3038 *J. Org. Chem.* **1983**, *48*, 3038-3043

Structures of Dication Ethers. Crystal and Molecular Structures of Bis(1,3-dimethyl-2-imidazoliniumyl) Ether Ditriflate and Bis[1,2-bis(dimethylamino)-3-cyclopropenyliumyl] Ether Ditriflate[1]

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The crystal structures of the title compounds, **3** and **4**, have been determined. Compound **3** crystallizes in space group $P2_1/c$, with $a = 11.503$ (8) Å, $b = 15.635$ (3) Å, $c = 12.060$ (8) Å, $\beta = 97.59$ (6)°, and $Z = 4$. **4** has space group $P\bar{1}$, with $a = 13.512$ (4) Å, $b = 12.455$ (3) Å, $c = 8.190$ (1) Å, $\alpha = 105.61$ (2)°, $\beta = 95.18$ (3)°, $\gamma = 101.36$ (2)°, and $Z = 2$. The geometry of the dication of **3** can be described as a bent-planar conformation around the C^+-O-C^+ linkage, one imidazolinium ring being tilted against this plane by 42.4°, the other one by 47.2°. For dication **4**, these values are 41.3° and 17.1°, respectively. The possibility of orbital overlap between the two carbenium π systems in each dication and the lone pairs of the bridging oxygen atom is discussed.

Despite the great variety and ubiquitous nature of carbocations, until recently bis(carbenium) ions linked by a single atom **1** were unknown. Dication ethers **2** represent

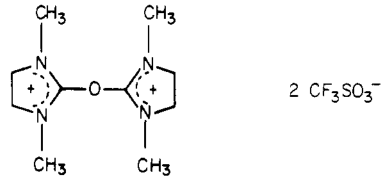
$$\underset{\mathbf{1}}{R^+\text{-}A\text{-}R^+\cdot 2X^-} \qquad \underset{\mathbf{2}}{R^+\text{-}O\text{-}R^+\cdot 2CF_3SO_3^-}$$

the first member of this novel class of compounds that have become easily available by the reaction of activated carbonyl compounds, such as $(4n + 2)$ π-annulenones, ureas, pyridones, etc., with triflic anhydride.[2] These dications owe their stability to an efficient charge delocalization which reduces Coulombic repulsion between the two positive charges. Interaction of the two cationic centers with the lone-pair electrons of the central oxygen atom in **2** is expected to determine the inversion and rotational barriers around the central COC bonds as well as the overall structure of the dications. Recent calculations,[3] by both semiempirical and ab initio methods, predict very low rotational barriers, such that at room temperature, these dictions are rotating freely. This is in agreement with ^1H and ^{13}C NMR spectra; however, because of experimental restrictions imposed by the low solubilities of these salts, no attempts could be made to freeze out rotamers or invertomers of the dication ethers.

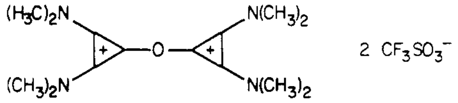
Depending on the particular cationic system, different conformations of **2** around the central COC bonds are predicted,[3] the preferred ones being bent-planar (**2a**), bent-perpendicular (**2b**), linear-planar (**2c**), and linear-perpendicular (**2d**). Considering only electronic stabilization of the conformers, the energy levels of **2a**-**2d** are very close to each other, so that the most stable conformation may be governed by local steric interactions in the particular conformation.

2a **2b** **2c** **2d**

Precise structural information is one of the most important unanswered questions about these novel dication ether salts. In particular the exact geometry and its concommitant effect upon possible cross-conjugation are important aspects for potential chemistry and use of these salts. Hence in order to determine to exact geometry and the preferred conformation in the solid state and to check on the validity of the theoretical predictions,[3] we undertook detailed X-ray studies on dications **3** and **4** and wish to report our results in this paper. Simultaneously and independently a similar study was undertaken by Childs and co-workers[5] on dication ether **5** previously prepared and described by us.[2]



3



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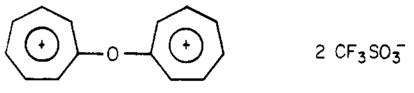

5

Experimental Section

Materials. The synthesis of **3** has been described before.[2b] Triflic anhydride[6] was redistilled from P_2O_5 just prior to use. As both **3** and **4** are moisture sensitive, all synthetic work was done under an argon atmosphere. Crystals for the X-ray data collection were selected from a suspension in Nujol and sealed in quartz glass capillaries.

Bis[2,3-bis(dimethylamino)cyclopropenyliumyl] Ether Ditriflate[7] (4). In an argon atmosphere, 0.42 mL (2.5 mmol) of triflic anhydride in 5 mL of CH_2Cl_2 was added dropwise to a

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(1) Dication Ethers and Related Compounds, 2.-1: Maas, G.; Singer, B. *Chem. Ber.* submitted for publication.

(2) (a) Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361-6362. (b) Stang, P. J.; Maas, G.; Smith, D. A.; McCloskey, J. A. Ibid. **1981**, *103*, 4837-4845.

(3) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1981**, *103*, 4258-4260.

(4) If the assumption is made that the central oxygen is sp^2 hybridized, the two oxygen lone pairs are energetically different; hence depending on which of the lone pairs interacts with an adjacent cationic center, different energy levels of the dication ether in each particular conformation result.

(5) Childs, R. F.; Faggiani, F.; Lock, C. J. L.; Rogerson, C. V. *J. Org. Chem.* Following paper in this issue. We thank Professor Childs for exchange of information and discussions prior to publication.

(6) Stang, P. J.; Dueber, T. E.; *Org. Synth.* **1974**, *54*, 79-84.

(7) This experiment was done by P. Sebald at Kaiserslautern.

0022-3263/83/1948-3038$01.50/0

Table I. Crystal Data for 3 and 4

	3	4
formula	$C_{12}H_{20}F_6N_4O_7S_2$	$C_{16}H_{24}F_6N_4O_7S_2$
fw	510.4	562.5
cryst dimens, mm	0.46 × 0.38 × 0.25	0.44 × 0.33 × 0.11
a, Å	11.503 (8)	13.512 (4)
b, Å	15.635 (3)	12.455 (3)
c, Å	12.060 (8)	8.190 (1)
α, deg	90.0	105.61 (2)
β, deg	97.59 (6)	95.18 (3)
γ, deg	90.0	101.36 (2)
space group	$P2_1/c$	$P\bar{1}$
Z	4	2
d_{calcd}, g·cm^{-3}	1.577	1.452
μ(Mo Kα) cm^{-1}	3.44	2.96

solution of 0.700 g (5.0 mmol) of 2,3-bis(dimethylamino)cyclopropenone[8] in 15 mL of CH_2Cl_2, cooled to 0 °C. Upon addition of anhydrous ether, a white precipitate separated, from which 0.900 g (64%) of 4 was obtained after recrystallization from acetonitrile/ether: mp 171 °C dec; IR (KBr) 1980 w, 1640 vs, 1492 m, 1413 s, 1394 s, 1265 vs, 1223 s, 1152 s, 1033 vs, 642 vs cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.30 s. Anal. Calcd for $C_{16}H_{24}F_6N_4O_7S_2$: C, 34.16; H, 4.30; N, 9.96. Found: C, 34.0; H, 4.27; N, 10.0.

2,3-Bis(dimethylamino)-1-hydroxycyclopropenylium Triflate[7] (6). A solution of 0.1 mL of trifluoromethanesulfonic acid in 5 mL of CH_2Cl_2 was added to a solution of 0.100 g of 2,3-bis(dimethylamino)cyclopropenone[8] in 5 mL of CH_2Cl_2. Upon addition of ether, a white crystalline solid precipitated, which after filtration and washing with ether yielded 0.095 g (45%) of 6, mp 70 °C. The compound readily takes up 0.5 mol of water. IR (KBr) ca 3000–2100 w, 1592, 1540, 1420, 1410, 1284, 1230, 1163, 1032, 641 (all s) cm^{-1}; ^{1}H NMR (CD_3CN) δ 3.09 (s, NMe_2), 3.17 (s, OH). Anal. Calcd for $C_8H_{13}F_3N_2O_4S$: C, 33.11; H, 4.52; N, 9.65. Found: C, 32.60; H, 4.64; N, 9.9.

X-ray Analysis of 3. A suitable crystal was sealed in a glass capillary. Pertinent crystal data are given in Table I. Lattice constants were determined from the diffractometer settings of 25 reflections, as an average over 31 measurements during the data collection. Data were obtained on a Philips PW 1100 four-circle diffractometer, using Mo K α radiation (scan speed 0.03°/s, scan width (1. + 0.35 tan Θ)°, Θ/2Θ scan). In the range $0 < \Theta \leq 21°$, 2307 unique reflections were measured. Three reference reflections (420, 080, 004) were monitored every hour; the intensities diminished to 93%, 92%, and 92%, respectively. This intensity loss was corrected linearly for all data. The structure was solved with MULTAN77[9] (361 E's > 1.40, three signpermuting reflections and four $\sum 1$ reflections in starting set). In the progress of refinement, hydrogen positions were partly localized in a difference Fourier map and partly calculated. In the final stages, all heavy atoms were refined anisotropically, hydrogen atoms isotropically with the fixed B value of their heavy neighbor atom. When 1600 reflections with $F_o > 3\sigma(F_o)$ and unit weights and refining 337 variables were used, the procedure converged at $R = 0.0784$, $R_w = (\sum w \cdot \Delta^2 F / \sum F_o^2)^{1/2} = 0.0694$.[9] No shift in positional parameters was larger than 0.23 times the corresponding esd at this point. Scattering factors were from the International Tables, Vol. III, in the representation of Fischer and Onken.[10]

The somewhat poor agreement factors are due in part to the high thermal motion of the triflate groups, for which the Gaussian ellipsoid model of thermal vibration is probably not adequate.

Table II. Coordinates (×10^4) of the Non-Hydrogen Atoms of 3[a]

atom	x/a	y/b	z/c
S1	2561 (2)	1291 (2)	4056 (2)
S2	7266 (2)	1382 (2)	10071 (2)
F1	816 (8)	380 (8)	4335 (8)
F2	529 (7)	1108 (8)	2925 (9)
F3	1582 (10)	45 (7)	2976 (11)
F4	8218 (8)	2784 (6)	9591 (10)
F5	6364 (6)	2871 (5)	9607 (7)
F6	7532 (7)	2814 (6)	11099 (8)
O1	2676 (5)	1493 (4)	7423 (5)
O2	2943 (9)	1547 (9)	3052 (9)
O3	3299 (7)	706 (5)	4647 (7)
O4	2155 (9)	1932 (7)	4670 (11)
O5	8375 (6)	1106 (5)	10585 (7)
O6	6336 (6)	1242 (6)	10722 (9)
O7	7057 (11)	1166 (8)	8983 (8)
N1	897 (6)	1492 (5)	8030 (8)
N2	2415 (7)	1099 (5)	9255 (6)
N3	4539 (5)	1253 (4)	7066 (6)
N4	3412 (6)	117 (4)	7148 (6)
C1	2032 (7)	1343 (6)	8259 (7)
C2	398 (11)	1363 (9)	9079 (13)
C3	1413 (12)	1074 (8)	9900 (11)
C4	259 (9)	1795 (8)	6998 (12)
C5	3607 (10)	1055 (7)	9746 (9)
C6	3532 (7)	947 (5)	7232 (7)
C7	5273 (8)	548 (6)	6776 (8)
C8	4513 (9)	−236 (6)	6857 (9)
C9	4879 (9)	2149 (6)	7073 (9)
C10	2312 (9)	−355 (7)	6967 (8)
C11	1317 (11)	676 (8)	3512 (11)
C12	7364 (9)	2514 (8)	10055 (10)

[a] Esd values are given in parentheses.

Final heavy atom coordinates are given in Table II. Hydrogen positions and a list of structure factors have been deposited in supplementary material.

X-ray Analysis of 4. The compound crystallized in transparent, colorless thin columns. A crystal coated with Nujol was enclosed in a quartz glass capillary. Crystal data are listed in Table I. Lattice constants were obtained from the diffractometer angles of 21 reflections with $15.0° \leq 2\Theta \leq 23.5°$. Intensity data were collected on a Philips PW 1100 diffractometer (Θ/2Θ scan, scan width (1.20 + 0.35 tan Θ)°, scan speed 0.03°/s^{-1}). In the range $1.50° \leq \Theta \leq 23.80°$, 3943 independent reflections with indices $\pm h, \pm k, +l$ were measured. Three reference reflections which were monitored every hour, suffered a loss of intensity, which amounted to 2.3% at the end. To account for this, a linear correction was made. No absorption correction was applied. From intensity statistics, a centrosymmetric intensity distribution was evident, and space group $P\bar{1}$ was later confirmed by a successful refinement.

The phase problem was solved with MULTAN77,[9] using 450 E's > 1.58 and 5000 out of 5197 phase relationships. With 1603 reflections having $F_o > 4\sigma(F_o)$, the structure was refined by block-diagonal least-squares methods[9] (one atom per block). Hydrogen atoms were located in a ΔF map and included in the structure-factor calculation with isotropic temperature factors (B = 7.0 Å^2). After three cycles in which the "heavy" atoms were refined anisotropically, an R value of 0.092 was obtained. Because of the high vibrational amplitudes of the fluorine and oxygen atoms in both anions and because of the presence of some unassigned peaks (with electron density somewhat higher than for hydrogens) in the anion regions of a ΔF map, disorder of the anions was assumed. According to this, a disordered triflate group rotated by 60° around the S1–C15 bond (staggered conformation) with an occupancy factor of 0.12 and B = 7.0 Å^2 was included in the refinement. Spurious peaks in the region of the second triflate goup, however, did not fit an acceptable geometry and were not taken into account. Three high-indexed reflections ($\bar{9}\bar{6}7$, $\bar{7}47$, $\bar{7}08$) with exceedingly high $w \cdot \Delta^2 F$ were excluded from refinement and the structure factor calculation, thus leaving 1600 reflections for 335 varied parameters (hydrogen atoms were held constant). The final R values were $R = 0.0905$, $R_w = (\sum w \cdot \Delta^2 F / \sum w F_o^2)^{1/2} = 0.0866$, where $w = 1/(\sigma^2 + 0.00625 F_o^2)$.

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[8] (a) Weiss, F.; Hertel, M. University of Erlangen—Nürnberg, unpublished results. (b) Wilcox, C.; Breslow, R. *Tetrahedron Lett.* **1980**, 3241–3242.

[9] The following programs were used: MULTAN77 (Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; and Declerq, J. P.; Universities of York (England) and Louvain (Belgium); BLKLS—A Crystallographic Block-Diagonal Least-Squares Program (Bartlett, M. W.; ETH Zürich (Switzerland); 1972); BLFLS—A modified version (Spilker, J.; Eichhorn, K.; University of Saarbrücken (West Germany)) of the ORFLS program. Also, Johnson's ORTEP program and some smaller programs from Stewart's X-RAY 76 system were used. All calculations were carried out on a TR 440 compouter at the computing center at Kaiserslautern.

[10] Onken, H.; Fischer, K. F. *Z. Kristallogr.* **1968**, *127*, 188.

Table III. Positional Parameters of the Non-Hydrogen Atoms of 4[a]

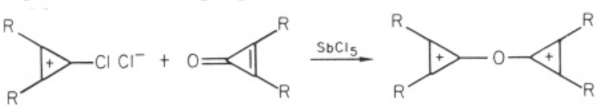
atom	*x/a*	*y/b*	*z/c*
S1	3587 (2)	2593 (3)	2333 (4)
S2	1206 (3)	7282 (3)	4184 (5)
O1[b]	7958 (5)	8419 (5)	2564 (9)
O2[b]	3940 (8)	3027 (8)	1028 (11)
O3[b]	2529 (7)	2170 (9)	2165 (18)
O4	4060 (8)	3379 (8)	3959 (11)
O5	1329 (11)	7099 (9)	2439 (12)
O6	408 (8)	7854 (10)	4500 (17)
O7	1184 (10)	6340 (8)	4775 (13)
F1[b]	3788 (7)	569 (7)	754 (12)
F2[b]	3865 (8)	909 (8)	3437 (12)
F3[b]	5122 (7)	1631 (9)	2320 (17)
F4	2425 (10)	9264 (9)	4921 (15)
F5	2293 (9)	8608 (11)	6957 (11)
F6	3093 (7)	7932 (13)	5159 (18)
N1	5282 (6)	7189 (8)	2508 (11)
N2	7222 (6)	5569 (7)	3032 (11)
N3	9030 (6)	6460 (6)	−657 (10)
N4	10443 (6)	9385 (6)	1560 (10)
C1	6227 (7)	7094 (8)	2617 (12)
C2	6979 (7)	6471 (8)	2825 (12)
C3	7231 (7)	7529 (8)	2633 (13)
C4	9089 (6)	7433 (7)	446 (11)
C5	9631 (7)	8568 (7)	1347 (11)
C6	8702 (7)	8153 (7)	1650 (12)
C7	5042 (9)	8227 (11)	2269 (17)
C8	4460 (8)	6231 (12)	2546 (17)
C9	6452 (11)	4569 (11)	3122 (18)
C10	8294 (9)	5544 (12)	3371 (19)
C11	8087 (9)	5563 (9)	−1142 (15)
C12	9880 (9)	6254 (10)	−1551 (17)
C13	11302 (8)	9218 (9)	678 (16)
C14	10570 (9)	10451 (10)	2959 (16)
C15	4120 (9)	1384 (10)	2228 (16)
C16	2298 (10)	8321 (12)	5408 (18)
O2′[c]	310 (5)	258 (5)	357 (9)
O3′[c]	439 (5)	350 (5)	248 (9)
O4′[c]	303 (5)	212 (5)	85 (9)
F1′[c]	477 (4)	155 (5)	372 (7)
F2′[c]	740 (4)	116 (5)	106 (7)
F3′[c]	353 (4)	35 (4)	209 (7)

[a] For atoms O2′, O3′, O4′, F1′, F2′, and F3′ parameters are $\times 10^3$; for all others they are $\times 10^4$. [b] Occupancy factor 0.88. [c] Occupancy factor 0.12.

Final positional parameters of the non-hydrogen atoms are given in Table III. Hydrogen coordinates and the list of observed and calculated structure factors are deposited as supplementary material.

Results and Discussion

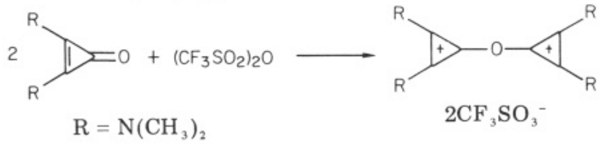
Syntheses and Properties of 4. A dication ether similar to 4 has been prepared before by the reaction in eq (1).[11] For the preparation of 4, however, we chose the reaction of 2,3-bis(dimethylamino)cyclopropenone with trifluoromethanesulfonic anhydride (eq (2)), a general route to these dication ether salts.[2] The ^{1}H NMR spectrum of 4 at room temperature shows only one signal for all protons, in agreement with a dication rotating freely around the COC and N–C(ring) bonds.[12] At lower temperatures, the somewhat broadened signal shows a coalescence phenomenon and splits into two sharp singlets, which at 253 K are 7.5 Hz apart. This dynamic behavior is well-known for dimethylamino-substituted cyclopropenylium systems[13] and is caused by hindered rotation around the N–C(ring) partial double bond as expressed by the resonance structures **4a** ↔ **4b** ↔ **4c**. A $\Delta G^{\ddagger}$ (298) = 15.4 ± 0.2 kcal·mol^{-1} was calculated for this process.[14] Dication ether 4 is readily hydrolyzed to give the hydroxycyclopropenylium cation 6 also prepared independently by reaction of the cyclopropenone with triflfuoromethanesulfonic acid. Contrary to other protonated (4*n* + 2) π-annulenones,[2] 6 is a rather weak acid, and no neutral ketone can be detected in the NMR spectrum of the aqueous acetonitrile solution of 6. The ketone is, however, formed quantitatively in an alkaline medium.



(1)

R = N(i-C$_3$H$_7$)$_2$

$SbCl_6^-$



(2)

R = N(CH$_3$)$_2$

$2CF_3SO_3^-$

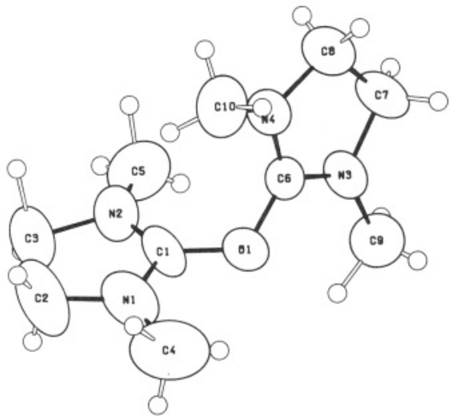


Figure 1. ORTEP plot of **3**. Thermal ellipsoids represent a 50% probability.

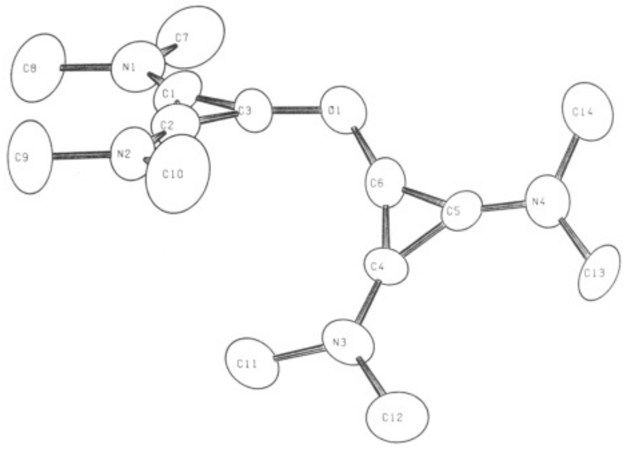
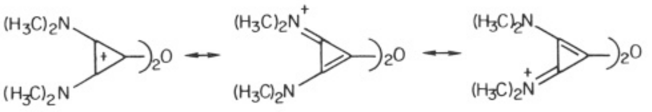


Figure 2. ORTEP plot of **4**.



4a **4b** **4c**

Structures of 3 and 4. A. The Dications. Figures 1 and 2 show the dication portion of **3** and **4**, respectively.

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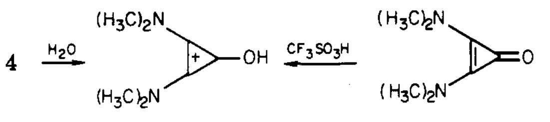
[11] Priesner, C. Ph. D. Thesis, University of Müchen, 1977.

[12] Of course, this observation may also have other reasons. A static conformation like **2c** or **2d** and freely inverting **2a** or **2b** would all lead to the equivalence of all methyl groups (assuming freely rotating NMe$_2$ groups).

[13] Yoshida, Z.-I. *Top. Curr. Chem.* **1973**, *40*, 47–72.

[14] The equation $\Delta G^{\ddagger} = 4.57T_c(9.97 + \log (T_c/\delta\nu))$ was used, where T_c is the coalescence temperature, and $\delta\nu = \nu_A - \nu_B$ in the slow exchange spectrum.



6 $CF_3SO_3^-$

The full list of bond distances and angles is given in Tables IV and V. The charge delocalization over the formamidinium system in **3** becomes evident from the C1–N and C6–N bond lengths (average 1.30 Å), which are much shorter than the N–CH_2 single bonds (average 1.47 Å) in both rings and very close to a C=N double bond (1.29 Å).[15] Also the average N–C(methyl) bond is shorter (1.44 Å) than the usual N–C single bond distance of 1.47 Å.[15] Virtually the same values have been found in the *N*-methylurenium cation[16] and other O-protonated or O-alkylated ureas.[17] As a consequence of sp^2 hybridization and π conjugation in the formamidinium (NCN) system, the five-membered rings are close to planarity, thus forcing the hydrogen atoms of the CH_2 groups into nearly eclipsed positions. No ring atom deviates by more than 0.017 Å from the least-squares plane defined by all five atoms of the respective ring. On the other hand, all four methyl groups are tilted out of the plane of the formamidinium system to which they are bonded, in the direction of the less crowded molecular site. This deviation from the plane is small for the C4 and C9 methyl groups (0.04 and 0.05 Å), yet significant, as the standard deviations in the atomic coordinates amount to only 0.009–0.014 Å. However, C5 deviates by 0.25 Å from the plane defined by the N2–C1–N1 fragment and points in the direction away from the second heterocycle, and C10 is displaced by 0.39 Å from the N4–C6–N3 plane such that the C5–C10 distance becomes longer. These distortions around the N2 and N4 nitrogen atoms tend to minimize the steric interaction between the C5 and C10 methyl groups. The closest intramolecular distances between the four methyl groups are C5–C10 4.122 ± 0.015 Å, C4–C10 4.110 ± 0.017 Å, C5-C9 4.087 ± 0.015 Å. The van der Waals radius of the methyl group is about 2.0 Å,[18] so the actual conformation of dication ether **3** together with the distortions around N2 and N4 allows a symmetrical distribution of nonbonded interactions between the methyl groups.[19]

Charge delocalization according to resonance **4a** ↔ **4b** ↔ **4c** is also evident from the bond lengths in dication ether **4**. The average N–C(ring) distance is 1.29 Å and compares well with the corresponding value of **3** (1.30 Å) or the *N*,*N*-dimethylisopropylideneiminium ion[20] (1.302 Å) and the expected C=N double bond length (1.29 Å).[15] Similar values have also been found in other dimethylamino-substituted cyclopropenylium cations[21,22] and in a bis(dimethylamino)cyclopropenylidene–Pd complex[23] for which contributions from resonance structures like **4b** and **4c** were also invoked. The bond length asymmetry in the three-membered rings with one long and two short distances may, in part, also be assigned to pronounced contributions of resonance structures **4b** and **4c** to the overall bonding state of the cyclopropenylium systems. It should, however, be mentioned that the geometry of three-membered rings is also influenced by conjugative interactions of the substituents with the in-plane Walsh orbitals of the ring.[24] It has been predicted from ab initio calculations that OH, like other lone-pair substitutents, will cause a shortening of the adjacent bonds and a lengthening of the distal bond in a cyclopropane ring.[25] it seems that this theory also holds for cyclopropenes and cyclopropenylium salts, even though data for such systems bearing donor subsitutents are sparse.[24] The bond length asymmetry in the dication ether **4** may also be partly caused by the oxygen substituent.

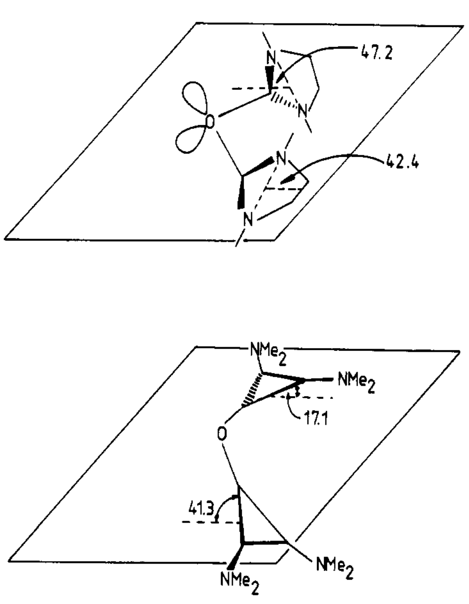


Figure 3. Angles between planes in cations **3** (top) and **4** (bottom). For the direction of the lone pairs on oxygen, see discussion.

In tris(dimethylamino)cyclopropenylium cations, it has been found that the nitrogens and methyl carbons deviate significantly from the plane of the three-membered ring in a fashion so as to reduce steric interactions between the methyl groups.[21,22] In ion **4** oxygen atom O1 and nitrogens N1, N2, N3 are displaced by less than 1.5 standard deviations from the plane of the ring they are attached to; only N4 deviates by 0.05 Å, in the direction away from the second ring. For the methyl carbons C7–C14 displacements by 0.01, –0.05, –0.03, 0.16, 0.13, –0.07, 0.01, –0.10 Å (signs refer to the respective ring plane) are observed. Similar to ion **3** discussed above, the high deviations of C10 and C11 are in opposite directions and thereby diminish steric interaction between both methyl groups. However, this contact is markedly shorter (3.69 ± 0.02 Å) than the contacts between methyl groups in **3** (see above). Similar short distances are observed between other methyl carbons not belonging to the same ring: C10–C12, 3.79 ± 0.02 Å; C8–C11, 3.60 ± 0.016 Å.

Of specific interest to the present study is the geometry and conformation around the central C–O–C bonds of the

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(18) Reference 15, Chapter 24.

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(24) Allen, F. H. *Tetrahedron* **1982**, *38*, 645–655; *Acta Crystallogr., Sect. B* **1980**, *B36*, 81–96.

(25) Durmaz, S.; Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942–6945. This work points out that neither π donation by the lone pair nor the σ-acceptor character of a substituent bring about the changes in bond geometry. "Increased ring strain caused by local effects such as changes in hybridization" is considered to be the actual governing factor.

Table IV. Bond Lengths (Å) and Bond Angles (deg) in 3[a]

cations				anions			
C1-O1	1.349 (10)	C6-O1	1.345 (9)	S1-O2	1.400 (9)	S2-O5	1.411 (7)
C1-N1	1.319 (11)	C6-N3	1.294 (10)	S1-O3	1.381 (8)	S2-O6	1.425 (8)
C1-N2	1.281 (12)	C6-N4	1.307 (10)	S1-O4	1.364 (9)	S2-O7	1.345 (9)
C2-N1	1.471 (15)	C7-N3	1.459 (11)	S1-C11	1.776 (14)	S2-C12	1.773 (13)
C2-C3	1.498 (12)	C7-C8	1.516 (14)	C11-F1	1.297 (15)	C12-F4	1.265 (12)
C3-N2	1.473 (13)	C8-N4	1.466 (11)	C11-F2	1.269 (16)	C12-F5	1.329 (13)
N1-C4	1.439 (16)	N3-C9	1.453 (12)	C11-F3	1.240 (17)	C12-F6	1.334 (15)
N2-C5	1.422 (14)	N4-C10	1.456 (12)				
C1-O1-C6	120.3 (7)			O4-S1-O3	115.9 (7)	O7-S2-O6	116.7 (8)
N2-C1-N1	117.2 (8)	N3-C6-N4	116.3 (7)	O4-S1-O2	115.4 (9)	O7-S2-O5	112.7 (6)
N2-C1-O1	126.8 (7)	N3-C6-O1	118.9 (7)	O3-S1-O2	113.2 (7)	O6-S2-O5	114.4 (5)
N1-C1-O1	116.0 (8)	N4-C6-O1	124.8 (7)	O4-S1-C11	106.3 (6)	O7-S2-C12	103.1 (1)
N1-C2-C3	104.5 (9)	N3-C7-C8	103.8 (7)	O3-S1-C11	104.0 (6)	O6-S2-C12	102.3 (5)
N2-C3-C2	103.8 (9)	N4-C8-C7	103.6 (7)	O2-S1-C11	99.5 (6)	O5-S2-C12	104.8 (5)
C1-N1-C4	128.1 (9)	C6-N3-C9	127.0 (7)	F3-C11-F2	109.8 (1.4)	F4-C12-F5	111.1 (1.0)
C1-N1-C2	106.5 (9)	C6-N3-C7	108.4 (7)	F3-C11-F1	106.2 (1.3)	F4-C12-F6	106.0 (1.1)
C4-N1-C2	125.2 (9)	C9-N3-C7	124.5 (7)	F2-C11-F1	105.1 (1.2)	F5-C12-F6	104.2 (9)
C1-N2-C5	126.7 (8)	C6-N4-C10	126.5 (7)	F1-C11-S1	109.2 (1.0)	F4-C12-S2	113.1 (8)
C1-N2-C3	107.9 (8)	C6-N4-C8	107.9 (7)	F2-C11-S1	113.6 (1.0)	F5-C12-S2	111.8 (9)
C5-N2-C3	123.9 (9)	C10-N4-C8	122.3 (7)	F3-C11-S1	112.5 (1.0)	F6-C12-S2	110.1 (8)

[a] Numbers in parentheses are esd values.

Table V. Bond Distances (Å) and Bond Angles (deg) in 4[a]

cations				anions			
C1-C2	1.419 (14)	C4-C5	1.418 (12)	S1-O2	1.402 (9)	S2-O5	1.416 (11)
C1-C3	1.356 (13)	C4-C6	1.361 (12)	S1-O3	1.403 (9)	S2-O6	1.411 (11)
C2-C3	1.349 (13)	C5-C6	1.331 (12)	S1-O4	1.428 (9)	S2-O7	1.381 (9)
C3-O1	1.346 (11)	C6-O1	1.348 (11)	S1-C15	1.779 (13)	S2-C16	1.771 (14)
C1-N1	1.302 (12)	C4-N3	1.285 (11)	C15-F1	1.324 (15)	C16-F4	1.324 (18)
N1-C7	1.451 (15)	N3-C11	1.462 (13)	C15-F2	1.321 (14)	C16-F5	1.223 (16)
N1-C8	1.471 (15)	N3-C12	1.445 (13)	C15-F3	1.318 (15)	C16-F6	1.274 (16)
C2-N2	1.280 (12)	C5-N4	1.304 (11)				
N2-C9	1.481 (14)	N4-C13	1.441 (14)				
N2-C10	1.458 (14)	N4-C14	1.470 (14)				
C3-O1-C6	116.0 (7)						
C1-C2-C3	58.6 (7)	C4-C5-C6	59.2 (6)	O4-S1-O3	115.6 (8)	O7-S2-O6	117.0 (8)
C2-C3-C1	63.3 (7)	C5-C6-C4	63.6 (6)	O4-S1-O2	109.1 (6)	O7-S2-O5	114.9 (7)
C3-C1-C2	58.1 (7)	C6-C4-C5	57.2 (6)	O3-S1-O2	116.6 (7)	O6-S2-O5	208.6 (8)
C1-C3-O1	147.6 (9)	C4-C6-O1	152.7 (8)	O4-S1-C15	103.6 (6)	O7-S2-C16	105.2 (7)
C2-C3-O1	149.1 (9)	C5-C6-O1	143.7 (8)	O3-S1-C15	105.0 (6)	O6-S2-C16	103.0 (6)
C3-C1-N1	150.7 (10)	C6-C4-N3	151.9 (8)	O2-S1-C15	105.4 (6)	O5-S2-C16	106.8 (7)
C2-C1-N1	151.2 (9)	C5-C4-N3	150.9 (8)	F3-C15-F2	109.6 (11)	F4-C16-F5	107.2 (13)
C1-N1-C7	119.5 (9)	C4-N3-C11	121.6 (8)	F3-C15-F1	104.7 (12)	F4-C16-F6	106.6 (13)
C1-N1-C8	120.2 (9)	C4-N3-C12	120.4 (8)	F2-C15-F1	105.9 (10)	F5-C16-F6	106.9 (14)
C7-N1-C8	120.2 (9)	C11-N3-C12	117.8 (8)	F1-C15-S1	112.0 (9)	F4-C16-S2	111.2 (10)
C1-C2-N2	150.2 (9)	C4-C5-N4	147.8 (9)	F2-C15-S1	105.9 (10)	F5-C16-S2	115.0 (10)
C3-C2-N2	151.2 (9)	C6-C5-N4	152.8 (9)	F3-C15-S1	112.7 (8)	F6-C16-S2	109.5 (11)
C2-N2-C9	122.3 (9)	C5-N4-C13	122.5 (8)				
C2-N2-C10	120.1 (8)	C5-N4-C14	118.9 (8)				
C9-N2-C10	117.3 (9)	C13-N4-C14	117.8 (8)				

[a] Esd's in parentheses.

dication ethers **3** and **4**. The C–O bond lengths are equal within the error limits, with an average of 1.347 Å in both ions. These values are in the range of 1.33–1.38 Å found for the C(sp^2)–O bond in other ethers.[26,27] The C–O–C angles in **3** (120.3 ± 0.7°) and **4** (116.0 ± 0.7°) differ significantly, but comparison with other C(sp^2)–O–C angles shows that this value may vary in a wide range (ca. 114°–121°).

For the conformation around the ether linkage it is best to check the angle between the central C^+–O–C^+ plane and the planes of the rings attached to it (Figure 3 and Table G of the supplementary material). It can be seen that in **3** one formamidinium (NCN) system is rotated by 42.4° out of the C1–O1–C6 plane, and the second by 47.2° in the opposite direction. In **4**, one cyclopropane ring is tilted by 41.3° against the C3–O1–C6 plane, the second one by only 17.1°. Thus, the cation of **3** can be described as having a bent–perpendicular conformation around the C^+–O–C^+ linkage, but not in a sense visualized by formula **2b**, which implies that one ring and the C–O–C unit lie in the same plane. This conformation may be rationalized by the possibility of each of the two formamidinium π systems overlapping with a different lobe of the two lone pairs of sp^3-hybridized oxygen (see top of Figure 3). The exact hybridization of oxygen in ethers (i.e., sp^2 or sp^3 hybridized) is an unanswered question. The conformational similarity between ethers and alkanes has been taken as an indication for sp^3 hybridization of the oxygen.

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(26) Brown, J. N.; Meyers, E. A. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1178–1183.

(27) For structural parameters of the ether group, see: Goldberg, I. In "The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues"; Patai, S., Ed.; Wiley-Interscience: New York, 1980; Supplement E, pp 175–180.

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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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[28] Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 654–667.

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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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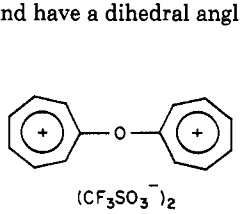
The X-ray crystal structure of ditropenyliumyl ether bis(trifluoromethanesulfonate) $[(C_7H_6^+)_2O][CF_3SO_3]^-{}_2$, has been determined. The crystals are orthorhombic, *Pcnb* (No. 60), with cell dimensions a = 7.985 (2) Å, b = 18.571 (6) Å, c = 12.984 (3) Å, and Z = 4. Intensities were measured with 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.


$(CF_3SO_3^-)_2$

1

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.

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