

# *N*-Allylaldiminium Cation as $\pi$ -Ligand: Synthesis and Crystal Structure of $[(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{CuX}_2$ ( $\text{X} = \text{Cl}, \text{Br}$ ) Compounds

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**Abstract**—The  $[(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{CuX}_2$  [ $\text{X} = \text{Cl}$  (**I**) or  $\text{Br}$  (**II**)] complexes were prepared by an electrochemical synthesis from *N*-allyl-4-(*N,N*-dimethylamino)benzaldehyde (ADBA) and ethanol solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{CuBr}_2$ , respectively, and their crystal structures were determined [DARCh diffractometer,  $\text{MoK}_\alpha$  radiation, 989 ( $F \geq 4\sigma(F)$ ) and 965 ( $F \geq 3\sigma(F)$ ) reflections,  $R = 0.035$  and  $0.053$  for **I** and **II**, respectively]. The compounds are isostructural, space group  $P2_1/a$ ,  $Z = 4$ . Unit cell parameters are  $a = 27.74(1)$ ,  $b = 7.253(3)$ ,  $c = 6.852(6)$  Å,  $\beta = 91.05(5)^\circ$  for **I** and  $a = 28.175(8)$ ,  $b = 7.392(2)$ ,  $c = 7.000(2)$  Å,  $\beta = 90.18(3)^\circ$  for **II**. The copper coordination polyhedron is a trigonal pyramid formed by three halogen atoms and a C=C bond. The structure is built from the centrosymmetric  $\text{Cu}_2\text{X}_4(\text{ADBAH})_2$  dimers joined together by the hydrogen bonds  $\text{C}-\text{H} \cdots \text{X}$  [ $\text{H} \cdots \text{Cl}$  2.85–2.87(8) Å]. The geometry of the  $\text{ADBAH}^+$  cation is indicative of its partial transformation from the aromatic to quinoid form, owing to the stabilization of the aldiminium cation under the +*M*-effect of the  $(\text{CH}_3)_2\text{N}$  group. Net atomic charges are calculated for **I**.

Previous studies have shown that allyl- and diallylamine are capable of being  $\pi$ -coordinated to copper(I) both as neutral species and in nitrogen-protonated forms [1, 2]. Earlier, we prepared and structurally characterized the first copper(I)  $\pi, \sigma$ -complexes with *N*-allylaldimines and studied their structures [3], but attempts at obtaining ionic copper(I)  $\pi$ -complexes with nitrogen-protonated Schiff bases resulted, because of hydrolysis, in the known copper(I) allylammonium  $\pi$ -complexes, e.g.,  $[\text{C}_3\text{H}_5\text{NH}_3]\text{CuCl}_2$  [4]. The reason was that iminium salts were rapidly hydrolyzed, so that they should be prepared under strictly anhydrous conditions [5]. That is why the more stable *N*-allyl-4-(*N,N*-dimethylamino)benzaliminium cation ( $\text{ADBAH}^+$ ) was used as a ligand in the synthesis of the copper(I)  $\pi$ -complexes with *N*-allyl-substituted iminium salts in this work. The crystal  $\pi$ -complexes  $[\text{ADBAH}]\text{CuX}_2$  [ $\text{X} = \text{Cl}$  (**I**) and  $\text{Br}$  (**II**)] were prepared and structurally characterized.

## EXPERIMENTAL

The ADBA ligand was prepared by the condensation of allylamine with 4-(*N,N*-dimethylamino)benzaldehyde [6]. High-quality single crystals of **I** and **II** were synthesized by an ( $U = 0.3$  V) electrochemical reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$  on copper electrodes in ethanol solutions containing ADBA and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{CuBr}_2$ , respectively. Acid was not introduced into the reaction mixture. Rather air-stable crystals **I** and **II** grew as monoclinic prisms in a day and retained their stability during the X-ray experiment.

After the preliminary photographic study, the structures were solved using the diffraction arrays collected on a DARCh single-crystal diffractometer; intensities of reflection were corrected for the Lorentz and polarization effects.

Crystallographic and intensity collection data are reported in Table 1.

The structures were solved by direct methods; light and H atoms were located from difference Fourier syntheses. Full-matrix anisotropic refinement of all non-hydrogen atoms (isotropic for hydrogen atoms) and absorption correction (DIFABS program) were carried out using the CSD program package [7].

Atomic coordinates and thermal parameters for **I** and **II** are given in Table 2, and bond lengths, bond angles, and torsion angles for **I** and **II** are listed in Table 3.

## RESULTS AND DISCUSSION

Compounds **I** and **II** are isostructural. The copper atom has a trigonal-pyramidal environment comprised of three halogen atoms and the C=C bond in one of the equatorial positions. The modest offset of the copper atom from the plane of equatorial ligands (0.29 Å for **I** and 0.37 Å for **II**) is consistent with the observed axial elongation of  $\text{Cu}-\text{X}(2)$  [2.733(5) Å in **I** and 2.814(4) Å in **II**] [1]. The  $\tau$  angle between the plane of equatorial ligands and the C=C bond is equal to  $14^\circ$  in **I** and  $15^\circ$  in **II**. The structures are built from the centrosymmetric  $\text{Cu}_2\text{X}_4(\text{ADBAH})_2$  dimers formed due to the elongated Cu–X contacts. The ligand cation is coordinated to cop-

**Table 1.** Crystallographic and intensity collection data for **I** and **II**

Parameter	<b>I</b>	<b>II</b>
<i>M</i>	323.7	412.6
<i>F</i> (000)	664	808
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> , Å	27.74(1)	28.175(8)
<i>b</i> , Å	7.253(3)	7.392(2)
<i>c</i> , Å	6.852(6)	7.000(2)
β, deg	91.05(5)	90.18(3)
<i>V</i> , Å <sup>3</sup>	1379(2)	1458(1)
<i>Z</i>	4	4
ρ(calcd), g/cm <sup>3</sup>	1.560(3)	1.880 (2)
μ <sub>Mo</sub> , cm <sup>-1</sup>	20.07	73.40
Radiation	MoK <sub>α</sub>	MoK <sub>α</sub>
Diffractionmeter	DARCh	DARCh
Scan mode	θ/2θ	θ/2θ
Number of reflections:		
measured	1144	1158
unique with <i>F</i> ≥ <i>nσ</i> ( <i>F</i> )	989	965
<i>n</i>	4	3
2θ <sub>max</sub> , deg	51.68	53.01
Number of refined parameters	222	222
<i>R</i>	0.035	0.053
<i>R</i> <sub>w</sub>	0.036	0.054
Weight scheme	[σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> + 0.0008 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	[σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> + 0.0022 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>
GOOF	1.08	1.14

per(I) only through the C=C bond. The hydrogen atom at the aldimine nitrogen atom prevents Cu–N interaction and forms a N(1)–H(N)···X hydrogen bond in the dimer. Each dimer is associated with four analogous dimers by the hydrogen bonds C(11)–H(11.3)···X(2) and C(12)–H(12.3)···X(1), thus forming layers arranged in the (001) plane (figure) and joined together by the van der Waals forces. The parameters of selected hydrogen bonds are given in Table 4.

Zwitterionic complexes **I** and **II** are structurally similar to the copper(I) chloride π-complex with diallylammonium [(CH<sub>2</sub>=CH–CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]CuCl<sub>2</sub> (**III**) [8], in which the ligand cation furnishes only one C=C bond for the coordination to the Cu atom. Structure **III** has the same symmetry. It is also composed of the dimeric inorganic Cu<sub>2</sub>Cl<sub>4</sub><sup>2-</sup> fragments, and the conformation of the coordinated allyl group [the C(1)=C(2)–C(3)–N angle is equal to 157.7°] is the same as in structures **I**

(156.7°) and **II** (152.7°). Curiously, the replacement of Cl by Br in **III** results in an anisostructural [(CH<sub>2</sub>=CH–CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]CuBr<sub>2</sub> compound [9]. Although its structure contains the Cu<sub>2</sub>Br<sub>4</sub><sup>2-</sup> anions, its unit cell is base-centered, and the C(1)C(2)C(3)N torsion angle in the coordinated allyl group is equal to 101.1°. Two copper(I) halide π-complexes with allylammonium, [CH<sub>2</sub>=CH–CH<sub>2</sub>–NH<sub>3</sub>]CuCl<sub>2</sub> (92.2°) and [CH<sub>2</sub>=CH–CH<sub>2</sub>–NH<sub>3</sub>]CuBr<sub>2</sub> (102.3° and 153.6° in the two independent allylammonium cations), both containing inorganic fragment Cu<sub>2</sub>X<sub>4</sub><sup>2-</sup>, are also anisostructural [4]. Therefore, the replacement of halogen atoms in this group of π-complexes is a crucial structure-changing factor. This differentiates them from isostructural complexes **I** and **II** and evidences the greater role of the ADBAH<sup>+</sup> cation in structure formation.

**Table 2.** Atomic coordinates\* and thermal parameters\*\* for structures **I** and **II**

Atom	x	y	z	B, Å <sup>2</sup>	Atom	x	y	z	B, Å <sup>2</sup>
Cu	0.47303(3)	0.7099(1)	-0.0166(1)	3.14(2)	H(N)	0.570(2)	0.657(7)	0.260(8)	2(1)
	0.47326(8)	0.7078(4)	-0.0120(3)	3.30(7)		0.576(6)	0.65(2)	0.25(2)	4(4)
Cl(1)	0.41882(6)	0.7104(3)	-0.2703(2)	3.23(5)	H(1.1)	0.425(3)	0.75(1)	0.25(1)	5(2)
Br(1)	0.41686(7)	0.7249(3)	-0.2707(2)	3.06(5)	H(1.2)	0.418(5)	0.79(2)	0.25(2)	1(4)
Cl(2)	0.54809(6)	0.6325(3)	-0.1252(2)	3.00(5)		0.427(2)	0.952(9)	0.154(9)	2(2)
Br(2)	0.55163(7)	0.6342(3)	-0.1329(3)	2.89(5)	0.431(4)	0.94(2)	0.16(1)	1(3)	
N(1)	0.5655(2)	0.7251(9)	0.3399(8)	3.4(2)	H(2.1)	0.508(2)	0.972(9)	0.184(9)	5(2)
	0.5652(5)	0.724(2)	0.331(2)	2.7(4)		0.509(6)	0.95(2)	0.19(2)	3(4)
N(2)	0.7939(2)	0.8378(8)	0.1978(9)	3.9(2)	H(3.1)	0.504(2)	0.640(8)	0.392(7)	1(1)
	0.7921(6)	0.821(2)	0.207(2)	3.8(5)		0.505(5)	0.64(2)	0.40(2)	4(3)
C(1)	0.4403(3)	0.853(1)	0.205(1)	3.4(2)	H(3.2)	0.515(2)	0.82(1)	0.51(1)	5(2)
	0.4433(6)	0.854(2)	0.201(2)	2.2(4)		0.509(7)	0.83(3)	0.50(3)	8(6)
C(2)	0.4890(2)	0.8626(9)	0.2364(9)	2.6(2)	H(4.1)	0.591(2)	0.926(8)	0.495(8)	4(1)
	0.4879(6)	0.865(2)	0.240(2)	2.3(5)		0.589(6)	0.92(2)	0.50(2)	6(5)
C(3)	0.5144(3)	0.748(1)	0.386(1)	3.2(3)	H(6.1)	0.671(2)	0.030(7)	0.512(8)	3(1)
	0.5142(7)	0.744(2)	0.377(2)	3.3(6)		0.671(5)	0.01(2)	0.53(2)	2(3)
C(4)	0.5990(3)	0.829(1)	0.401(1)	3.1(2)	H(7.1)	0.748(2)	0.04(1)	0.46(1)	7(2)
	0.5997(6)	0.814(2)	0.409(2)	2.7(5)		0.740(8)	0.98(3)	0.45(3)	3(7)
C(5)	0.6483(2)	0.823(1)	0.348(1)	3.1(2)	H(9.1)	0.723(2)	0.634(8)	0.068(8)	2(1)
	0.6475(7)	0.814(2)	0.351(2)	2.6(5)		0.723(5)	0.64(2)	0.09(2)	1(3)
C(6)	0.6815(3)	0.937(1)	0.444(1)	4.1(2)	H(10.1)	0.646(2)	0.642(7)	0.158(7)	1(1)
	0.6798(6)	0.919(3)	0.447(3)	3.7(6)		0.647(6)	0.63(2)	0.15(2)	2(4)
C(7)	0.7292(3)	0.942(1)	0.401(1)	4.0(2)	H(11.1)	0.817(3)	0.058(9)	0.31(1)	3(2)
	0.7256(9)	0.921(3)	0.403(3)	4.9(7)		0.818(5)	0.06(2)	0.31(2)	4(3)
C(8)	0.7471(2)	0.831(1)	0.250(1)	3.4(2)	H(11.2)	0.836(3)	0.89(1)	0.44(1)	9(3)
	0.7448(7)	0.808(3)	0.256(3)	3.3(5)		0.829(8)	0.91(3)	0.42(3)	11(7)
C(9)	0.7137(3)	0.711(1)	0.156(1)	4.0(2)	H(11.3)	0.861(3)	0.98(1)	0.23(1)	11(3)
	0.7122(9)	0.702(3)	0.164(3)	5.0(8)		0.85(1)	0.93(4)	0.22(4)	13(9)
C(10)	0.6668(3)	0.709(1)	0.202(1)	3.7(2)	H(12.1)	0.809(3)	0.62(1)	0.07(1)	8(4)
	0.6655(8)	0.697(3)	0.210(3)	3.7(6)		0.812(6)	0.61(2)	0.09(2)	6(5)
C(11)	0.8282(3)	0.955(2)	0.300(2)	5.2(3)	H(12.2)	0.788(3)	0.74(1)	-0.08(1)	6(2)
	0.8272(9)	0.932(3)	0.301(3)	6.6(9)		0.787(6)	0.74(2)	-0.07(2)	4(4)
C(12)	0.8114(3)	0.726(2)	0.042(2)	5.5(4)	H(12.3)	0.847(2)	0.754(8)	0.02(1)	5(2)
	0.8093(8)	0.709(4)	0.055(3)	7.0(9)		0.842(6)	0.77(2)	0.02(2)	5(4)

\* Atomic coordinates and thermal parameters in the upper and lower rows correspond to compounds **I** and **II**, respectively.

\*\* For non-hydrogen atoms  $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \hat{a}_i \hat{a}_j$ .

The  $\pi$ -coordinated C=C bond effectively interacts with the copper atom in structure **I** [Cu–*m*(1,2) 1.96(1) Å, C(1)CuC(2) 38.3(3)°] and is elongated to 1.36(2) Å. By contrast, the Cu–*m*(1,2) distance in structure **II** is elongated to 1.99(2) Å, and the apparent shortening of the double bond to 1.29(3) Å [the C(1)CuC(2) angle is 35.8(6)°] results in a noticeable difference (0.12 Å) between the Cu–C(1) and Cu–C(2) bond

lengths (Table 3). A similar, though more pronounced shortening of a partially disordered C=C bond [C(1)=C(2) 1.21(1) Å] is found in structure **III** and presumably explained by the involvement of the hydrogen bonds (=C)–H···X in the formation of the polar Cu<sup>δ+</sup>...C<sup>δ-</sup>–H<sup>δ+</sup>...X<sup>δ-</sup> contacts. This enhances electrostatic interactions in the Cu(I) coordination polyhedron and the disorder of the C=C bond [8].

**Table 3.** Bond lengths\*, bond angles ( $\omega$ ), and torsion angles\*\* ( $\varphi$ ) in structures **I** and **II**

Bond	<i>d</i> , Å		Angle	$\omega$ , deg	
	<b>I</b>	<b>II</b>		<b>I</b>	<b>II</b>
Cu–X(1)	2.28(1)	2.409(6)	X(1)CuX(2)	110.1(4)	110.4(2)
Cu–X(2)	2.29(1)	2.429(8)	X(1)CuX(2)'	97.5(3)	98.8(2)
Cu–X(2)'	2.733(5)	2.814(4)	X(1)Cum(1,2)	122.9(5)	120.9(5)
Cu–C(1)	2.06(1)	2.03(2)	X(2)CuX(2)'	95.4(3)	98.7(2)
Cu–C(2)	2.097(9)	2.15(2)	X(2)Cum(1,2)	121.6(5)	120.8(5)
Cu– <i>m</i> (1,2)	1.96(1)	1.99(2)	X(2)'Cum(1,2)	100.0(4)	100.6(5)
			C(1)CuC(2)	38.3(3)	35.8(6)
C(1)–C(2)	1.36(2)	1.29(3)	C(2)C(1)H(1.1)	117(5)	137(10)
C(1)–H(1.1)	0.92(8)	0.9(2)	C(2)C(1)H(1.2)	116(4)	117(8)
C(1)–H(1.2)	0.87(6)	0.8(1)	H(1.1)C(1)H(1.2)	126(7)	101**
C(2)–C(3)	1.49(1)	1.50(3)	C(1)C(2)C(3)	122.4(9)	125(2)
C(2)–H(2.1)	1.02(6)	1.0(2)	C(1)C(2)H(2.1)	120(4)	125(10)
			C(3)C(2)H(2.1)	116(4)	110(10)
C(3)–N(1)	1.47(2)	1.48(3)	C(2)C(3)N(1)	111.0(8)	113(2)
C(3)–H(3.1)	0.83(6)	0.8(1)	C(2)C(3)H(3.1)	114(4)	120(10)
C(3)–H(3.2)	1.00(8)	1.1(2)	C(2)C(3)H(3.2)	107(4)	97
			N(1)C(3)H(3.1)	104(4)	106(10)
			N(1)C(3)H(3.2)	104(4)	112
			H(3.1)C(3)H(3.2)	117(6)	109
N(1)–C(4)	1.26(1)	1.29(2)	C(3)N(1)C(4)	124.8(9)	126(2)
N(1)–H(N)	0.75(5)	0.8(2)	C(3)N(1)H(N)	113(4)	124
			C(4)N(1)H(N)	121(4)	110
C(4)–C(5)	1.42(2)	1.41(3)	N(1)C(4)C(5)	127.0(9)	127(2)
C(4)–H(4.1)	0.98(6)	1.0(2)	N(1)C(4)H(4.1)	119(4)	114(10)
			C(5)C(4)H(4.1)	115(4)	117(10)
C(5)–C(6)	1.40(1)	1.37(3)	C(4)C(5)C(6)	119.3(9)	120(2)
C(5)–C(10)	1.40(1)	1.41(3)	C(4)C(5)C(10)	124.8(9)	123(2)
			C(6)C(5)C(10)	116.0(9)	117(2)
C(6)–C(7)	1.36(2)	1.33(3)	C(5)C(6)C(7)	123.4(9)	123(2)
C(6)–H(6.1)	0.88(5)	0.9(1)	C(5)C(6)H(6.1)	120(4)	123(9)
			C(7)C(6)H(6.1)	115(4)	114(9)
C(7)–C(8)	1.41(1)	1.43(3)	C(6)C(7)C(8)	120.0(9)	122(2)
C(7)–H(7.1)	0.99(7)	0.7(2)	C(6)C(7)H(7.1)	116(4)	118
			C(8)C(7)H(7.1)	122(4)	120
C(8)–C(9)	1.42(1)	1.37(3)	C(7)C(8)C(9)	116.6(9)	115(2)
C(8)–N(2)	1.36(1)	1.38(3)	C(7)C(8)N(2)	121.7(9)	120(2)
			N(2)C(8)C(9)	121.6(9)	125(2)
C(9)–C(10)	1.35(2)	1.36(3)	C(8)C(9)C(10)	121.8(9)	124(2)
C(9)–H(9.1)	0.87(6)	0.8(1)	C(8)C(9)H(9.1)	120(4)	114
			C(10)C(9)H(9.1)	118(4)	122
C(10)–H(10.1)	0.81(5)	0.8(2)	C(9)C(10)C(5)	122.1(9)	120(2)
			C(9)C(10)H(10.1)	127(3)	121
			C(5)C(10)H(10.1)	111(3)	120

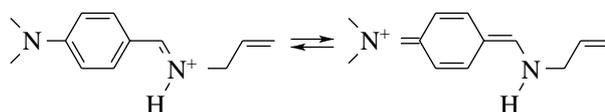
**Table 3.** (Contd.)

Bond	<i>d</i> , Å		Angle	$\omega$ , deg	
	I	II		I	II
N(2)–C(11)	1.45(2)	1.44(3)	C(8)N(2)C(11)	121.3(9)	126(2)
N(2)–C(12)	1.43(2)	1.44(3)	C(8)N(2)C(12)	121.0(9)	118(2)
			C(11)N(2)C(12)	118(1)	116(2)
C(11)–H(11.1)	0.81(7)	1.0(2)	N(2)C(11)H(11.1)	109(5)	114(8)
C(11)–H(11.2)	1.1(1)	0.9(2)	N(2)C(11)H(11.2)	107(5)	112
C(11)–H(11.3)	1.07(8)	0.9(3)	N(2)C(11)H(11.3)	115(5)	105
			H(11.1)C(11)H(11.2)	114(8)	98
			H(11.1)C(11)H(11.3)	103(7)	106
			H(11.2)C(11)H(11.3)	109(7)	122
C(12)–H(12.1)	0.8(1)	0.74(2)	N(2)C(12)H(12.1)	110(7)	111
C(12)–H(12.2)	1.04(9)	1.1(2)	N(2)C(12)H(12.2)	110(5)	106(8)
C(12)–H(12.3)	1.01(7)	1.1(2)	N(2)C(12)H(12.3)	109(4)	102(8)
			H(12.1)C(12)H(12.2)	100(9)	119
			H(12.1)C(12)H(12.3)	109(8)	113
			H(12.2)C(12)H(12.3)	118(6)	104
Angle	$\phi$ , deg		Angle	$\phi$ , deg	
	I	II		I	II
CuX(2)Cu'X(1)	100.0	102.9	C(7)C(8)C(9)C(10)	3.1	1.6
CuC(1)C(2)C(3)	–102.8	–95.3	C(7)C(8)N(2)C(11)	2.0	4.9
C(1)C(2)C(3)N(1)	156.7	152.7	C(7)C(8)N(2)C(12)	–179.3	–178.3
C(2)C(3)N(1)C(4)	–91.8	–97.7	N(2)C(8)C(9)C(10)	–177.3	–177.2
C(3)N(1)C(4)C(5)	174.4	171.2	C(8)C(9)C(10)C(5)	1.1	3.8
N(1)C(4)C(5)C(6)	–173.8	–178.7	C(9)C(8)N(2)C(11)	177.5	179.8
N(1)C(4)C(5)C(10)	–6.6	–7.7	C(9)C(8)N(2)C(12)	–1.1	–2.9
C(4)C(5)C(6)C(7)	179.4	177.8	C(9)C(10)C(5)C(4)	–179.0	–178.5
C(5)C(6)C(7)C(8)	–1.8	–1.8	C(9)C(10)C(5)C(6)	–0.7	–4.7
C(6)C(7)C(8)C(9)	–3.4	–0.5	C(10)C(5)C(6)C(7)	–0.3	–3.8
C(6)C(7)C(8)N(2)	–177.0	–176.3			

\* X corresponds to Cl in structure **I** and Br in structure **II**; *m*(1,2) is the midpoint of the multiple C(1)=C(2) bond.

\*\* If the deviation for the  $\omega$  angle is not indicated, it is greater than 10°.

An analysis of the geometry of the ADBAH<sup>+</sup> cation in structures **I** and **II** reveals that it is partially transformed from an aromatic to quinoid form. This is evidenced by the redistribution of the bond lengths in the aromatic ring and by the presence of the short C(4)–C(5) and C(8)–N(2) distances (Table 3). Such a behavior is in agreement with the +*M*-effect of the (CH<sub>3</sub>)<sub>2</sub>N group. The latter takes on a part of the positive charge and thus stabilizes the aldiminium cation. The canonical resonance forms can be represented as follows:



To reveal how the positive charge is stabilized on the ADBAH<sup>+</sup> cation, atomic charges in structure **I** were calculated using the HYPERCHEM program and the modified version of the iterative SCF LCAO MO method in the INDO approximation [10] (ZINDO/1). The structure of the complex was represented by a cluster comprised of 340 atoms (900 initial AOs were taken

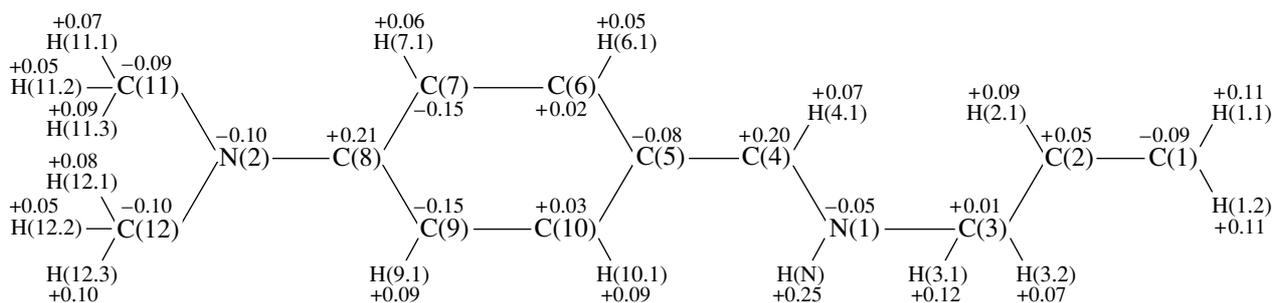
**Table 4.** Geometry of hydrogen bonds in structures **I** and **II**\*

A–H...B bond	Distance, Å			AHB angle, deg**
	H...B	A...B	A–H	
C(1)–H(1.2)...X(2)	3.10(6)	3.58(1)	0.87(6)	137(5)
	3.2(1)	3.64(2)	0.8(1)	140
C(2)–H(2.1)...X(1)	3.13(6)	4.08(1)	1.02(6)	148(4)
	3.2(2)	4.11(2)	1.0(2)	146
C(3)–H(3.1)...X(2)	3.04(5)	3.70(1)	0.83(6)	138(4)
	3.2(1)	3.76(2)	0.8(1)	131
N(1)–H(N)...X(1)	2.68(5)	3.226(7)	0.75(5)	131(5)
	2.8(2)	3.39(2)	0.8(2)	129
N(1)–H(N)...X(2)	2.70(5)	3.284(8)	0.75(5)	136(5)
	2.8(1)	3.34(1)	0.8(2)	127
C(11)–H(11.3)...X(2)	2.85(8)	3.87(2)	1.07(8)	161(6)
	3.1(3)	3.91(3)	0.9(3)	142
C(12)–H(12.3)...X(1)	2.87(7)	3.73(2)	1.01(7)	144(5)
	2.9(2)	3.83(2)	1.1(2)	142

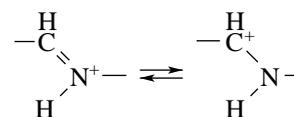
\* The values in the upper and lower rows correspond to compounds **I** and **II**, respectively.

\*\* In structure **II**, deviations of the AHB angle are  $\geq 10^\circ$ .

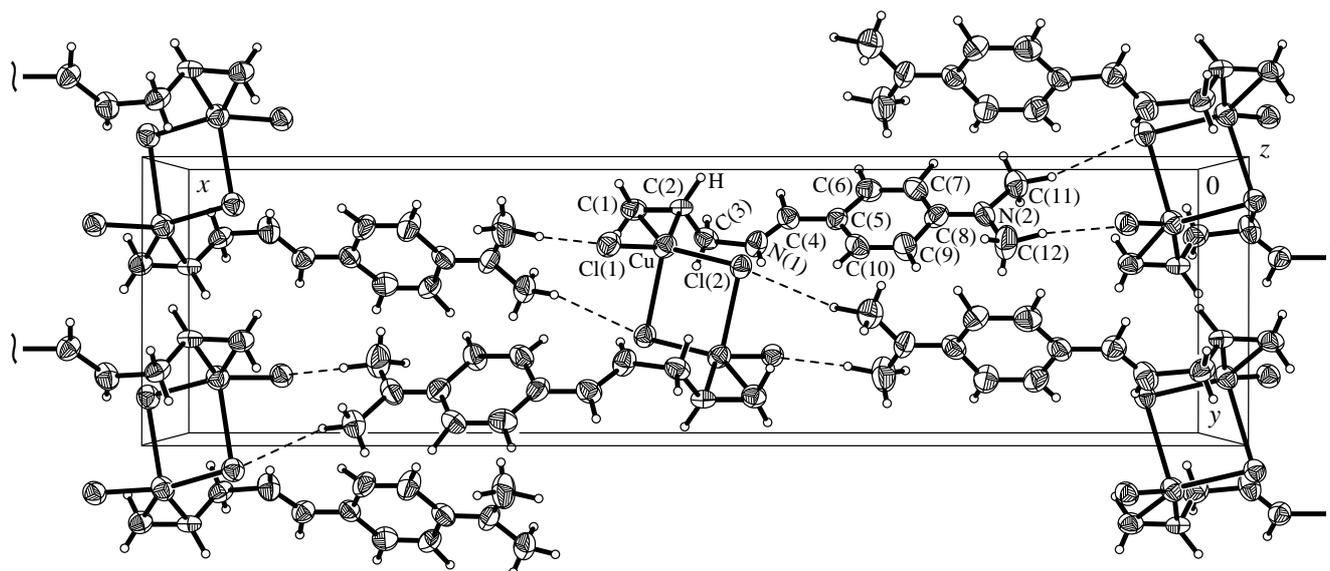
into account). The computational results are presented in the following scheme:



Owing to the Cl–Cu  $p-d_\pi$  interaction, the copper atom in **I** bears a small net charge  $-0.04\bar{e}$ . The hydrogen-bond-induced polarization results in the buildup of a significant negative charge at the chlorine atoms:  $-0.65\bar{e}$  and  $-0.54\bar{e}$  at Cl(1) and Cl(2), respectively. The following trend is also distinctly observed: the hydrogen atoms involved in hydrogen bonding bear a somewhat greater positive charge. Small and close in magnitude, negative charges on the nitrogen atoms are evidence for the weakening of their basicity and substantial  $+M$ -effect of the  $(\text{CH}_3)_2\text{N}$  group. Rather high positive charges on the C(4), C(6), C(10), and C(8) atoms are noteworthy. They point to a certain contribution of the resonance structures with a charge transfer to the carbon atoms, e.g.,



Therefore, a pure  $\pi$ -complex (containing no  $\sigma$ -donating nitrogen atoms in the Cu coordination sphere) with the protonated Schiff base is synthesized (in the presence of traces of water). Compounds **I** and **II** were obtained without adding acid to the reaction mixture. Note that compounds **I** and **II** are the first representatives of this class among the copper(I)  $\pi$ -complexes. Interestingly, the  $2\text{CuCl} \cdot \text{L}$   $\pi, \sigma$ -complexes formed by copper(I) chloride with the unprotonated Schiff bases *N*-allyl-2-furylaldimine and *N*-allylbenzaldimine (L) exhibit radically different structure, in which the copper atoms have a virtually planar-trigonal environment



Fragment of structure I.

with separate  $\sigma$ - and  $\pi$ -coordination, while the  $\text{Cu}_4\text{Cl}_4$  cycle plays the role of an inorganic fragment [3].

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