

β,β -Dichlorovinylidiazonium or Dichloro(diazomethyl)carbenium Ion? Crystal Structure and Electron Density Distribution of β,β -Dichlorovinylidiazonium Hexachloroantimonate¹

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The crystal structure of β,β -dichlorovinylidiazonium hexachloroantimonate, $2 \cdot \text{SbCl}_6$, and the topological electron density analysis of **2** provide compelling evidence for the importance of chlorine-stabilized carbenium ion resonance forms for the stabilization of vinylidiazonium ions by β -substitution.

While aliphatic diazonium ions in general and the parent vinylidiazonium ion² in particular are highly reactive and unstable, Bott discovered that various β,β -disubstituted vinylidiazonium ions with substituents with lone pairs are surprisingly stable.³ Significant contributions by resonance forms **II–IV** were considered to be responsible for this extraordinary stabilization by β -substitution and to explain their reactions with nucleophiles.^{4–6} As part of our physical and theoretical organic studies of the chemistry of aliphatic diazonium ions and of the origin of this substituent effect, we recently reported the first crystal structure of an aliphatic diazonium ion, β,β -diethoxyvinylidiazonium hexachloroantimonate, $1 \cdot \text{SbCl}_6$.⁷ We have now succeeded in the determination of the single-crystal X-ray structure of β,β -dichlorovinylidiazonium hexachloroantimonate, $2 \cdot \text{SbCl}_6$. The crystal structure of **2** allows a greater insight into the interesting bonding situation since **2** can be compared with a variety of *gem*-dichloroalkenes.

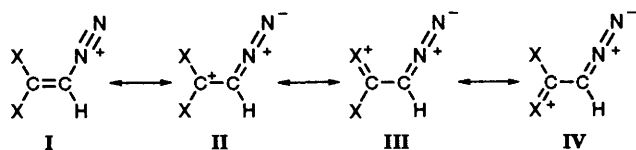
The salt $2 \cdot \text{SbCl}_6$ was prepared according to the procedure reported by Bott.⁸ Toluene-*p*-sulfonohydrazide was reacted with chloral hydrate at 5 °C to give the trichloroaldehyde *p*-tolylsulfonylhydrazone. Reaction of the hydrazone with SbCl_5 for 50 h at 0 °C yielded $2 \cdot \text{SbCl}_6$.[†] A solution of $2 \cdot \text{SbCl}_6$ in ethylene chloride was covered with a layer of dry *n*-hexane and left standing in a glove box under N_2 atmosphere. Pale yellow single crystals suitable for X-ray diffraction[‡] formed at the interface after three days.

There are two symmetry-independent cations **A** and **B** (Fig. 1) in the asymmetric unit of the monoclinic unit cell of $2 \cdot \text{SbCl}_6$. This finding explains the doublet peak for the NN stretching mode at 2238 cm^{-1} in the solid-state IR spectrum. Both ions **A** and **B** have C_s symmetry and structural differences between **A** and **B** are small except for the CN bond which is about 0.035 Å longer in **A** than in **B**.

To evaluate the importance of the resonance forms **I–IV** for the bonding in **2**, the structural argument relies on the relative lengths of the C=C and the C–Cl bonds. Pertinent reference data for this analysis are provided by the crystal structures of

gem-dichloroalkenes, **3–13**, which we have compiled in Table 1. Although the molecules **3–13** cover a wide range of C–Cl and C=C bond lengths and Cl–C–Cl angles, the respective values in **2** all are extreme. The C=C bond lengths of 1.344 and 1.350 Å for **2** are significantly longer than the typical bond length range of 1.313–1.330 Å found for **3–11**, and alkenes **12** and **13** have even shorter C=C distances of 1.300 and 1.302 Å, respectively. The bond angles $\angle \text{Cl–C–Cl}$ of **2** (117.8, 118.7°) are larger than the range for **3–13**. Most significantly however, all C–Cl bond lengths in **2** are rather short, in the range 1.673(6)–1.692(7) Å, and they are much shorter compared to all the *gem*-dichloroalkenes **3–13**. In X-ray crystallography the reference value for the $\text{C}(\text{sp}^2)\text{–Cl}$ bond length is 1.734 Å.¹⁹ Although the C–Cl distances for most of the *gem*-dichloroalkenes are shorter than this value, their average length (*ca.* 1.72 Å) still remains significantly above the C–Cl bond lengths of **2**. In fact, the C–Cl bonds in **2** are almost as short as the $\text{C}^+\text{–Cl}$ bond length of the chloro-substituted carbocation reported recently by Laube *et al.*;²⁰ note that the differences between our C–Cl distances and the short $\text{C}^+\text{–Cl}$ bond of 1.668(8) Å reported by Laube are within the standard deviations. Thus, the analysis of the crystal structure of **2** provides compelling structural evidence for the importance of the resonance forms **II–IV** for the stabilization of **2**. This finding also is corroborated by the CN bond lengths: Their lengths (1.362, 1.397 Å) are much shorter compared to normal C–N bonds (1.47 Å) and instead they are in better agreement with typical conjugated C=N bond length (1.36 Å).²¹

The comparisons of the structures and spectroscopic properties of **1** and **2** allows the bonding in these vinylidiazonium ions to be examined depending on the nature of the β -substituent. The following observations all clearly indicate that the importance of resonance forms **II–IV** is even greater for **1** than for **2**. Both **A** and **B** of **2** have C=C bond lengths of 1.344–1.350 Å and NN bond lengths of 1.079–1.085 which are on average about 0.03 and 0.02 Å, respectively, shorter than those of **1**. On the other hand, the C–N bonds of **2** are longer by 0.03 Å compared to **1**. Moreover, the IR peak correspond-



[†] Selected spectroscopic data: ν_{NN} (KBr) 2238 cm^{-1} ; ^1H NMR (CD_2Cl_2) δ 8.43; ^{13}C NMR (CD_2Cl_2) δ 171 and 104 (J_{CH} 228.5 Hz), m.p. 129–130 °C; elemental analyses were satisfactory.

[‡] Crystal data: $\text{C}_2\text{HN}_2\text{Cl}_8\text{Sb}$, $M = 458.41$, monoclinic, space group $P2_1/c$, $a = 14.052(5)$, $b = 12.3250(2)$, $c = 15.558(6)$ Å, $\beta = 108.538(8)^\circ$, $V = 2554.7(14)$ Å³, $Z = 8$, $F(000) = 1712$, $D_c = 2.384$ g cm^{-3} , $\mu(\text{Mo–K}\alpha) = 2.87$ mm^{-1} , $2\theta \leq 2\theta \leq 26$; graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å); Enraf-Nonius CAD4 diffractometer, 3541 unique reflections from 3696 measured reflections at 173 K; θ – 2θ scan mode ($2\theta_{\text{max}} = 46^\circ$). Structure solutions were obtained by Patterson techniques. Final $R = 0.029$, $R_w = 0.054$ and $S = 1.51$ for 3130 reflections with $I > 2.5\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

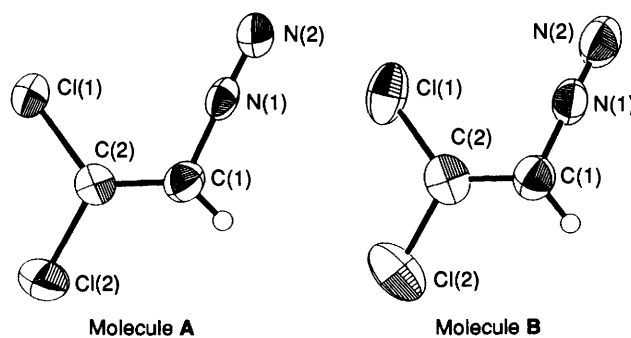


Fig. 1 ORTEP drawings of the symmetry-independent β,β -dichlorovinylidiazonium ions **A** and **B**. Selected structural parameters for **A**, with data for **B** in square brackets: C(1)–C(2) 1.344(9) [1.350(10)], C(1)–N(1) 1.397(9) [1.362(10)], C(1)–H(1) 0.87(7) [0.93(7)], C(2)–Cl(1) 1.679(6) [1.677(7)], C(2)–Cl(2) 1.673(6) [1.692(6)], N(1)–N(2) 1.085(8) [1.079(1)] Å; C(2)–C(1)–N(1) 116.9(6) [116.2(6)], C(2)–C(1)–H(1) 131(4) [126(4)], C(1)–C(2)–Cl(1) 123.5(5) [122.7(6)], C(1)–C(2)–Cl(2) 119.1(5) [118.5(6)], Cl(1)–C(2)–Cl(2) 117.8(4) [118.7(4)], C(1)–N(1)–N(2) 178.5(6) [178.9(6)]°.

Table 1 C(sp²)-Cl and C=C bond lengths and Cl-C-Cl angles of various *gem*-dichloroalkenes and related systems^a

Compound	Compound	C-Cl	C=C	Cl-C-Cl	Ref.
1-SbCl ₆	β,β-Diethoxyvinylidiazonium hexachloroantimonate		1.374, 1.378		7
2-SbCl ₆	β,β-Dichlorovinylidiazonium hexachloroantimonate	1.673-1.692	1.344, 1.350	117.8, 118.7	
3	4-Chloro-5-dichloromethylenefuran-2-one	1.702, 1.716	1.321	114.5	9
4	5-Chloro-6-dichloromethylene-4-methoxy-1-methyl-4-trichloro-methylhexahydropyrimidin-2-one	1.705, 1.722	1.321	113.6	10
5	1,1-Dichloro-2,2-bis(<i>p</i> -chlorophenyl)ethylene	1.729, 1.743	1.320, 1.322	109.9, 110.7	11
6	1,1-Dichloro-2,2-bis(<i>p</i> -methoxyphenyl)ethylene	1.728	1.326	110.3	12
7	<i>N</i> -(2,2-dichlorovinyl)-2,3-epoxy-6-azabicyclo[3.1.0]hexane	1.715, 1.723	1.313	113.9	18
8	2,2'-(2,2-Dichlorovinylidene)-bis(4-chloro-6-nitrophenol)	1.719	1.330	108.3	13
9	4,4'-(2,2-Dichlorovinylidene)-bis(2-chloro-6-nitrophenol)	1.73, 1.72	1.33	111	13
10	Perchloro[4]radialene	1.708, 1.716	1.326, 1.329	113.7, 114.0	14
11	Vinylidene chloride ^b	1.710	1.324	114.5	15
12	(<i>Z</i>)-2-Chloro-3,3-dimethyl-2-(trichlorovinyl)cyclopropane carboxylic acid	1.695, 1.708	1.300	114.4	16
13	<i>rel</i> -(α <i>R</i>), (1 <i>R</i> , <i>trans</i>)-α-Cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate	1.692, 1.735 ^c	1.302	112.4	17
14-SbF ₆	Chlorobisphenylcarbenium hexachloroantimonate	1.668(8)			20

^a In Å and (°). ^b By the visual method using non-sectored and sectored plates and by the sector-microphotometer method. ^c Statistical disorder of the vinyl group was considered responsible for the short C-Cl bond.

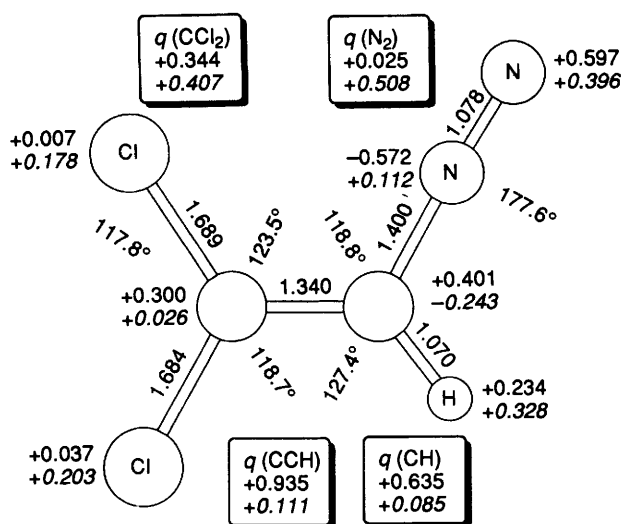


Fig. 2 RHF/6-31G* optimized structure of β,β-dichlorovinylidiazonium ion, **2**, together with integrated Bader charges and NBO charges (italics)

ing to the NN stretching mode of **2** occurs about 62 cm⁻¹ higher than that of **1**. The ¹H and ¹³C NMR spectra also are indicative of a larger positive charge at C_β for **1** than for **2**: the chemical shifts are δ 8.43 (C_α-H) and δ 104 (C_α) for **2** and they are shifted to higher field, δ 6.14 (H) and 56 (C_α), for **1**.§

Finally, in comparing **1** and **2** it is worth noting that the ∠Cl-C-C angle for the Cl that is *cis*(*trans*) with regard to the N₂ group is about 4° larger (5° smaller) than the respective ∠O-C-C angle. While the X_{*cis*}-C-C angle in **2** is larger than 120°, the corresponding angle in **1** is smaller. These angles indicate attractive neighbouring group interaction between the N₂ group and the *cis*-β-substituent in **1** but repulsive interaction in **2**.²²

We have studied the electronic structure of the β,β-dichlorovinylidiazonium ion **2**, using topological electron density analysis²³ as well as the natural population analysis (NPA) method.²⁴ The RHF/6-31G* structure shown in Fig. 2 is in

excellent agreement with the crystal structure of 2·SbCl₆. The integrated atomic charges clearly indicate that the overall charge on the N₂ group is very small and that instead the positive charge is located primarily on the CH group and C_β. We have shown previously that small N₂ charges are characteristic of diazonium ions in general²⁵ and the pertinent question for the vinyl systems concerns the charge distribution within the Cl₂CCH fragment. Importantly, the Cl atoms are found to carry only minor positive charges and most of the charge (+0.935) is assigned to the CCH fragment. The NPA analysis assigns about half of the positive charge to the N₂ group and only a small charge to the CH group. Similar differences between the topological and NPA analysis were found and discussed in our recent comparative population analyses of diazonium ions and an explanation was given.²⁶ The NPA and integrated charges of the CCl₂ fragment agree well but, in contrast to the topological analysis, the NPA analysis indicates moderate charge transfer (*ca.* 0.2) from each Cl atoms leading to an almost neutral C_β. The NPA method thus assigns significant positive charge to the N₂ group and each Cl but only a small charge of +0.111 to the least electronegative hydrocarbon fragment, while it is a great advantage of the topological method to provide charges that agree with electronegativities. The NN bond length in **2** becomes crucial in judging the relative value of these population analyses; the NPA charge of the N₂ group clearly would predict a lengthening of the NN bond. However, the NN bond in **2** is actually shorter than in N₂ itself, a finding that is fully consistent with the overall charge and polarity of the N₂ group as determined with the topological method.

Laube *et al.*²⁰ suggested that the C⁺-Cl bond is shortened owing to π-back-donation leading to a positively charged chlorine (*e.g.* C=Cl⁺).²⁷ While this interpretation is based solely on structural data, our topological analysis of the electron density distribution suggests that the Cl atoms stabilize the adjacent positive centre *via* polarization of the density in the Cl regions towards C_β but without significant back-donation, that is, without significant Cl→C_β charge transfer.²⁶ We conclude that the electronic structures indicate a higher importance of **II** compared to **III** and **IV** while the analysis of structures alone cannot distinguish between **II**-**IV**. This finding emphasises the importance of the atom anisotropy for the interpretation of Lewis structures which we have recently discussed.²⁶

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§ While there are no general charge *vs.* ¹³C NMR chemical shift relations, we are comparing CH fragments in very similar bonding environments.

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