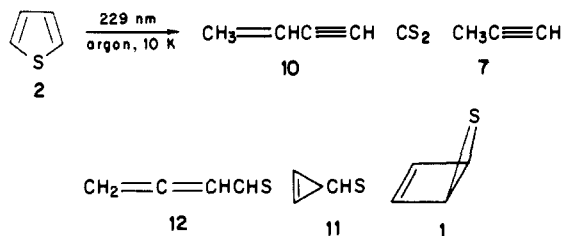


Scheme II



By analogy with the furan system the species responsible for the IR bands at 1150 and 855  $\text{cm}^{-1}$  in the matrix photolysis of thiophene has been assigned to cyclopropene-3-thiocarbonyl (11) while the absorptions at 1950 and 1920  $\text{cm}^{-1}$  have been assigned to 2,3-butadienylthiol (12). We have also photolyzed matrix-isolated  $\text{C}_4\text{D}_4$  in which the 1150- $\text{cm}^{-1}$  band remained essentially unchanged in agreement with its assignment to a thiocarbonyl absorption. The Dewar thiophene structure 1 has been assigned, *vide infra*, to the thiophene photoproduct responsible for the strong absorption at 740  $\text{cm}^{-1}$ . Irradiation (254 nm) of the thiophene photolyzate caused the disappearance of the absorption bands assigned to 11 and 1 with a concomitant increase of the thiophene spectrum. Dewar thiophene also underwent photolysis at long wavelength ( $\lambda = 280 \text{ nm}$ ) and even at  $\lambda > 320 \text{ nm}$  albeit very slowly.

In the earlier<sup>2</sup> solution-phase photolysis of thiophene we also trapped the Dewar isomer when thiophene was irradiated in a rigid glass at  $-170 \text{ }^\circ\text{C}$  followed by reaction with furan in the dark, thereby demonstrating that 1 was formed and intercepted under matrix conditions.

As a model for Dewar furan and Dewar thiophene, the matrix photolysis of cyclopentadiene (13) was investigated. van Tamelen et al.<sup>11</sup> reported the formation of bicyclo[2.1.0]pent-2-ene (14) as the sole product of UV photolysis of 13, but no IR spectrum of 14 has been reported. Our matrix photolysis of cyclopentadiene resulted in the formation of essentially a single new product with only two strong absorptions at 720 (100%) and 770 (50%)  $\text{cm}^{-1}$  and weak absorptions (<1.5%) in particular at 860 and 920  $\text{cm}^{-1}$ . This new product was subsequently distilled from the matrix and the structure determined by 400-MHz  $^1\text{H}$  low-temperature NMR to be the bicyclic isomer 14. Unexpectedly red-shifted UV absorptions have been previously reported for 14<sup>12</sup> and perfluoro-tetramethyl Dewar thiophene.<sup>13,14</sup> Indeed, the photolysis (260 nm) of the argon-matrix-isolated cyclopentadiene photolyzate (and slowly with  $\lambda = 280 \text{ nm}$ ) resulted in the destruction of 14 and regeneration of 13.

In our matrix photolysis of furan, thiophene, and cyclopentadiene we have found in each instance a strong IR absorption in the 700–800- $\text{cm}^{-1}$  region<sup>15</sup> and moreover those absorptions which we have assigned to the bicyclic isomers could be selectively destroyed by irradiation at wavelength  $\lambda \geq 280 \text{ nm}$ . Thus, we are forced to conclude that the Dewar forms of both furan and thiophene are primary products of the photolysis of 2 and 3.

Further studies are in progress.

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## Structures of Two Cyclopropylcarbiny Cations<sup>1</sup>

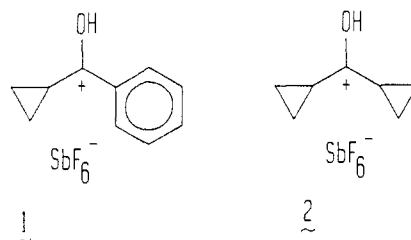
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Cyclopropylcarbiny cations have been the subject of many investigations over the past 20 years.<sup>2</sup> However, until now there have been no direct examinations of the structures of these cations. As stated by Sorensen:<sup>3</sup> "X-ray data on cyclopropylcarbiny salts are badly needed because no experimental bond distance data is available for comparison with the calculations".

We have now prepared two substituted cyclopropylcarbiny cations as crystalline salts and have determined their structures by single-crystal X-ray diffraction techniques. Both the hydroxycyclopropylphenylmethyl cation (1) and hydroxycyclopropylmethyl cation (2) ions were prepared as their hexafluoro-



antimonate salts by protonation of the corresponding cyclopropyl ketones with  $\text{HF/SbF}_5$ . NMR spectra of solutions of these salts agree well with previously reported spectra of these ions.<sup>4</sup>

There are two independent cations in the asymmetric unit of 1 with very similar geometries. The structure of one of these is shown in Figure 1 and important parameters are summarized in Table I.<sup>5</sup> It is clear from these data that the cyclopropyl ring in 1 has adopted a conformation close to the expected "bisected" geometry. For the two molecules in each asymmetric unit, the angles made between the plane defined by the cyclopropyl carbons and the plane defined by the atoms around the formal cation center are 83.4° and 87.8°. The phenyl group, on the other hand, lies in a plane much closer to the plane around the cation center with angles between these planes of only 25.3° and 28.6°. These structures give a very beautiful demonstration of the different conformations required for effective conjugation of cyclopropyl and phenyl groups with an adjacent positive charge.

(1) This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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(5) X-ray analyses 1: space group  $P2_1/c$ ; unit cell,  $a = 13.204$  (5) Å,  $b = 9.178$  (3) Å,  $c = 21.369$  (6) Å,  $\beta = 102.70$  (3)°; 3976 unique reflections; solved using direct and difference methods; full-matrix least-squares refinement (three hydrogens were not found); final  $R_1 = 0.058$ ,  $R_2 = 0.036$ . 2: space group  $P2_1/m$ ; unit cell,  $a = 7.000$  (1) Å,  $b = 8.549$  (2) Å,  $c = 10.849$  (2) Å,  $\beta = 119.63$  (1)°; 1061 unique reflections; solved using Patterson synthesis and difference methods; full-matrix least-squares refinement; final  $R_1 = 0.025$ ,  $R_2 = 0.037$ . Neither of the cations appear to be perturbed by strong interactions with the counterions in the crystal lattice other than a hydrogen bonding interaction of the hydroxy proton with a fluorine in an  $\text{SbF}_6^-$  (O–H...F distances: 1, 2.608 (5) Å, 2.787 (7) Å; 2, 2.565 (6) Å. This type of interaction is present in all the structures of protonated ketones we have determined and of course will be present in solution. A more detailed discussion of the structure of the protonated carbonyl group will be presented in a forthcoming publication.

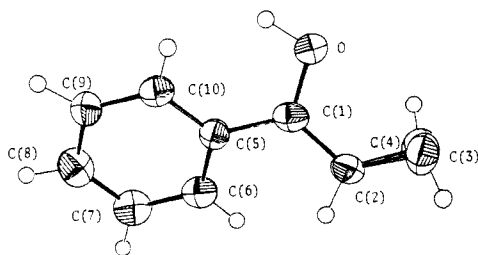


Figure 1. Structure of one of the two molecules of **1**. (One hydrogen on each of C(3) and C(4) was not found.)

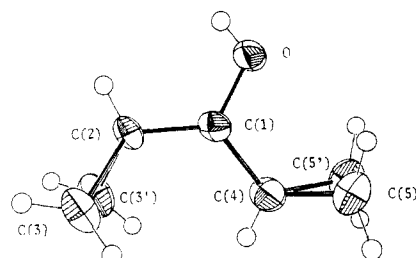


Figure 2. Structure of **2**.

Table I. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

1, Molecule A			
C(1)-O	1.302 (9)	O-C(1)-C(2)	116.1 (6)
C(2)-C(3)	1.535 (10)	C(2)-C(3)-C(4)	62.2 (5)
C(3)-C(4)	1.444 (11)	C(4)-C(2)-C(1)	117.7 (6)
C(1)-C(2)	1.409 (8)	C(2)-C(1)-C(5)	123.8 (6)
C(2)-C(4)	1.541 (10)	C(1)-C(2)-C(3)	120.1 (6)
C(1)-C(5)	1.464 (9)	C(3)-C(4)-C(2)	61.8 (5)
		C(4)-C(2)-C(3)	56.0 (5)
1, Molecule B			
C(1)-O	1.288 (10)	O-C(1)-C(2)	117.2 (6)
C(2)-C(3)	1.550 (10)	C(2)-C(3)-C(4)	61.6 (5)
C(3)-C(4)	1.452 (13)	C(4)-C(2)-C(1)	117.6 (7)
C(1)-C(2)	1.424 (9)	C(2)-C(1)-C(5)	122.1 (7)
C(2)-C(4)	1.540 (11)	C(1)-C(2)-C(3)	116.5 (7)
C(1)-C(5)	1.448 (10)	C(3)-C(4)-C(2)	62.3 (5)
		C(4)-C(2)-C(3)	56.1 (5)
2 <sup>a</sup>			
C(1)-O	1.290 (8)	O-C(1)-C(2)	120.8 (6)
C(2)-C(3)	1.524 (7)	C(2)-C(3)-C(3')	61.3 (3)
C(1)-C(4)	1.432 (9)	C(2)-C(1)-C(4)	123.7 (6)
C(5)-C(5')	1.470 (6)	C(4)-C(5)-C(5')	61.4 (2)
C(1)-C(2)	1.428 (6)	C(4)-C(1)-O	115.6 (4)
C(3)-C(3')	1.465 (5)	C(1)-C(2)-C(3)	119.3 (5)
C(4)-C(5)	1.534 (5)	C(3)-C(2)-C(3')	57.5 (3)
		C(1)-C(4)-C(5)	117.8 (5)
		C(5)-C(4)-C(5')	57.3 (3)

<sup>a</sup> In **2**, a mirror plane exists through atoms O, C(1), C(2), and C(4), giving rise to a symmetric structure in which atoms C(3) and C(5) are equivalent to C(3') and C(5'), respectively.

The structure of **2** is shown in Figure 2.<sup>6</sup> Again it is clear that both cyclopropyl rings adopt a bisected geometry. The ion has an overall "sickle" shape in contrast to the "W" shape suggested by Olah for this ion based on his analysis of the structure of the parent dicyclopropylmethyl cation.<sup>7</sup> This sickle conformation is probably the result of an increased steric interaction between the protons on C(3) and C(3') with the substituent on C(1) as the hydrogen atom on C(1) in the parent cation is replaced by a hydroxy group on this carbon in **2**.

It is of interest to examine the bond lengths found for these cyclopropylcarbanyl cations. It can be seen on comparison of the bond distances observed in **1** and **2** with those of a typical cyclopropyl ketone (Figure 3)<sup>8</sup> that a substantial lengthening of the C(1)-O bonds and shortening of the C(1)-cyclopropyl and C(1)-phenyl bonds has occurred on protonation of the ketones. These changes are consistent with conjugation of the cyclopropyl and phenyl rings with the protonated carbonyl group and the transfer of positive charge onto these rings.

The cyclopropyl bond distances observed in these cations are of particular interest. The two vicinal bonds in **1** have the same

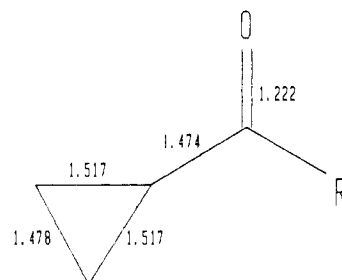


Figure 3. Bond lengths for a typical cyclopropyl ketone.<sup>8</sup>

internuclear distance with an average bond distance of 1.542 (5) Å in the two examples of **1**. This is some 0.030 Å longer than that found in free cyclopropane.<sup>9</sup> In contrast, the distal bond is shortened to 1.448 (9) Å, some 0.064 Å shorter than that of cyclopropane. The same pattern of bond length changes was observed in each of the cyclopropyl rings of **2**.

The average cyclopropyl bond distances in **1** and **2** are the same as those normally found for a cyclopropane despite the very large distortions that are found here in the individual bond lengths. In each case the elongation of the two vicinal bonds is matched by a corresponding diminution of the distal bond of twice the magnitude. The pattern of changes observed here is the same but substantially larger than that found by Allen in his analysis of the structure of cyclopropyl ketones.<sup>8</sup> In the case of **1**, the magnitude of the distortion of the cyclopropyl bonds is 2.3 times that found by Allen. With **2** the distortion is only 1.6 times as large as normally found for a cyclopropyl ketone suggesting that less charge is delocalized onto an individual cyclopropyl group in **2** than is found for **1**. Taking this argument further, this suggests that a cyclopropyl ring is more effective at stabilizing a positive charge on an adjacent carbon than is a phenyl ring.<sup>7,10</sup>

Overall, the structures of these two cations are fully in accord with those expected for bisected cyclopropylcarbanyl type cations. The hydroxy and phenyl groups help stabilize the positive charge and even larger bond length distortions in the cyclopropyl ring would be expected in other less-substituted derivatives and in the parent cation. When these structures become available, it will be interesting to see whether the average cyclopropyl bond distance remains the same as that of cyclopropane itself. Published calculations on the parent cation when held in a bisected conformation suggest that this will not be the case.<sup>11</sup>

**Supplementary Material Available:** Tables of crystal data, atomic positions, bond lengths and angles, anisotropic temperature factors, and final observed and calculated structure factors for C<sub>10</sub>H<sub>11</sub>O<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (**1**) and C<sub>7</sub>H<sub>11</sub>O<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (**2**) as Tables A-M (36 pages). Ordering information is given on any current masthead page.

(6) In an earlier report of the structure of **2** presented at the International Symposium in Novel Aromatic Compounds, St. Andrews, Scotland, July 15-19, 1985, the two vicinal cyclopropyl bonds in each ring were given different distances, although the differences were within the error limits of the determination. Further examination of the structure revealed that a mirror plane exists and the final refinement was done by using a higher symmetry space group.

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