TMS), $(10^8 + f)$ is the frequency of the lock signal, and f is the frequency of the manual oscillator. Use of the factor 10^8 assumes an absolute ν_1 = 100 MHz for TMS on the Varian HA-100D spectrometer employed. The HA-100D spectrometer employed in this work was found to have a frequency range of 100,001,600.0–100,001,900.0 Hz, and the appropriate corrections have been made in the tabulated tin frequencies.

The tin chemical shifts are relative to a 50% solution of tetramethyltin in methylene dichloride, with a positive sign used to denote a shift upfield from tetramethyltin. This "standard solution" was found to have a tin-119 resonance frequency of 37,290,662 ± 2 Hz. This value compares favorably with that reported by McFarlane, *et al.*, for a 95% solution 37,290,665 ± 2 Hz).[6] Tin frequencies were calibrated with the standard after each run.

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The Crystal and Molecular Structure of 2,2′-Bis(6-methyl-3-pyridinol)

L. H. Vogt, Jr.,* and J. G. Wirth

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Abstract: 2,2′-Bis(6-methyl-3-pyridinol) is a highly fluorescent homolog of a new family of 3-pyridinol dimers. The structure of the 6-methyl dimer was determined by single-crystal X-ray diffraction methods to better understand its physical properties. The compound crystallized in space group $P2_1/n$ with a = 7.62, b = 4.61, c = 20.59 Å, β = 134.07°, and Z = 2. The positions of all eight nonhydrogen atoms in the asymmetric unit were located by the symbolic addition method. A difference Fourier gave the six hydrogen atom positions. Full-matrix least-squares refinement (eight atoms anisotropic, six hydrogens isotropic) using 592 reflections ($F > 3\sigma$) resulted in a conventional R factor of 0.071. The molecules are discrete and planar and contain strong intramolecular hydrogen bonds (N–O, 2.568 Å); there are no intermolecular hydrogen bonds. The 1.347-Å C–O and 1.459-Å C–C (bridge) bonds are about halfway between the typical double and single bond distances. This is consistent with other evidence which suggests the existence of a tautomeric equilibrium involving a form with quinoid character.

In the course of an investigation of the oxidation of heterocyclic phenols,[1] a pale yellow crystalline compound was isolated from a reaction medium consisting of PbO_2, 6-methyl-3-pyridinol, and petroleum ether. The yellow compound fluoresced a brilliant yellow-green when excited with uv light. Nmr and ir spectra, molecular weight, and elemental analyses indicated that the compound was a 2,2′ dimer of 6-methyl-3-pyridinol with an empirical formula of $C_{12}H_{12}N_2O_2$ and contained a strong hydrogen bond.[1] In order to verify these findings and firmly establish the details of the molecular structure, we undertook a single-crystal X-ray diffraction analysis. In particular, we wanted to define those features of the structure that could be useful in understanding the mechanism of the exceptionally intense fluorescence, *viz.*, whether the molecule shows any quinoid character (why it is yellow rather than colorless), whether it is planar, if there are any intermolecular interactions, and whether the hydrogen bond is as strong as suggested by the ir spectrum.

Experimental Section

The compound was prepared by the oxidation of 6-methyl-3-pyridinol as described earlier[1] and was recrystallized from petroleum ether (30–60°) to give long, thin, pale yellow plates. Preliminary cell and space group data were collected on precession and Weissenberg cameras using Cu Kα radiation. The long direction of the crystal corresponded to the b axis of the monoclinic unit cell. A General Electric automated (Datex) XRD-6 diffractometer, with a quarter-circle goniostat, was used to obtain the final cell parameters based on Cu Kα_1 1.54051 Å and to collect the integrated intensity data (using θ–2θ scans and a 4° takeoff angle). Table I gives the pertinent experimental data. The intensity of the 020 reflection, monitored twice daily during the data collection, remained essentially constant, indicating that the crystal was stable during this period. Corrections were applied to the data for Lorentz and polarization effects but not for absorption or extinction.

Table I. Experimental Data

a, Å	7.62 ± 0.02
b, Å	4.61 ± 0.04
c, Å	20.59 ± 0.02
β, deg	134.07 ± 0.02
ρ(X-ray), g/cm^{-3}; ρ(measd)	1.38; 1.36 ± 0.01
Space group[a]	$P2_1/n$
Molecules/unit cell	2
Total obsd reflections[b]	592
$\langle\lvert E\rvert\rangle$	0.751
$\langle\lvert E^2 - 1\rvert\rangle$	0.916
Crystal size, mm	0.50 × 0.07 × 0.02

[a] The equivalent positions are $\pm(x, y, z)$ and $\pm(x + {}^1/_2, y - {}^1/_2, z + {}^1/_2)$ with b as the unique axis. [b] The intensities of 1095 reflections ($2\theta \leq 154°$) were measured, but only those whose F's were $>3\sigma$ were considered as observed.

The standard deviation of $|F_o|$ $(=\sqrt{I})$, where the integrated intensity I is $I = TC - (B_1 + B_2)(t_c/2t_b)$, was assumed to be[2]

$$\sigma(F) = [TC + (t_c/2t_b)^2(B_1 + B_2) + 0.05I)^2]^{1/2}/2F$$

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* Address correspondence to this author at G. E. Chemical Products Business Section, Cleveland, Ohio 44110.

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Table II. Fractional Coordinates and Thermal Parameters ($\beta_{ij} \times 10^4$)[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	0.2514 (6)	0.7616 (8)	−0.0447 (2)	330 (12)	473 (26)	39 (1)	32 (14)	70 (4)	5 (5)
O	0.5979 (6)	0.9873 (8)	−0.0979 (2)	531 (14)	711 (25)	58 (2)	−90 (16)	139 (5)	−25 (5)
C1	0.4203 (7)	0.8985 (9)	−0.0375 (2)	321 (14)	443 (30)	34 (2)	54 (16)	67 (4)	12 (5)
C2	0.4355 (7)	0.8517 (9)	−0.1011 (2)	376 (16)	434 (28)	39 (2)	74 (18)	81 (5)	13 (6)
C3	0.2752 (9)	0.6579 (11)	−0.1699 (3)	514 (20)	534 (34)	42 (2)	22 (21)	102 (6)	−16 (7)
C4	0.1062 (9)	0.5205 (12)	−0.1753 (3)	412 (18)	550 (34)	35 (2)	−7 (20)	56 (5)	−14 (7)
C5	0.0961 (7)	0.5749 (10)	−0.1120 (2)	321 (14)	432 (29)	35 (2)	16 (16)	52 (4)	−4 (5)
C6	−0.0856 (12)	0.4349 (17)	−0.1146 (5)	429 (22)	764 (46)	67 (3)	−142 (28)	109 (8)	−35 (11)
H1	−0.1748 (112)	0.5662 (167)	−0.1066 (44)	12.02 (225)[b]					
H2	−0.0142 (105)	0.3208 (130)	−0.0648 (41)	9.98 (198)[b]					
H3	−0.2023 (107)	0.3387 (135)	−0.1678 (42)	9.93 (185)[b]					
H4	0.2904 (65)	0.6094 (84)	−0.2140 (24)	5.129 (136)[b]					
H5	−0.0114 (78)	0.3912 (106)	−0.2270 (32)	6.702 (1152)[b]					
H6	0.6986 (94)	0.0921 (136)	−0.0423 (40)	9.33 (167)[b]					

[a] The coordinates are expressed in fractions of the cell parameters. Esd's in the last significant figures are in parentheses. Anisotropic parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters, B, are in Å^2.

TC represents the total counts during a 2° scan (1° on each side of the Cu K$\bar{\alpha}$-1.5418 Å peak) at a rate of 1°/min, t_c is the time for the scan, and t_b is the time (10 sec) for each background (B_1 and B_2).

A General Electric 605 computer was used to execute the following programs: EFACT, WILSON, and SORTE-66 (symbolic addition), written by A. L. Bednowitz (IBM Watson Research Center, Tarrytown, N. Y.; BNLSI (full-matrix least-squares in which $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$, is minimized), W. C. Hamilton's (Brookhaven National Laboratory, Upton, N. Y.) modification of the Busing-Martin-Levy[3a] program; DISTAN (distance and angles), written by A. Zalkin (Lawrence Radiation Laboratory, University of California, Berkeley, Calif.); ORFFE (error function program), the BNL modification of the Busing-Martin-Levy program;[3b] ORTEP (stereoscopic plotting), written by C. K. Johnson[3c]; and FORDAP, the BNL version of A. Zalkin's Fourier program.

Atomic scattering factors for neutral C, N, and O were taken from the International Tables[4] and those for H were by Stewart, *et al.*[5]

Structure Analysis

The structure was solved by the symbolic addition method.[6] The first E map, based on 266 reflections having E values between 3.6 and 1.0, showed all eight nonhydrogen atoms. Isotropic least-squares refinement of these positions, using unit weights, gave a conventional R value ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.45; anisotropic refinement reduced this to 0.18. A difference Fourier immediately showed the six hydrogen atoms (the electron density for these atoms was between 0.3 and 0.5 e/Å^3). Final least-squares refinement using anisotropic temperature factors for all but the hydrogen atoms and rejecting all reflections having $|F_o| \leq 3\sigma$ gave an unweighted R of 0.071, a weighted R of 0.073, and a "goodness of fit" of 1.79.[7] The final difference Fourier showed no electron density higher than 0.2 e/Å^3, and the coordinates for the greatest density did not correspond to any chemically significant position. Table II gives the fractional coordinates and thermal parameters for all 14 of the atoms in the asymmetric unit. Selected bond distances and angles are shown in Figure 1.

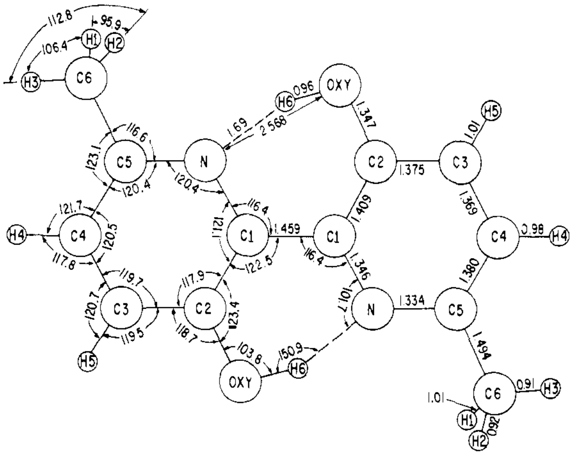
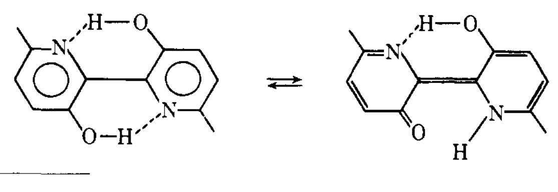


Figure 1. Bond distances and angles. Esd's for bonds not involving hydrogen range from 0.004 to 0.009 Å, and with hydrogen, from 0.04 to 0.07 Å. The esd's for angles not involving hydrogen are 0.4–0.5° and with hydrogen the range is from 1.9 to 4.7°, except for the methyl hydrogens, where the range is from 5.3 to 5.5°.

Discussion

The dimer molecules are seen to be essentially planar with all but the three methyl hydrogen atoms within 3σ of the least-squares plane through the molecule (Table III). Figure 2 is a stereoscopic[8] drawing of the molecule and shows that the magnitude and orientation of the 50% probability thermal ellipsoids for all of the nonhydrogen atoms are reasonable and not unexpected. The bond distances shown in Figure 1 suggest a considerable resonance contribution to the structure, probably of a quinoid character, which may give rise to the yellow color of the dimer, *e.g.*



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(3) (a) W. R. Busing, K. L. Martin, and H. A. Levy, Report No. ORNL-TM-305; 1962; (b) ORNL-TM-306, 1964; (c) C. K. Johnson, ORNL-3794, 1965.

(4) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962; (a) J. A. Ibers, p 202; (b) O. Kennard, p 275.

(5) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(6) J. Karle and I. L. Karle in "Transactions of the American Crystallographic Association," Vol. 2, American Crystallographic Association, Pittsburgh, Pa., 1966, p 46.

(7) A table of the absolute values of the observed and calculated structure factors (×10) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(8) A satisfactory viewer for examining these stereoscopic drawings is available from Gordon Enterprises, North Hollywood, Calif. 91601. It is designated as a Pocket Stereoscope, Type 120 G.E., and costs $15.

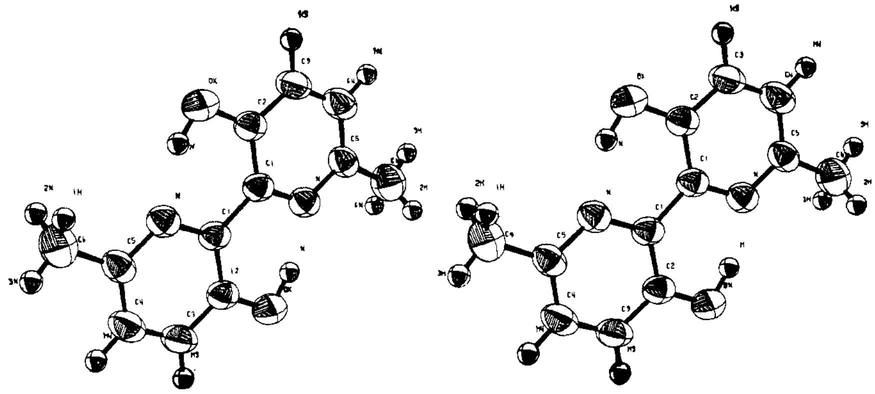

Figure 2. Stereoscopic drawing of the dimer molecule. The hydrogen atoms were drawn in with fixed radii of 0.1 Å to afford a clear representation of the main molecular framework.

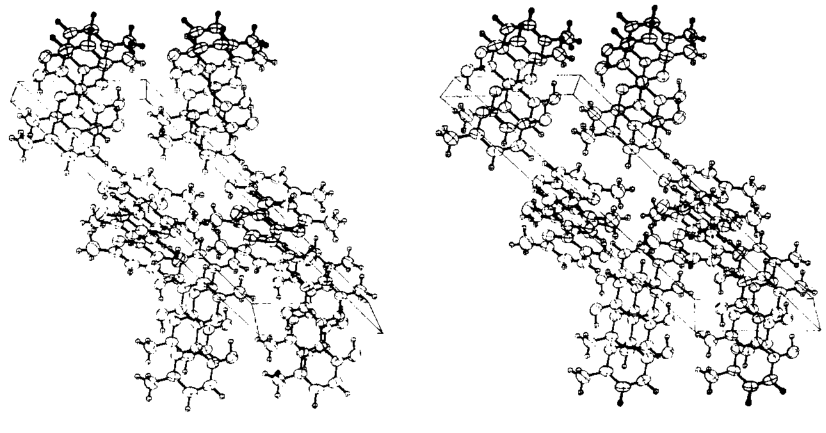

Figure 3. Stereoscopic drawing illustrating the molecular packing. The longest axis is *a*, the shortest is *b*, and *c* is horizontal.

The C1—C1 and C2—O distances are about halfway between the accepted values for single and double bond distances (C—C, 1.541; C═C, 1.337; C—O, 1.43; C═O, 1.23 Å).[4b] Strong intramolecular hydrogen bonding is indicated by the very short N–O distance of 2.568 Å and is consistent with the same conclusion drawn from ir and nmr data.

Table III. Deviations (Å) of Atoms from the Least-Squares Plane[a]

Atom	$Ax + By + Cz - D = 0$[b] Distance from plane, Å
N	−0.002 ± 0.003
O	−0.012 ± 0.004
C1	0.010 ± 0.004
C2	0.003 ± 0.004
C3	0.007 ± 0.005
C4	0.003 ± 0.005
C5	−0.004 ± 0.004
C6	−0.025 ± 0.008
H4	0.070 ± 0.037
H5	−0.043 ± 0.045
H6	−0.083 ± 0.055

[a] The positions of all but the three methyl hydrogen atoms were used to compute the least-squares plane. The dihedral angle between the plane defined by the three methyl hydrogen atoms (H1, H2, H3) and three atoms of the pyridine ring (N, C2, C4) is 87.7 ± 3.4°. [b] x, y, and z are in terms of fractional coordinates of the unit cell. $A = 2.7101$; $B = -3.4287$; $C = 3.2803$; $D = -2.0744$.

The methyl groups are not freely rotating, since the difference Fourier shows specific peaks rather than a ring of electron density in the region where the three methyl hydrogens should be. However, the relatively large isotropic thermal parameters for these three hydrogen atoms suggest that either the methyl groups are undergoing hindered rotation or they are disordered.

Figure 3 shows a stereoscopic drawing of the molecular packing in the unit cell and illustrates that the dimers are present as discrete molecular units. If just the C, N, and O atoms are considered, there is only one *intermolecular* contact that is less than 3.47 Å (a 3.368-Å distance between the oxygen atom of one molecule and the methyl carbon of an adjacent molecule). This is significantly larger than the calculated van der Waals distance for a C–H · · · O hydrogen bond of 3.0 Å.[9]

The closest intermolecular contact when the hydrogen atoms are considered is 2.576 Å, which is the distance between the H5 atoms on adjacent molecules. Thus, there are no *intermolecular* hydrogen bonds or other significant *intermolcular* contacts in the crystal.

The molecules are stacked in the crystal with their planes parallel, but not eclipsed, and with a 3.429-Å interplanar spacing. Figure 3 shows that the stacks run through the crystal in two different directions. The planes through the molecules in each stack make a dihedral angle with each other of 84.0 ± 1.9°. There are no chemical or crystallographic differences between the molecules in these stacks. Thus, in the solid, the fluorescence is almost certainly of intramolecular origin. The molecular structure and spectroscopic data suggest that the fluorescence mechanism may involve a tautomeric shift analogous to that proposed for the

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(9) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 16.

salicylanils.[10] A more detailed discussion of the fluorescence will appear in a future communication.

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Acknowledgments. L. H. Vogt would like to thank Dr. J. S. Kasper for the use of his Datex atuomated G. E. diffractometer.

Electronic Spectra of 2-Aminonaphthalene-6-sulfonate and Related Molecules. I. General Properties and Excited-State Reactions[1]

Carl J. Seliskar[2] and Ludwig Brand*

Contribution from the McCollum–Pratt Institute, The Johns Hopkins University, Baltimore, Maryland 21218.

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Abstract: The absorption and luminescence spectra of 2-aminonaphthalene-6-sulfonate and its derivatives suggest the importance of intramolecular charge transfer in the spectral properties of these molecules. The lone-pair electrons on the nitrogen atom are principally involved in the lower energy electronic transitions in all of these molecules, and this suggests that the two lowest energy absorptions can be assigned as $a_\pi \leftarrow l$ transitions. The excited-state reactions of 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate are presented and rationalized on the basis of the $a_\pi \leftarrow l$ transition.

Substituted naphthalene derivatives have been used as fluorescence probes to obtain information about enzymes,[3] mitochondrial membranes,[4] and nerve excitation.[5] Interpretation of fluorescence changes related to biological function requires an understanding of the excited states involved. The aim of this research was a partial characterization of the lower electronic states of a series of 2-aminonaphthalene-6-sulfonate derivatives.

The spectroscopy of these molecules is of interest in its own right. The low-energy electronic transitions in aromatic amines, especially aniline, have been interpreted in terms of a "composite molecule" approach.[6–8] In this theory, aromatic hydrocarbons having strongly conjugating groups, such as an amine, are treated as being made up of two component molecules. The electronic states of the whole molecule would then be some combination of the local states of both parts *plus* a certain percentage of electron-transfer states between the two components. In the case of the anilines the theory has been worked out extensively[9–12] and Kimura, *et al.*,[13,14] have obtained experimental results that agree well with theoretical predictions. The discussion of the electronic states of 2-aminonaphthalene-6-sulfonate and its derivatives studied here will be treated in the general terms of this theory.

Experimental Section

Solvents. *tert*-Butyl alcohol was obtained from Matheson Coleman and Bell and redistilled through a 40-cm Vigreux column. The middle fraction boiling at 82 ± 0.5° was collected and used.

Absolute ethanol was obtained from Publicker Industries, Inc. (Philadelphia, Pa.), and used as such for all the fluorescence measurements at 300°K. No significant fluorescence was observed from the solvent itself. Ethanol used for the measurements of fluorescence and phosphorescence at 77°K was refluxed for more than 3 hr over metallic magnesium and then distilled through a 38-cm column of Rhashig rings. The middle fraction boiling at 78 ± 0.5° was collected and immediately used. Absolute ethanol treated in this manner formed crack-free glasses at 77°K. Water was either distilled from an alkaline permanganate solution and then again, or processed by a Hydro, Inc., water processing unit. In either case no fluorescence or significant ultraviolet absorption could be detected from pure water above 2000 Å.

Aqueous solutions of acids were obtained by diluting commercially available reagents (Baker Chemical Co.). Solid sodium and potassium hydroxides were obtained from Baker Chemical Co., and their solutions were prepared gravimetrically.

Aqueous solutions of the compounds studied here containing dissolved oxygen showed no increase in their fluorescence quantum yields after outgassing with pure nitrogen gas. However, when these molecules were dissolved in more nonpolar solvents, such as ethanol, increased fluorescence yields were found after outgassing with dry nitrogen gas. However, there were no changes in the shapes of the emission bands after outgassing any of the solvents. Thus, fluorescence quantum yields in organic solvents were measured only after outgassing to maximum quantum yield with ultrapure dry nitrogen gas (Air Products, Baltimore, Md.), whereas energies and bandwidths of emission were determined on air-equilibrated solutions.

Organic Syntheses and Purifications. The following compounds were used in this study.

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[1] Contribution No. 644 from the McCollum–Pratt Institute. This research was supported by NIH Grant No. G. M. 11632. A preliminary account of this work has appeared in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969.

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