one deuterium atom in the 4-position of the coumarin ring.

Based on the results obtained with enol acetate 6, we propose that the photoisomerization of 1 → 2 proceeds via photoreaction of the enol (or enolate) tautomer of 1. To test this conclusion, we have studied the photochemistry of the corresponding enolate anion. Addition of sodium methoxide to a methanolic solution of 1 caused a very rapid change in the absorption spectrum with new maxima appearing at 314 and 239 nm. The extinction coefficients for these new maxima were on the order of $\epsilon \sim 10^4$. The sodium enolate of 1 could also be generated by addition of sodium methoxide to solutions of 6. When a thoroughly deareated methanolic solution of 6 was first treated with sodium methoxide and then irradiated with light of wavelength >300 nm, an extremely rapid and clean conversion to methyl 3-(2-hydroxyphenyl)-3-phenylpropionate (10) was observed. The identity of 10 was
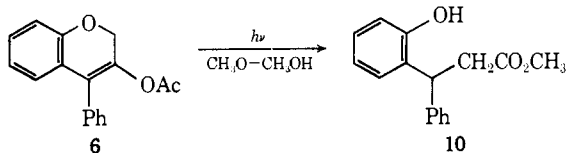


determined by its straightforward spectral characteristics as well as its facile conversion to 2 on heating. Structure 10 is not the primary photoproduct of the reaction but rather is derived by attack of methoxide on dihydrocoumarin 2. A control experiment clearly demonstrated that when trace amounts of sodium methoxide were added to a methanolic solution of 2, ester 10 was formed in quantitative yield.

In addition to being a cleaner reaction than that observed with either 1 or 6, the base-catalyzed photolysis of 6 proceeded with a much higher quantum efficiency (i.e., $\Phi(6{\rightarrow}1)^{\text{base}} = 0.24$, $\Phi(1{\rightarrow}2) = 0.007$). The difference in reaction efficiency can be readily attributed to the high concentration of the reactive enolate tautomer present in solution during the photolysis of 6 in basic methanol. Further work on the photochemistry of carbonyl compounds which proceed through the enol form is in progress and will be reported at a later date.

(15) Alfred P. Sloan Foundation Fellow, 1968–1972; NATO Senior Postdoctoral Fellow, 1973.
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## Molecular Structure of an N-Substituted Azonine. Demonstration of Polyenic Character in a Member of This Class of Compounds

*Sir:*

Among π-excessive heteromonocycles, the 10π-electron heteronins (1) are deemed potentially aromatic by Hückel's $4n + 2$ rule. A group of heteronins[1] has recently been synthesized and studied by Anastassiou and collaborators.[2–4] The thermodynamic stability and spectral characteristics suggest that some of the N-substituted azonines (1; X = NR) be considered polyenic,[5] and it is expected that reducing the availability of the electron pair on the heteroatom will result in a gradual transition from aromatic to polyenic character. In an effort to elucidate the detailed molecular geometry of the nitrogen-containing or azonine nine-membered ring, we have carried out a three-dimensional X-ray study on N-(N,N-dimethylcarbamyl)azonine (2).[1]
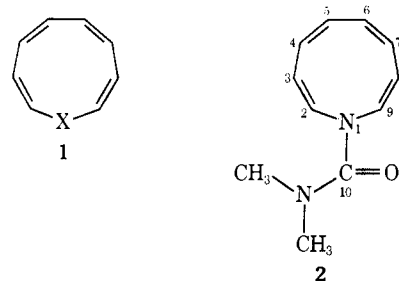


The crystals of 2 belong to the monoclinic system with $a = 11.119\,(3)$, $b = 6.499\,(1)$, $c = 16.617\,(5)$ Å, and $\beta = 118°14'\,(1')$. There are four molecules of $C_{11}H_{14}N_2O$ in the unit cell, and the space group is $P2_1/c$. A total of 853 independent nonzero ($2\theta \leq 90°$) values was measured on a Picker FACS-1 diffractometer using Cu $K\alpha$ radiation. The crystals are quite stable at 0° but decompose over a period of a few days at room temperature.[6] The structure was solved by the symbolic addition method and has been refined by full-matrix least-squares procedures to an $R$ factor of 0.061 on all observed data. Anisotropic temperature factors were included for the carbon, nitrogen, and oxygen atoms, while the hydrogen atoms were refined with isotropic temperature factors. See paragraph at end of paper regarding supplementary material.

The molecular structure of 2 in the crystal is shown in Figure 1. Some molecular dimensions are shown in Figure 2. The molecule is significantly nonplanar and exists in a boat conformation relative to the reasonably good plane (maximum deviation 0.046 Å) through the four atoms C(2), C(3), C(6), and C(7), with C(4), C(5), C(8), C(9), and N(1) lying 0.918, 0.955, 0.826, 1.352, and 1.178 Å, respectively, from this plane. The double bond lengths, 1.301–1.334 Å, are definitely localized at C(2)–C(3), C(4)–C(5), C(6)–C(7), and C(8)–C(9), while the C(3)–C(4), C(5)–C(6), and C(7)–C(8) lengths (1.460–1.469 Å) are in the range expected for $C(sp^2)$–$C(sp^2)$ single bonds.[7–9] This bond alternation is in contrast to

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(5) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, 1133 (1970).
(6) Two crystals were used to accumulate the data. The first crystal was discarded after the standards fell to 75% of their initial value and the second when they fell to 85% of their initial value. We did not attempt to collect data beyond this point as we found that the high order reflections began to lose intensity quite soon after a crystal was irradiated and thus we felt that little increase in precision would be obtained due to crystal decomposition and the uncertainties in scaling additional decomposing crystals.
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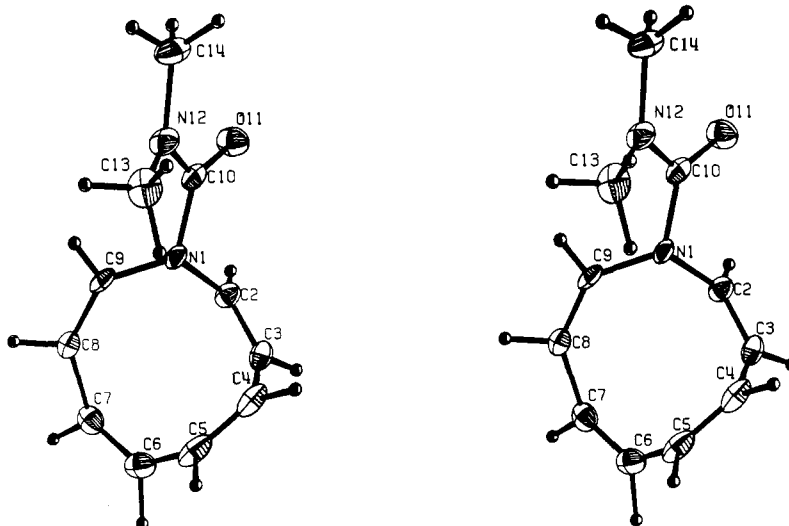
Figure 1. Stereoscopic drawing of a single molecule of 2. The probability level of the ellipsoids is 25%.

the situation believed to exist in the parent 1$H$-azonine,[10] which has been classified as aromatic on the basis of its nmr and uv spectra. Octamethylcyclooctatetraene,[7] [16]annulene,[8] and a derivative of 1$H$-azepine[9] exhibited similar patterns of bond alternation. The endocyclic bond angles at C(8), C(9), and N(1) are all much greater than usual. A Dreiding model of the azonine ring reveals a rigid structure with considerable strain in the C(8)–C(9)–N(1) region of the molecule. Apparently this strain is partially offset by considerable bond angle deformation at the C(8)–C(9) double bond. The ring nitrogen atom lies 0.181 Å from the plane of its three-bonded neighbors suggesting hybridization intermediate between sp$^2$ and sp$^3$. Inspection of Figure 1 shows that the p orbital of the nitrogen atom (assuming sp$^2$ hybridization) will be in a position to conjugate with the $\pi$-system of the C(8)–C(9) bond (the C(8)–C(9)–N(1)–C(10) torsion angle is 173°) rather than with that of the C(2)–C(3) bond. Such an effect could be responsible for the N(1)–C(9) bond (1.391 (9) Å) being significantly shorter than the N(1)–C(2) bond (1.433 (8) Å) or than the N(1)–C(10) bond (1.424 (8) Å). The torsion angles in the ring are listed in Table I.

Table I. Torsion Angles in the Azonine Ring

| | $\tau$, deg | | $\tau$, deg |
|---|---|---|---|
| C(9)–N(1)–C(2)–C(3) | −82 | C(5)–C(6)–C(7)–C(8) | −7 |
| N(1)–C(2)–C(3)–C(4) | 4 | C(6)–C(7)–C(8)–C(9) | 47 |
| C(2)–C(3)–C(4)–C(5) | 80 | C(7)–C(8)–C(9)–N(1) | 8 |
| C(3)–C(4)–C(5)–C(6) | 1 | C(8)–C(9)–N(1)–C(2) | 19 |
| C(4)–C(5)–C(6)–C(7) | −67 | | |

An important aspect of the structure is the large twist of the exocyclic carbonyl group about the N(1)–C(10) bond; the C(2)–N(1)–C(10)–O(11) and C(9)–N(1)–C(10)–O(11) torsion angles are 24.9 and −131.3°, respectively. These values, together with the relatively

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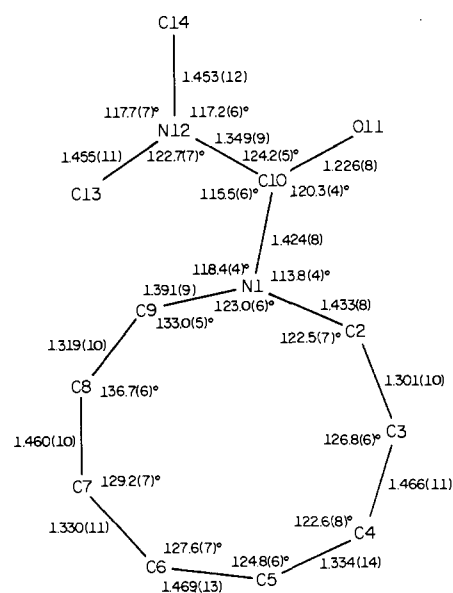(10) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970).



Figure 2. Bond lengths and angles in the molecule of 2.

long N(1)–C(10) bond and the significant nonplanarity at N(1), suggest incomplete $\pi$-electron delocalization from N(1) to the exocyclic carbonyl group. If the $\pi$-electrons from nitrogen were completely available for delocalization throughout the nine-membered ring, then a 10$\pi$-system would exist and Hückel's rule would predict a planar structure with effectively equal C–C bond lengths. In view of this well-defined example of essentially complete bond alternation with considerable nonplanarity observed in 2, further structural evidence would be desirable to clarify the factors governing questions of planarity and bond alternation in this series of compounds.

Supplementary Material Available. A listing of structure factor amplitudes and atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche

(105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-1636.

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## Copper Complexes of Dopa. Control of the Bonding Mode

*Sir:*

Catecholamines and catecholamino acids are important intermediates in many neurological and other biochemical reactions.[1] The coordination chemistry of these compounds is complicated by their ability to act as ambidentate or bridging ligands.[2,3] Thus, for example, L-dopa (3,4-dihydroxyphenylalanine), used in the treatment of Parkinson's disease, can coordinate as a bidentate ligand through either the catecholate (O, O) or the amino acid (O, N) end of the molecule. Furthermore, it is known that divalent transition metal ions such as Mn,[4] Cu,[5] and possibly Ni[6] also have biologically significant roles which in part involve interactions with the catechol amines. It thus seemed appropriate to investigate in greater detail the nature of the coordination compounds formed between these ligands and metal ions. In this paper we report what we believe to be the first isolated complexes of dopa with the transition metal ion Cu and discuss those conditions which lead to the different modes of binding observed.

When $Cu^{2+}$ and dopa in 1:2 mole ratio are placed in water and aqueous ammonia is added to bring the pH to 5.0, a blue-purple complex can be isolated from the solution.[7] This complex is sparingly soluble in water and methanol but quite soluble in DMF and DMSO. In DMF its electronic spectrum exhibits a peak at 16,130 cm$^{-1}$ ($\epsilon$ = 97). The complex in DMSO can be reduced in two reversible one-electron steps by cyclic voltametric techniques at potentials of −0.04 and −0.53 V vs. sce.[8] These results can be compared with

the known complex $Cu(tryptophan)_2$[9] wherein a peak at 16,130 cm$^{-1}$ ($\epsilon$ = 85) and potentials of −0.04 and −0.53 V are found. Since the tryptophan complex almost certainly binds through its amino acid end, we conclude that this blue-purple complex involves bonding of dopa through the amine carboxylate linkage. The infrared spectrum further substantiates this, showing the absorptions characteristic of free catechol OH's. These data taken together with elemental analysis[7] lead us to formulate the isolated complex as $Cu(O,N\text{-}dopa)_2 \cdot H_2O$, containing I, wherein the electronic spec-



trum and epr properties[10] are consistent with a trans square planar coordination geometry

When the pH of the solution is further raised by addition of ammonia (still under nitrogen), complex I redissolves and the solution color changes to olive green. If a cold 1:1 mixture of ethyl acetate and isopropyl alcohol is added to the 1:2 Cu–dopa solution at pH 9.5 an olive green solid can be obtained.[11] This solid is extremely soluble in water but insoluble in methanol. In water it displays absorption bands at 15,800 ($\epsilon$ = 62) and 23,000 cm$^{-1}$ ($\epsilon$ = 100), and reversible voltametric waves at −0.15 and −0.30 V. It lacks the infrared bands characteristic of free catechol. The data are to be compared with the $Cu(catecholate)_2{}^{2-}$ complex[12] which absorbs at 14,900 ($\epsilon$ = 70) and 24,800 cm$^{-1}$ ($\epsilon$ = 210) and shows voltametric waves at −0.15 and −0.39 V.[8] These comparisons together with elemental analysis[11] lead us to formulate this complex as $(NH_4)_2Cu(O,O\text{-}dopa)_2 \cdot 4H_2O$, with a square planar $CuO_4$ coordination sphere, II.

When II is dissolved in neutral unbuffered water the pH is found to be 6.4 and the spectrum indicates the presence of exclusively the complex II. This indicates



that even below the nominal physiological pH range the O,O-bound form is a viable species (at least kinetically inert over the period of a few hours). On the other hand simply mixing 2:1, dopa–$Cu^{2+}$ at pH 7.3 does not give 100% formation of the O,O complex

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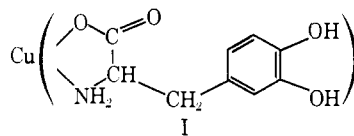(4) U. Meiri and R. Rahamimoff, *Science*, 176, 308 (1972).

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(7) All operations are carried out under nitrogen. $CuCl_2 \cdot 2H_2O$ (0.26 g) is dissolved in 2 ml of $H_2O$, and *d,l*-dopa (0.55 g) suspended in 3 ml of $H_2O$ is added to the solution. The pH is brought up to 5 by slowly adding dilute ammonia over 45 min. The mixture is stirred for an additional 30 min and the blue-purple solid is collected by filtration, washed with water, methanol, and *n*-pentane, and dried under vacuum, decomposition point 220–223°. *Anal.* Calcd for $Cu(C_9H_{10}NO_4)_2 \cdot H_2O$: C, 45.57; H, 4.64; N, 5.90. Found: C, 46.08, H, 4.39; N, 5.66.

(8) Voltametric methods utilized a dropping Hg electrode with Pt as counter and sce as reference electrodes. Tetraethylammonium perchlorate (0.1 *M*) was supporting electrolyte in DMSO while KCl was used in water. Complex concentration was roughly $10^{-3}$ *M*.
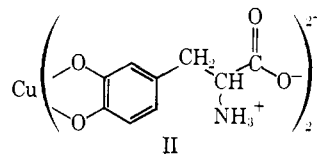
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(11) All operations are carried out under nitrogen. A solution of $CuCl_2 \cdot 2H_2O$ (0.26 g) in 0.4 ml of $H_2O$ plus 0.73 ml of aqueous $NH_3$ is added to a suspension of 0.55 g of *d,l*-dopa in 0.5 ml of $H_2O$ and stirred for 30 min whereupon the pH is 9.5. A small amount of unreacted dopa is filtered off and the olive green filtrate is cooled in ice. Ice cold 1:1 ethyl acetate–isopropyl alcohol is added slowly and the solution is then decanted from the resulting olive green oil. The oil is washed with 1:1 ethyl acetate–isopropyl alcohol and then vigorously scratched in the presence of the ice cold liquid. The resultant solid is filtered, washed with 1:1 ethyl acetate–isopropyl alcohol, isopropyl alcohol, and ether and dried under vacuum, decomposition point 124°. *Anal.* Calcd for $(NH_4)_2Cu(C_9H_9NO_4)_2 \cdot 4H_2O$: C, 38.47; H, 6.10; N, 9.97. Found: C, 38.97; H, 5.93; N, 9.88.

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