The Crystal Structure of the Dication Ether Salt $\{[(Me_2N)_2C]_2O\}^{2+}$ $(CF_3SO_3^-)_2$. Bonding and Charge Delocalization in Ethers

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The crystal structure of the title compound has been determined from 2279 independent reflections measured at −135 °C on a CAD 4 diffractometer. The salt crystallizes in the monoclinic space group $P2_1/n$ with $a=8.246(1)$, $b=23.830(3)$, $c=11.371(2)$ Å, $\beta=101.65(1)°$ and $Z=4$.

The structure was solved by direct methods and refined by fullmatrix least-squares methods to $R=0.052$. The dication ether is bent with a central C3−O−C4 angle of 122.4(4)°. All four nitrogen atoms as well as C3 and C4 appear to be completely sp^2 hybridized, and this is in agreement with delocalization of the positive charge on these atoms. The corresponding C---N and C---O bond lengths have average values of 1.311(9) and 1.366(4) Å. Due to steric interaction of the methyl groups, and possibly also to electronic effects, the cation is far from planar.

Alternative schemes for π-bonding in the central C−O−C system in dication ethers are discussed. These novel ethers are also compared to neutral aromatic and aliphatic ethers.

In previous papers[1,2] we have shown that trifluoromethanesulfonic anhydride reacts with hexamethylphosphoramide to give the diphosphonium salt $[(Me_2N)_3P-O-P(NMe_2)_3]^{2+}$-$(CF_3SO_3^-)_2$ with a linear P−O−P sequence. The dication was stabilized by delocalization of the positive charge over the six nitrogen atoms and the P−O−P group.[2] Similar salts were prepared from triphenylphosphine oxide[1] and later from other phosphoric amides.[3]

We have recently extended our work to include the quite analogous reactions of amides and ureas with trifluoromethanesulfonic anhydride.[4] Here the reaction products are dication ether salts. With ureas they are of the type $[(R_2N)_2C-O-C(NR_2)_2]^{2+}(CF_3SO_3^-)_2$.[4] In addition to the compounds reported in Ref. 4, we have prepared three salts $[(R_1R_2C)_2O]^{2+}(CF_3SO_3^-)_2$ where $R_1=Me_2N$, $R_2=H$; $R_1=H_2N$, $R_2=MeO$ and $R_1R_2C=$
$\overline{CH_2CH_2CH_2C-N}-Me$. Presently we are investigating cyclization reactions using dicarbonyl and diphosphoryl compounds; $e.g.$ $Me_2NC(O)CH_2CH_2C(O)NMe_2$ gives the cyclic dication ether salt $[Me_2NC-\overset{\circ}{\overline{CH_2CH_2C}}NMe_2]^{2+}(CF_3SO_3^-)_2$. Quite independently Maas and Stang also prepared a series of non-cyclic dication ether salts,[5,6] and structures of such salts have just been solved by their group[7] and by R. Childs et al.[8]

$$1 \qquad\qquad\qquad 2 \qquad\qquad\qquad 3$$

Their structural results show a bent, central C−O−C group in the dicarbonium ions *1−3*.

The above ions are non-planar, the main deviations from planarity may be described in terms of rotation around the C−O bonds.[7,8] Theoretical calculations show surprisingly low barriers for the C−O rotations (20−50 kJ/mol),[9] and ^{13}C and ^{1}H NMR indicate that the ions rotate freely around the C−O bonds at room temperature.[7]

In the present investigation, we chose to examine the structure of the dication ether trifluoromethanesulfonate, *4*.

It differs from the dication ethers *1−3* by not containing rings. It should therefore be more flexible. Thus ^{13}C and ^{1}H NMR spectra indicate that there is free rotation around both C−O and N−C(O) bonds in *4*.[4] The single methyl signal at room temperature is split into

$$4$$

two sharp signals at −39 °C (coalescence temp. −26 °C), probably indicating that the C---N rotation is slowed first, since this bond has the highest rotation barrier.[9] Investigation of rotation barriers for N---C bonds in dithiocarbamates and O---C bonds in xanthates also indicates a higher rotation barrier in the first type of bond than in the latter.[10] With all types of rotations (and inversions) frozen, four different methyl signals should be found in such a dication with a C−O−C angle different from 180°.

An important aspect of the stability of these novel dicarbonium ions is the delocalization of charge, especially the possibility of conjugation across the central oxygen atom. With two dimethylamino groups bonded to each carbon in the central C−O−C system, steric interactions will be important in determining both the shape and the extent of cross conjugation in such a dicarbonium ion.

EXPERIMENTAL

The preparation of the crystals has been reported elsewhere.[4] Intensity data and data for determination of unit cell parameters were obtained on an Enraf-Nonius CAD 4 diffractometer at −135 °C. The crystal used had approximate dimensions 0.22×0.27×0.10 mm^3. Unit cell parameters were found from least-squares refinement of the setting angles of general reflections with 2θ between 14 and 18°. At −135 °C they are a=8.246(1), b=23.830(3), c=11.371(2) Å, β=101.65(1)°, Z=4, Dx=1.53 g/cm^{-1} and μ(Mo $K\alpha$)=3.19 cm^{-1}. The space group is $P2_1/n$.

Reflection intensities were collected using the omega scan technique with scan width $(1.00+0.35\mathrm{tg}\theta)°$ and graphite monochromated MoKα radiation. The scan rate varied between 1.5 and 10° min^{-1}. Of a total of 3428 unique reflections with $2\theta\leqslant48°$, 2279 were

observed [$I \geq 2\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Data collection and other computer programs used throughout this investigation belong to the Enraf-Nonius Structure Determination Pack, SDP-Plus 1982. For further details the reader is referred to an earlier paper.[2]

STRUCTURE DETERMINATION

The structure of the dication ether salt, (4), was solved by direct methods (MULTAN) and refined by full-matrix least-squares programs. Anisotropic temperature factors were used for all atoms except hydrogen. The function minimized is $\sum w(|F_o| - |F_c|)^2$, the weights correspond to counting statistics plus 2 % of the net intensity ($p = 0.02$).[2] The refinement converged at $R = 0.052$, $Rw = 0.061$ and $S = 1.12$.

A final difference map showed no peaks above 0.4 $e^-/\text{Å}^3$. Observed and calculated structure factors, tables of the final temperature parameters and of atomic coordinates for the hydrogen atoms are available from the authors on request. Coordinates for the other atoms are listed in Table 1. Bond lengths and angles are listed in Table 2. Some best planes as well as interplanar and torsional angles are shown in Table 3.

Table 1. Positional parameters and their estimated standard deviations.

Atom	x	y	z
O	0.1544(4)	0.3275(1)	0.3577(3)
C3	0.1990(5)	0.3826(2)	0.3520(4)
C4	0.2110(5)	0.2948(2)	0.4557(4)
N1	0.2092(5)	0.4142(2)	0.4483(3)
N2	0.2233(4)	0.3984(2)	0.2474(3)
N3	0.3650(5)	0.3007(2)	0.5152(4)
N4	0.1036(5)	0.2580(2)	0.4778(3)
C11	0.3157(7)	0.4641(2)	0.4691(5)
C12	0.1153(6)	0.4023(2)	0.5411(5)
C21	0.2048(6)	0.4565(2)	0.2066(5)
C22	0.2609(7)	0.3590(2)	0.1590(5)
C31	0.4973(6)	0.3237(2)	0.4607(5)
C32	0.4164(6)	0.2847(3)	0.6416(5)
C41	-0.0752(6)	0.2669(2)	0.4429(4)
C42	0.1532(7)	0.2053(2)	0.5417(5)
S1	-0.2434(2)	0.43254(5)	0.2772(1)
C1	-0.3076(8)	0.4649(3)	0.1324(5)
F11	-0.1893(5)	0.4760(2)	0.0777(3)
F12	-0.3733(7)	0.5164(2)	0.1486(5)
F13	-0.4215(4)	0.4352(2)	0.0594(3)
O11	-0.1206(4)	0.4694(2)	0.3408(3)
O12	-0.3910(5)	0.4286(5)	0.3201(4)
O13	-0.1756(6)	0.3798(2)	0.2475(4)
S2	0.4481(2)	0.18973(5)	0.3049(1)
C2	0.3689(7)	0.1185(2)	0.2822(5)
F21	0.2483(5)	0.1093(2)	0.3413(3)
F22	0.4861(5)	0.0808(1)	0.3161(4)
F23	0.3049(4)	0.1083(1)	0.1672(3)
O21	0.5137(5)	0.1923(2)	0.4317(3)
O22	0.3033(4)	0.2236(2)	0.2655(4)
O23	0.5693(4)	0.1923(2)	0.2307(3)

Table 2. Bond lengths (Å) and angles (°) in the dication ether salt.

Cation

C3−O	1.368(5)	C3−O−C4	122.4(4)
C4−O	1.363(5)	O−C3−N1	118.8(4)
C3−N1	1.318(6)	O−C3−N2	114.4(4)
C3−N2	1.300(6)	N1−C3−N2	126.8(4)
C4−N3	1.320(6)	O−C4−N3	119.6(4)
C4−N4	1.306(6)	O−C4−N4	114.1(4)
N1−C11	1.469(6)	N3−C4−N4	126.3(4)
N1−C12	1.457(6)	C3−N1−C11	122.2(4)
N2−C21	1.459(7)	C3−N1−C12	122.5(4)
N2−C22	1.453(7)	C11−N1−C12	115.4(4)
N3−C31	1.466(6)	C3−N2−C21	122.7(5)
N3−C32	1.465(7)	C3−N2−C22	122.7(4)
N4−C41	1.462(6)	C21−N2−C22	114.5(4)
N4−C42	1.468(7)	C4−N3−C31	123.0(4)
C−H (Ave)	0.95(6)	C4−N3−C32	122.2(4)
		C311−N3−C32	114.8(4)
		C4−N4−C41	122.5(4)
		C4−N4−C42	122.5(4)
		C41−N4−C42	115.0(4)

Anion 1

S1−O11	1.422(4)	O11−S1−O12	116.3(2)
S1−O12	1.402(4)	O11−S1−O13	112.7(2)
S1−O13	1.443(4)	O11−S1−C1	104.4(3)
S1−C1	1.799(6)	O12−S1−O13	115.4(3)
C1−F11	1.286(7)	O12−S1−C1	103.3(3)
C1−F12	1.368(8)	O13−S1−C1	102.4(3)
C1−F13	1.325(7)	S1−C1−F11	114.8(4)
		S1−C1−F12	108.2(5)
		S1−C1−F13	112.6(4)
		F11−C1−F12	103.8(6)
		F11−C1−F13	108.6(5)
		F12−C1−F13	108.3(5)

Anion 2

S2−O21	1.435(4)	O21−S2−O22	114.3(2)
S2−O22	1.436(4)	O21−S2−O23	115.1(2)
S2−O23	1.434(4)	O21−S2−C2	103.6(3)
S2−C2	1.818(6)	O22−S2−O23	115.2(2)
C2−F21	1.326(6)	O22−S2−C2	103.2(2)
C2−F22	1.319(6)	O23−S2−C2	103.3(2)
C2−F23	1.330(7)	S2−C2−F21	111.6(4)
		S2−C2−F22	112.0(4)
		S2−C2−F23	111.7(4)
		F21−C2−F22	108.6(5)
		F21−C2−F23	106.2(5)
		F22−C2−F23	106.5(4)

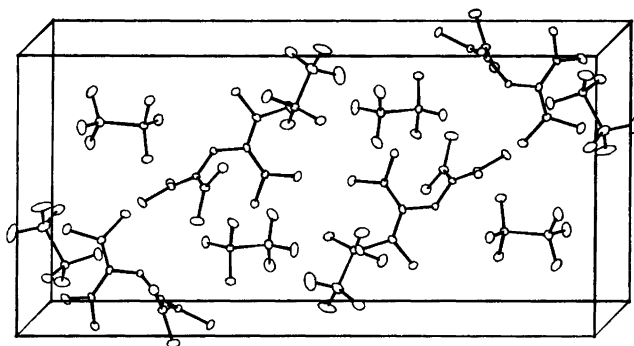*Fig. 1.* The unit cell contents of the dication ether trifluoromethanesulfonate.

RESULTS AND DISCUSSION

The structure of $\{[(Me_2N)_2C]_2O\}^{2+}(CF_3SO_3^-)_2$, (*4*), consists of discrete ions are indicated in the formula. There are no unusually short contacts between the ions. The packing in the unit cell is indicated in Fig. 1.

The structure of the dication ether. In Fig. 2, the structure of the dication ether is shown. From the figure it is seen that the ion has a bent, central C−O−C sequence. The C3−O−C4 angle is 122.4(4)°, indicating possible sp^2 hybridization of oxygen orbitals. Both C3 and C4 as well as the four nitrogen atoms are sp^2 hybridized. Angles centered on these atoms are all near 120° and their sum for each of the atoms is 360° within 0.1°. The appropriate best planes in Table 3 show the near coplanarity of the bonds from these atoms.
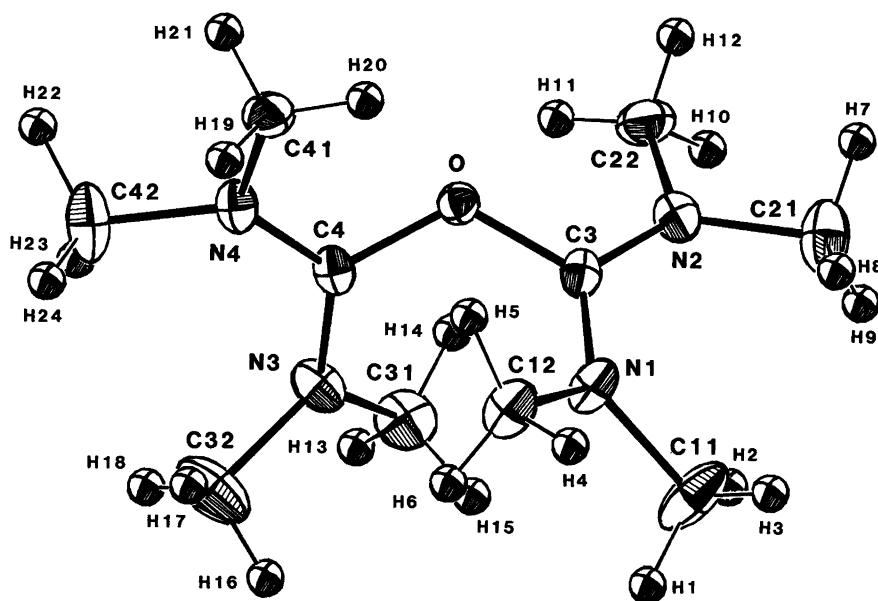

Fig. 2. The structure of the dication ether, as viewed along the normal to the central C−O−C plane.

Table 3. Best planes and dihedral and torsional angles in the cation.[a]

No. of plane	Atoms included	Dihedral angles (°)		Δ[b]
1	O, C3, C4	1–2	140.6 (=180−39.4)	0
2	O, C3, N1, N2	1–3	36.1	0.008
3	O, C4, N3, N4	2–3	114.4	0.015
4	C3, N1, C11, C12	2–4	26.3	0.002
5	C3, N2, C21, C22	2–5	23.0	0.020
6	C4, N3, C31, C32	3–6	25.5	0.001
7	C4, N4, C41, C42	3–7	25.7	0.006

Torsional angles

C4, O, C3, N1	−40.2	O, C3, N2, C21	154.3
C4, O, C3, N2	141.4	O, C3, N2, C22	−21.7
C3, O, C4, N3	−37.5	O, C4, N3, C31	−23.9
C3, O, C4, N4	141.4	O, C4, N3, C32	155.9
O, C3, N1, C11	154.6	O, C4, N4, C41	−27.5
O, C3, N1, C12	−25.7	O, C4, N4, C42	153.7

[a] Distances (Å) from the central O, C_3, C_4 plane: N1, −0.75; N2, 0.74; N3, 0.70; N4, −0.68; C11, −0.43; C12, −1.94; C21, 0.49; C22, 1.83; C31, 1.86; C32, 0.37; C41, −1.81; C42, −0.38. [b] Δ represents maximum distance (Å) of atoms included from the planes.

The dication ether, *4*, is far from planar, even if the methyl groups are ignored. This is mainly due to steric interactions between the methyl groups, and this effect is greater with a bent as compared to a linear C−O−C group. Deviations from planarity can be described in terms of rotations around the O−C and N−C(O) bonds. Fig. 2 illustrates these effects. There, the cation is viewed along the normal to the plane through the central C3−O−C4 group. From Table 3 it can be seen that the planar OC3N1N2 and OC4N3N4 groups are rotated ca. 38° around the O−C3 and O−C4 bonds so that N1 and N4 are on one side of the C−O−C plane while N2 and N3 are on the other. In addition, all Me_2NC groups (with near planar NC_3 skeletons) are rotated ca. 25° around the N−C(O) bonds so as to minimize methyl-methyl interactions. As a result, neighbour methyl carbons are on different sides of the OCN_2 planes (planes 2 and 3 in Table 3).

The shortest H--H contacts between methyl groups are 2.3 Å. These are found between methyl groups bonded to a common nitrogen atom as well as between the C12 and C41 and between the C22 and C31 methyl groups. Some hydrogen atoms belonging to the last four groups also approach the oxygen atoms closely (H---O=2.3−2.5 Å).

The cation has an approximate C_2 axis through the central oxygen atom and the

Table 4. Selected, average bond lengths (Å) and angles (°), in dication ethers.

Dication ether	C---O	N---C	N−C	∠C−O−C	C−O rot. angles	Ref.
1. $(C_{10}H_{20}N_4O)^{2+}$	1.347	1.300	1.455	120.3	42.4, 47.2	7
2. $(C_{14}H_{24}N_4O)^{2+}$	1.347	1.293[a]	1.460[a]	116.0	41.3, 17.1	7
3. $(C_{14}H_{12}O)^{2+}$	1.356			125.3	33.5, 33.5	8
4. $(C_{10}H_{24}N_4O)^{2+}$	1.366	1.311	1.462	122.4	36.1, 39.4	Present work

[a] The nitrogen atoms in these bonds are only indirectly connected to the C−O−C group.
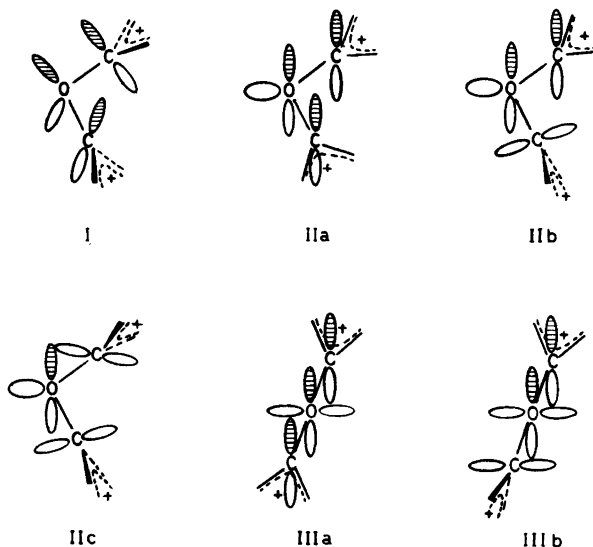
Fig. 3. Orbitals on the central C−O−C group in dication ethers that may participate in π-bonding. The C−O−C group is coplaner with the paper plane and the orbital lobes pointing up from the plane are shaded. Orbitals on carbon atoms are part of π-systems indicated by dashed curves. Hybridization of the oxygen orbitals are I: sp^3, II: sp^2, and III: sp. For further explanation, see text.

symmetry by analogy with diphenyl ethers[11] may be described as twisted with twist angles of ca. 38°. Also *1* and *3* have similar twisted configurations.

Bonding and charge delocalization in the dication ether. Average C−O and N−C(O) bond lengths are 1.366(4) and 1.311(10) Å, respectively. These values may be compared to the sum of the respective covalent radii[12] which are 1.40 and 1.44 Å, the radius for Csp^2 has been given a value of 0.74 Å.[13] From the above, a certain amount of double bonding is indicated, especially in the N−C(O) bonds. In Table 4, a comparison between the known structures of dication ethers are given. For all compounds *1−4*, the central C−O bond lengths have averages between 1.34 and 1.37 Å. This is close to the values found for the central C−O bonds in diaryl ethers[10,14−27] and C(aryl)−O in mixed aryl−alkyl ethers,[27−40] or for (>C=)C−O in unsaturated dialkyl ethers.[41,42] Do these short bond lengths indicate π-bonding in such compounds?

A characteristic feature of the dication ethers is the π-bonding within the two fragments bonded to the central oxygen atom. Such π-systems may interact with oxygen orbitals in three basic ways as indicated in Fig. 3.

I. Oxygen is sp^3-hybridized, the hybrid lone pair orbitals pointing up (shaded) or down relative to the central C−O−C plane. These orbitals form angles of ca. ±55° (half the tetrahedral angle) with the plane. As shown in Fig. 3, a rotation of the C−O bonds of ca. ±35° should make the direction of the $p\pi$ orbitals on the C and N atoms of the $CNMe_2$ groups in the present work, near parallel with the two filled sp^3 hybrid oxygen orbitals not participating in C−O σ-bonds. In such a system, π-bonding and charge delocalization can occur throughout the ion except for the methyl groups. The result will be a twist conformation.[11]

In the dicarbonium ions *1*, *2* and *4*, (see Table 4) the rotation of planar π-systems around C−O is between 47.2 and 33.5°. This is fairly close to 35° and may indicate that such π-bonding as discussed above is taking place in these dications. Their C−O−C angles, however, have values close to 120° as is expected for sp^2 hybridization, but these large angles may also be caused by steric interaction between the two groups bonded to oxygen.

II. Oxygen is sp^2 hybridized. In this case, there is a σ lone pair on oxygen, lying in the central C−O−C plane plus an unhybridized filled p-orbital at right angles to it. A π-system in a fragment coplanar with the C−O−C plane will overlap efficiently with the p-orbital above. On the other hand, such a planar fragment with a π-system may after a rotation around C−O of ca. 90°, possibly be able to overlap with the sp^2 lone pair orbital on oxygen.

The result may be a system with two planar π-bonded fragments being a) coplanar with C−O−C, b) nearly at right angles to C−O−C or c) one fragment being nearly at right angles, the other coplanar with C−O−C. The resulting conformations of the ether will be planar, butterfly or skewed and have C−O−C angles around 120°,[11] as shown in Fig. 3, IIa−c.

III. Oxygen is sp hybridized. Here the C−O−C sequence is linear, with p_y and p_z orbitals on oxygen not involved in σ-bonding. These orbitals can overlap with π-systems of the two molecular fragments bonded to oxygen when the fragments are at right angles to each other, Fig. 3, IIIb. If the fragments are coplanar, only one of the p-orbitals on oxygen is involved in π-bonding as shown in Fig. 3, IIIa.

The best overlap will probably take place in models containing a linear C−O−C system and possibly in a bent planar ion. No such conformations are found for ethers. In most cases skewed, twisted or intermediate conformations are found. That there are no bent planar conformations is probably due to steric interactions invariably occuring in bent, planar aromatic ethers. In the analogous diphosphonium ion, $[(Me_2N)_3P-O-P(NMe_2)_3]^{2+}$, we have found a linear P−O−P system, but outer d-orbitals on the phosphorus atoms are probably involved in the P−O bonding. Theoretical calculations, however, show that a linear C−O−C sequence is energetically favorable (comparable in energy to a bent sequence).[9] In the present investigation, steric interactions will prevent a planar ion, even one with a linear C−O−C sequence. Thus the adapted structure may be described as a compromise: A bent structure that allows a certain degree of overlap according to model I and at the same time minimizes steric repulsion.

Even cation 3,[8] with two small propenylium rings attached to the central oxygen atom, is not free of steric interactions in a bent, planar conformation.

A surprising fact is that the central C−O bond lengths varies so little in the dication ethers regardless of the relative rotations of the π-bonded fragments around these bonds. Thus the amount of π-overlap seems to play only a secondary role. (Ion *2* have rotations of fragments of 17.1 and 41.3°, respectively, while *3* has both rotations equal to 33.5°. This should give best π-overlap for *3*, but C−O bond lengths are slightly longer in *3* than in *2*.[1])

Diaryl thioethers also seem to have short C−S bonds even though the C−S−C thioether angle is close to 102°, a typical valency angle found in aliphatic sulfides.[43] In the skew conformation found, outer d orbitals on sulfur may, as in the P−O−P system mentioned above, participate in π-bonding. Quite recently, the first thio and seleno analogs of dication ethers have been prepared.[44] Their structures will probably be of the thioether type just mentioned, but perhaps with shorter C−S(Se) bonds due to the positive charge on the carbon atoms.

Stabilization of dication ethers by charge delocalization is evident also from preparative

data. Experience has taught us that replacing a dialkylamino group in a urea with an alkyl group, greatly diminishes the stability of the dication ether prepared. Assuming π-bonding through the central $C-O-C$ system, the cation (excluding methyl groups) may be described as follows:

Comparison with neutral ethers. There are three main types of ethers; namely dialkyl-, alkyl-aryl- and diaryl ethers. In the dialkyl ethers, the $C-O$ bond lengths are close to 1.43 Å,[30,44–46] the normal covalent $C-O$ bond length and the $C-O-C$ angle is usually close to 112°,[30,44–46] indicating sp^3 hybridization on the central oxygen atoms. For the alkyl-aryl ethers, the $C(alkyl)-O$ bond lengths are close to those found in the dialkyl ethers, whereas the $C(aryl)-O$ bond lengths are usually around 1.35–1.38 Å.[27–40] For these compounds, the $C-O-C$ angle is usually close to 118°, indicating sp^2-hybridization. Also dialkyl ethers (acetals) with one $C(sp^2)-O$ link have similar bond lengths and angles.[41,42]

For diaryl ethers, the $C-O$ ether linkages have average bond lengths close to 1.38 Å and the $C-O-C$ angles are mostly between 118 and 122°,[10,14–27] indicating again sp^2 hybridization on oxygen. With these last ethers, it is found that electron withdrawing substituents *ortho* and *para* to the ether linkage on one of the aromatic groups, lead to asymmetry in the $C-O$ ether bonds. A typical example is (4'-carbomethoxy-2'-nitrophenoxy)benzene, where the substituted phenyl groups has a $C-O$ ether link of 1.353(3) Å while the $C-O$ bond to unsubstituted phenyl is 1.409(3) Å.[24] In this ether, the $C-O-C$ group is nearly coplanar with the substituted phenyl group and the $C-O-C$ angle is 120.0(3)°. This indicates sp^2 hybridized oxygen and conjugation of its p_z orbital with this phenyl group. Also in most mixed alkyl-aryl ethers, the $C-O-C$ group is nearly coplanar with the aromatic group. However, steric hindrance may prevent such coplanarity as mentioned above in diaryl ethers, but without apparent effect on the bond lengths.[22]

From what is said above, the fact remains that positive charge on aromatic carbons created by electron withdrawing substituents shortens the $C-O$ ether linkage involving such carbon atoms.[17,19–22,24] This seems to support the idea of multiple bonding in diaryl- and mixed aryl-alkyl ethers.

That there is an electron transfer away from the ether oxygen atom in such compounds is supported by hydrogen bonding measurements. It shows clearly that the association constants in phenol-ether mixtures are very small for diaryl ethers, intermediate for alkyl-aryl ethers and highest for dialkyl ethers.[47] These findings are also supported by determination of solvatochromic parameters.[48]

In the dication ethers, there are two π-bonded, positively charged fragments bonded to ether oxygen. The ether linkage should therefore be expected to be similar to those found in diaryl ethers. From charge considerations, the $C-O$ bonds should be more like the corresponding bonds from aryl groups with *ortho* and *para* electron-withdrawing substituents i.e. close to 1.35–1.36 Å.[17,19–22,24] Inspection of Table 4 shows that this is indeed the case.

Comparison with the analogous diphosphonium salt. Only one structure of a diphosphonium salt is known, namely that of $[(Me_2N)_3P-O-P(NMe_2)_3]^{2+}(CF_3SO_3^-)_2$.[2] Here the central $P-O-P$ group is linear as compared to the bent $C-O-C$ group (angles close to 120°) in the dication ethers. The $P-O$ bond length found is 1.573(1) Å, which is a bit longer than 1.545 Å, the value found in the isolated phosphate ion (π-bond order$=\frac{1}{2}$).[49] This has

been interpreted in terms of a considerable amount of π-bonding based on overlap of empty d-orbitals on phosphorus with filled $p\pi$ orbitals on oxygen.[2] The main structural difference in the two types of dications is due to the difference in bending of the central $A-O-A$ group ($A=P,C$). However, the steric interactions of the methyl groups in the diphosphonium ion are so strong that they may prevent bending of the $P-O-P$ group in that particular salt.

Common for both types of salts is the extensive delocalization of charge which stabilizes the cations.

The structure of the anions. The trifluoromethyl sulfonate anions are quite normal with average $S-O$, $S-C$ and $C-F$ bond lengths of 1.429(15), 1.809(13) and 1.325(18) Å, respectively. These values are in agreement with those found in other dication ether salts and in the linear diphosphonium salt.[2,7,8]

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