However, the PES of ethers indicates that the two lone pairs are energetically different,[28] in accord with MO calculations[29] that points to steric and energetic differences for the two lone pairs. The situation is even less clear for cation 4. Regardless of whether a sp^2 or sp^3 hybridization of the oxygen atom is assumed, only one of the two cyclopropenylium π systems is in a geometry suited for efficient overlap with an oxygen lone pair.

Perhaps the conformations encountered in ions **3** and **4** are primarily dictated by the steric requirements of the cationic substituents. For example, a bent-planar conformation like **2a** may be excluded a priori, as the cations of both **3** and **4** could not fit into a plane because of severe steric interactions between the inside methyl groups (or NMe_2 groups) in this hypothetical structure. Similar reasons, but to a lesser extent, may prevent the molecule from assuming a bent-perpendicular structure like **2b**. However, such steric factors are much less important or nonexistent for the linear arrangements **2c** and **2d**, which, therefore, may occur even in dication ethers with very bulky substitutents.

B. The Anions and Crystal Structure. Because of high thermal motion as well as in part due to disorder, the geometry calculated for the triflate anions of both **3** and **4** is not very reliable. It should be mentioned that in trifluoromethansulfonic acid monohydrate, which is composed of oxonium ions and triflate anions, the following average distances and angles have been observed at room temperature:[30] S–O 1.436 Å,[31] C–F 1.307 Å, O–S–O 114.4°, O–S–C 104.0°, S–C–F 110.2°, F–C–F 108.7°.

The unit cell contents of **3** and **4** are depicted in Figures 4 and 5 (supplementary material). The closest contacts between cations and anions are found between sulfonate oxygen atoms and the atoms in the cation which share the positive charge; they are in the range of 3.12–3.19 Å in structure **3** and 2.93–3.14 Å in the crystal of **4**. No fluorine–cation contacts shorter than 3.40 Å (except for F6–C4 = 3.24 Å in **3**) exist in both crystal structures.

In summary, these X-ray determnations confirm and unambigiously establish the structure previously reported[2] for these novel dication ethers as well as provide important insight into their exact geometry and conformation in the solid state. Specifically, both cations investigated prefer a bent-nonplanar arrangement as the most stable conformation, despite the possibility of greater relief of steric strains as well as perhaps better overlap in a linear form.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft at Kaiserslautern and the NSF (CHE81-07629) at Utah. Access to the diffractometer at the Institute of Crystallography, University of Saarbrücken, is gratefully acknowledged.

Registry No. 3, 78581-33-6; 4, 86611-84-9; 6, 86611-86-1; triflic anhydride, 358-23-6; 2,3-bis(dimethylamino)cyclopropenone, 50338-18-6; trifluoromethanesulfonic acid, 1493-13-6.

Supplementary Material Available: Anisotropic thermal parameters of 3 and 4, lists of observed and calculated structure factors for 3 and 4 and hydrogen coordinates, angles between least squares planes, and stereoplots of the unit cells of 3 and 4 (7 pages). Ordering information is given on any current masthead page.

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[31] This value is probably not ideal for comparison with 3 and 4, as the oxygen atoms are involved in hydrogen bonds with the oxonium ion.

The Structure of Ditropenyliumyl Ether Bis(trifluoromethanesulfonate)

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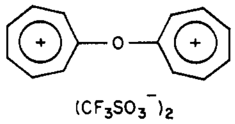
The X-ray crystal structure of ditropenyliumyl ether bis(trifluoromethanesulfonate) $[(C_7H_6^+)_2O][CF_3SO_3]^-{}_2$, has been determined. The crystals are orthorhombic, *Pcnb* (No. 60), with cell dimensions a = 7.985 (2) Å, b = 18.571 (6) Å, c = 12.984 (3) Å, and Z = 4. Intensities were measured with a Syntex $P2_1$ diffractometer and Mo Kα radiation. The structure was solved by Patterson and difference methods and refined to R_1 = 0.075, R_2 = 0.042 for 1209 reflections. The cation contains a bent C–O–C system (125.3 (4)°) and the C–O bonds (1.356 (3) Å) are short. There is extensive delocalization in the rings, and the average bond length (1.386 Å) may be shorter than in benzene. The two rings, which have a shallow boat structure, are twisted symmetrically about the C(1)–O–C(1) plane because of the interactions of the α-hydrogen atoms and have a dihedral angle of 113.0 (5)°.

Stang and co-workers[1,2] have recently described the preparation of a series of intriguing dication ether salts. These were obtained by the reaction of triflic anhydride with a variety of ketones. Ditropenyliumyl ether bis(trifluoromethanesulfonate) (**1**) is a typical example of such a salt.



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Several interesting structural questions arise with these dication salts. First there is the question of the correctness of the overall structure assignments. Second, one wonders how the conformations of these unusual ethers resemble those of the related diphenyl ethers[3] and whether the full

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[1] Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361.

[2] Stang, P. J.; Maas, G.; Smith, D. L.; McCloskey, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4837.

Table I. Selected Interatomic Distances (Å) and Angles (deg)

C(1)–C(2)	1.410 (6)	C(2)–C(3)	1.367 (6)	C(3)–C(4)	1.406 (7)
C(4)–C(5)	1.384 (7)	C(5)–C(6)	1.383 (7)	C(6)–C(7)	1.370 (7)
C(7)–C(1)	1.385 (6)	C(1)–O	1.356 (3)	S–O(1)	1.434 (3)
S–O(2)	1.436 (3)	S–O(3)	1.446 (3)	S–C	1.823 (5)
C–F(1)	1.325 (5)	C–F(2)	1.323 (6)	C–F(3)	1.324 (6)
C(7)–C(1)–C(2)	128.3 (5)	C(1)–C(2)–C(3)	127.6 (5)	C(2)–C(3)–C(4)	139.7 (5)
C(3)–C(4)–C(5)	127.3 (5)	C(4)–C(5)–C(6)	128.8 (5)	C(5)–C(6)–C(7)	129.1 (5)
C(6)–C(7)–C(1)	128.8 (5)	O–C(1)–C(2)	118.7 (3)	O–C(1)–C(7)	112.8 (3)
O(1)–S–O(2)	113.8 (2)	O(1)–S–O(3)	114.4 (2)	O(2)–S–O(3)	115.0 (2)
O(1)–S–C	103.4 (2)	O(2)–S–C	103.6 (2)	O(3)–S–C	104.7 (2)
F(1)–C–F(2)	107.6 (4)	F(1)–C–F(3)	107.9 (4)	F(2)–C–F(3)	107.2 (4)
F(1)–C–S	111.6 (4)	F(2)–C–S	110.8 (4)	F(3)–C–S	111.5 (4)
C(1)–O–C(1)′	125.3 (4)				

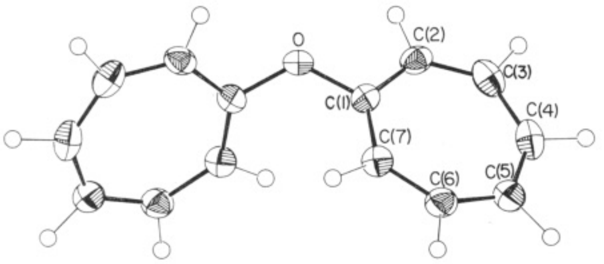


Figure 1. The cation $(C_7H_6)_2O^+$ showing the atom numbering.

positive charge on each ring gives them some distinctive geometries. In this latter regard Stang and co-workers in their original papers speculated on the various possible conformations available.[2] More recently Apeloig has reported calculations on the dicyclopropeniumyl and ditropenyliumyl ether salts.[4] The latter system at the MINDO/3 level was predicted to exist preferentially in a linear conformation (C–O–C angle = 180°) with the two seven-membered rings at right angles to each other. No collinear C–O–C bonds have been found crystallographically to the best of our knowledge, and this prediction alone merited experimental test. A third point of interest for the salt **1** is the presence of two tropenylium rings. There is a marked lack of structural data on simple tropenylium cations.[5]

For the above reasons we have determined the structure of **1** using single-crystal X-ray diffraction.[6]

Results

The salt **1** was prepared from tropone by the method reported by Stang et al.[1,2] Crystals were thermally stable at room temperature in the absence of moisture. The structure of **1** was determined by using X-ray diffraction as outlined in the Experimental Section. Bond lengths and angles are given in Table I.

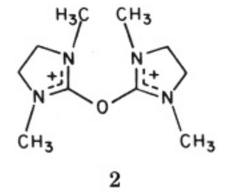
Discussion

The overall structure found for **1**, Figure 1, confirms that it is indeed a ditropenyliumyl ether as was suggested by Stang et al. It is also apparent, however, that the C–O–C angle (125.3 (4)°) is not 180°, as suggested by Apeloig.[4] Previous studies in this series have made use of solid-state CPMAS and solution ^{13}C NMR spectra to establish the conformational identity of cations in the crystalline state and in solution.[6] In this present case there was not enough distinctiveness in the carbon resonances of **1** to allow a meaningful comparison to be made.

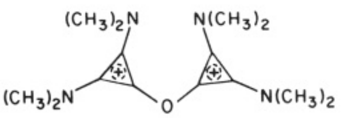
There are potentially four basic conformations for bent diaryl ethers. These are the planar, butterfly, twist, and skew conformations.[3a] All the diaryl ethers studied previously preferentially adopt skew conformations in which one aryl ring is close to being coplanar to the plane defined by the C–O–C atoms and the other ring tends to be at 90° to this plane. The twist conformation found here for **1** differs markedly from this pattern of behavior for diaryl ethers. The dication salt has a C_2 axis through the oxygen, and both rings are twisted by 33.5 (5)° from the C–O–C atom plane. Some twisting is necessary because of severe nonbonded interactions between the two ortho hydrogen atoms on the tropenylium ring. The H(2)$\cdots$H(2)′ distance of 2.9 (1) Å is possibly slightly larger than the van der Waals distance (2.58 Å), but it is clear that the twisted geometry is preferred over the skewed conformation. In comparing **1** with other diaryl ethers it should be borne in mind that the majority of other structures determined have markedly dissimilar substituents on the two aryl rings and in addition bulky groups in the ortho positions. In general the aryl ring with electron-withdrawing substituents tends to be coplanar with the C–O–C plane. The salt **1** possesses two equivalent rings, which are both electron withdrawing.

The C–O bond distance (1.356 (3) Å) in **1** is quite short and even shorter than the average of the two C–O bonds in aryl ethers. This suggests that there is significantly more multiple bonding in the C–O–C system of **1** arising from conjugation of the oxygen atom with the rings than with diaryl ethers. The C–O–C angle found here for **1** is comparable to that observed for diaryl ethers[3] and substantially larger than that for dialkyl ethers.[7] This again is consistent with conjugation between the rings and the oxygen atom.

In the accompanying paper, Stang and Maas[8] report the structure determinations of the two additional dication ether salts **2** and **3**. Both of these have bent rather than linear $^+$C–O–C$^+$ assemblies. Unlike the dication salt **1**



2



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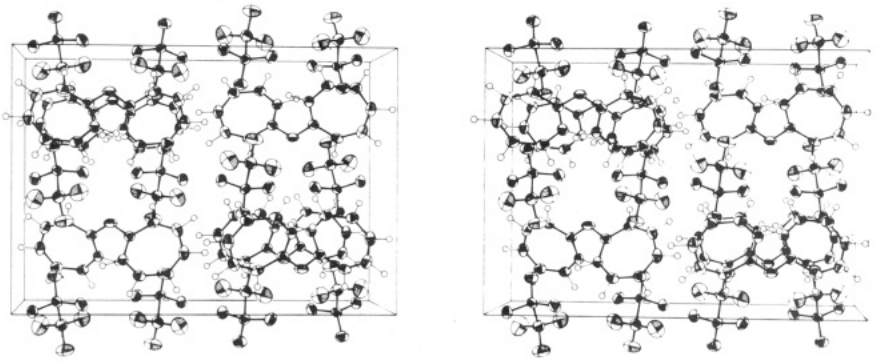

Figure 2. Packing of $[(C_7H_6)_2O][CF_3SO_3]$ within the unit cell; *b* and *c* are parallel to the bottom and side of the page respectively and view is down *a*.

studied here, these systems do not exhibit a C_2 symmetry axis through the oxygen atom and neither dication ether exists in a twist conformation. The C–O bond lengths are again short.

The cation **1** contains two equivalent tropenylium rings, each of which bears a positive charge. This dication represents the simplest tropenylium ions for which structural information is available.[5] The parent ion is disordered, and no accurate bond distances are known.[9] Other examples are complex fulvenylium type systems in which the positive charge is extensively delocalized over more than one ring.[10] The C–C bond lengths for **1** are, as would be expected, intermediate between expected single and double bond distances. Compared to tropone[11] the single–double bond alternation is reduced, although the increase in the "double bond" length is only significant in C(4)–C(5) furthest from the oxygen atom (1.385 (7) vs. 1.347 (9), 1.327 (9) Å). No significant increase is observed for the "double bonds" adjacent to the oxygen atom (1.367 (6) and 1.370 (7) vs. the range 1.348 (9)–1.365 (9) Å). The single bonds, however, are shortened (range 1.383 (7)–1.410 (6) vs. range 1.415 (9)–1.459 (9) Å). The residual alternation is consistent with some degree of conjugation of the oxygen atom with the seven-membered ring and reinforces the conclusions reached above on the length of the C–O bonds. The average C–C length in the seven-membered rings (1.386 Å) is substantially less than that estimated for the disordered parent ion.[9] Furthermore, it is interesting that the average C–C bond length obtained here for **1** may be somewhat shorter than that of the C–C bond length of benzene (1.395 Å)[12] although the errors preclude a definate conclusion. Calculations on the tropenylium ring suggest the reverse and that its bond distance should be greater than that of benzene.[13] More simple tropenylium ion structures need to be examined before the generality of this finding can be established.

The seven-membered rings in **1** are not completely planar but exist in a very shallow boat conformation. The conformation can be defined in terms of three planes involving C(1)C(2)C(7) (A), C(2)C(3)C(6)C(7) (B), and C(3)C(4)C(5)C(6) (C), with the angles between these planes being A–B 2.7 (5)° and B–C, 3.9 (5)°. The crystal structure of tropone itself[11] and several other simple tropones shows a similar very shallow boat conformation.[14] In addition to the bending of the ring, the oxygen atom is significantly out of the C(1)C(2)C(7) plane (0.116 (3) Å). The oxygen can be regarded as being in a pseudo-equatorial position of the very shallow boat conformation of the seven-membered ring.

The packing is shown in Figure 2. The cations are in layers parallel to the *ab* plane at $z = {}^1/_4, {}^3/_4$ with the cations roughly along *b*. Cation–cation contact along *b* is at $y = 0, {}^1/_2$, with the hydrogen atoms of the rings on adjacent cations (up *a*) interleaved. The anions are in similar layers at $z = 0, {}^1/_2$, but the anions align themselves across these planes parallel to *ac* and the two ends thus interleave with cations in a pair of parallel layers. Since the part of a cation above an anion (up *a*) is oriented in the same way as the translationally equivalent cation below, the twist in the cation is not designed to permit easier cation anion packing. Thus we conclude that the twist in the cation is not caused by packing. One final feature of the twisting of the cations and the packing is there are channels along *b* at $x = 0$, $z = 0$, and $x = 1/2$, $z = 1/2$ which are bordered solely by hydrogen and oxygen atoms, perhaps indicating some very weak hydrogen bonding in this region.

Molecular structure can be used as a criterion of aromaticity. Qualitatively, it is expected that an aromatic molecule will have C–C bond lengths that are intermediate between those of conventional single and double bonds.[15] This approach to the definition of aromaticity has been quantified by taking the mean square deviations of the bond lengths from the average value.[16] When this approach is used, the aromaticity constant (*A*) of each tropylium ring of **1** is 0.97 as compared to benzene where *A* = 1. Thus on this geometric definition of aromaticity, the tropylium ion, as exemplified by **1**, is essentially as aromatic as benzene. This result agrees with the conclusions reached by Dauben and co-workers based on a comparison of the magnetic susceptibility exaltations of benzene and tropylium ions[17] and is in line with other estimated[18,19] or calculated values.[13] It should be noted that the *A* value

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Table II. Crystal Data

compound	$[(C_7H_6)_2O]^{2+}[CF_3SO_3^-]_2$, $C_{16}H_{12}F_6O_7S_2$
fw	494.4
cryst size (mm)	0.30 × 0.30 × 0.35, rough cube
systematic absences	$hk0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$; $0kl$, $l = 2n + 1$
space group	*Pcnb*
unit cell, Å	$a = 7.985$ (2); $b = 18.571$ (6); $c = 12.984$ (3)[a]
volume, Å^3	1925.6 (9)
Z	4
ρ_{calcd}, g cm^{-3}	1.705
μ, cm^{-1}	3.76
max 2θ, reflctns meas	45°, $h,k,\pm l$
standard reflctns (esd)	3 0 3 (0.043); 2 2 3 (0.013)
temp, °C	−55
unique reflctns	1274
no. with $I > 0$	1209
no. of variables	160
final R_1; R_2[b]	0.075; 0.042
final shift/error max (av)	0.027, 0.002
final difference map max; min e Å^{-3}	0.40; −0.53
x (secondary extinction)	0.00079
weighting	$w = \sigma(F)^{-2}$
error in an observation of unit wt	1.0785

[a] This cell can be transformed to the standard setting, *Pbcn*, $a = 7.985$ (2), $b = 12.984$ (3), $c = 18.571$ (6), R by the matrix (100/00-1/010). [b] $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

Table III. Atomic Positional Parameters (×10^4)

atom	x	y	z
S	2618 (2)	3889 (1)	335 (1)
L(1)	1717 (4)	3222 (2)	278 (2)
O(2)	1655 (4)	4504 (2)	20 (2)
O(3)	3570 (4)	3985 (2)	1272 (2)
C	4191 (7)	3802 (3)	−645 (4)
F(1)	3497 (4)	3684 (2)	−1586 (2)
F(2)	5097 (4)	4396 (2)	−747 (3)
F(3)	5238 (4)	3266 (2)	−482 (2)
C(1)	4114 (6)	1975 (2)	2803 (4)
C(2)	3193 (6)	2153 (2)	1913 (3)
C(3)	2206 (6)	1708 (2)	1334 (4)
C(4)	1918 (6)	965 (3)	1432 (4)
C(5)	2449 (7)	517 (2)	2219 (4)
C(6)	3433 (6)	682 (3)	3063 (4)
C(7)	4177 (6)	1323 (3)	3318 (4)
O	5000	2500	3283 (3)

of 1 found here differs markedly from those estimated for various tropones.[14a]

Experimental Section

All manipulations were carried out in a drybox under a nitrogen atmosphere. Solvents were dried with freshly activated molecular sieves prior to use.

Ditropenyliumyl ether (trifluoromethanesulfonate) was prepared by the method of Stang et al.[2] Crystals of the salt were obtained as pentagonal prisms by precipitation from an acetonitrile solution, diethyl ether being added by vapor diffusion.

Collection of the X-ray Data. A near cubic crystal was sealed in a Lindemann tube with a nitrogen atmosphere, transferred to a Syntex P2$_1$ diffractometer, and cooled to −55 °C. Unit cell parameters were obtained from a least-squares fit of χ, and 2θ for 15 reflections in the range 20.4° < 2θ < 32.1° were recorded on the diffractometer with use of graphite monochromated Mo Kα_1 radiation (λ 0.70926 Å). Crystal data are summarized in Table II. The density of the crystal was not measured because of its instability. Intensities were measured with the P2$_1$ diffractometer with use of a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[20,21] Corrections were made for Lorentz–polarization factors but not for absorption. This will make a maximum error in F_0 of 2.0%.

Solution of the Structure. The sulfur atom was found from a three-dimensional Patterson synthesis, and all other atoms were found from electron density difference syntheses. The coordinates of all non-hydrogen atoms were refined with the use of full-matrix least-squares minimizing $\sum \omega(|F_0| - |F_c|)^2$, until the maximum shift/error was 0.1. At this stage the positional parameters of all atoms were refined. The non-hydrogen atoms were then refined a further three cycles until the shift/error was 0.01. Throughout the scattering curves were taken from the International Tables.[22] Secondary extinction corrections were applied by using SHELX. The positional parameters for non-hydrogen atoms are given in Table III;[23] temperature factors and parameters for hydrogen atoms have been deposited.

Acknowledgment. This work was supported by the National Sciences and Research Council of Canada. We thank Drs. Stang and Maas for discussion and release of their results before publication.

Registry No. 1, 75359-40-9.

Supplementary Material Available: Four tables giving anisotropic temperature factors, hydrogen atom positional factors, distances and angles involving hydrogen atoms, and least-squares planes, dihedral angles, and torsional angles (4 pages). Ordering information is given on any current masthead page.

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