Dication Ethers. Part 8.[1] The *X*-Ray Crystal Structures of 9,9′-Oxybis-(10-methylacridinium) Bis(tetrafluoroborate) and the Neutral Ether 9,9′-Oxybisacridine

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The *X*-ray crystal structures of 9,9′-oxybis-(10-methylacridinium) bis(tetrafluoroborate) (**3**) and 9,9′-oxybisacridine (**4**) have been determined. Both compounds have twist conformations around the ether structural fragment. The angles between the acridine rings and the C–O–C plane are 46.3, 46.3° in (**3**) and 57.4, 51.1° in (**4**). The most significant difference between (**3**) and (**4**) is the shortening of the ether bond by *ca.* 0.06 Å in the dication ether (**3**).

In biscarbenium ethers ('dication ethers'), R_2C^+–O–$^+CR_2$, electronic interaction between the positive charges and the lone pairs of the oxygen atoms can be expected, which, among others, should exert an influence on the overall conformation of the dication. According to theoretical predictions,[2] the following conformations should have minimum energies, depending on the nature of R_2C^+: bent-planar (**1A**), bent-perpendicular (**1B**), linear-planar (**1C**) and linear-perpendicular (**1D**).

So far, the crystal structures of the dication ether salts (**2a**),[3] (**2b**),[4] (**2c**),[3] and (**2d**)[5] have been determined. In all dications, the R_2C^+ moieties are tilted against the C^+–O–C^+ plane in opposite directions, and the valence angle at oxygen is *ca.* 120°. The twisted conformations around the ether bonds result from the dominating influence of *steric* interactions between the two R_2C^+ parts of the dication.

When comparing the structures of a dication ether, R_2C^+–O–$^+CR_2$, and a related neutral ether, R_3C–O–CR_3, one should have a better chance to work out the consequences of *electronic* interaction with respect to molecular conformation and bonding geometry. Therefore, we have undertaken structure analyses of compounds (**3**) and (**4**).

Experimental

Compound (**3**) was obtained by anion exchange from 9,9′-oxybis-(10-methylacridinium) bistrifluoromethanesulphonate[6] with tetra-n-butylammonium tetrafluoroborate in acetonitrile and precipitation with ether; 90% yield, m.p. 238 °C (decomp.) (Found: C, 58.2; H, 3.9; N, 5.3. $C_{28}H_{22}B_2F_8N_2O$ requires C, 58.4; H, 3.85; N, 4.9%). Crystals were grown by evaporation of an acetonitrile solution. Crystals of (**4**)[6] were grown from methanol.

Crystal Data for (3).—$(C_{28}H_{22}N_2O)^{2+}\cdot 2BF_4^-$, M_r = 576.1, monoclinic, $C2/c$, a = 23.251(1), b = 5.761(1), c = 18.748(3) Å, β = 100.22(2)°, V = 2 472 Å^3, Z = 4, D_c = 1.548 g cm^{-3}, μ(Mo-K_α) = 1.3 cm^{-1}, $F(000)$ = 1 176, final R value 0.044 for 1 014 reflections with $I > 3\sigma(I)$.

Crystal Data for (4).—$C_{26}H_{16}N_2O$, M_r = 372.4, monoclinic, $P2_1/c$, a = 12.137(2), b = 13.170(2), c = 11.554(2) Å, β = 96.36(1)°, V = 1 836 Å^3, Z = 4, D_c = 1.348 g cm^{-3}, μ(Mo-K_α) = 0.8 cm^{-1}, $F(000)$ = 776, final R value 0.0426 for 1 960 reflections with $I > 3\sigma(I)$.

Crystal Structure Determination for (3) *and* (4).—Data collection for both compounds was carried out at 297 K on an Enraf–Nonius CAD4 diffractometer [monochromatized Mo-K_α radiation, θ–2θ scan, scan width $(0.85 + 0.35 \tan\theta)$°, scan speed 1.5—5° min^{-1}]. Cell constants were obtained from diffractometer settings of 25 reflections. The phase problem was solved with MULTAN 82.[7] Refinement (on F) was done by a full-matrix, least-squares procedure. Programs of the Enraf–Nonius[8] 'Structure Determination Package' were used.

(**3**): prismatic crystal enclosed in a quartz capillary, crystal size 0.55 × 0.15 × 0.32 mm. R_{int} = 0.011 for averaged symmetrically equivalent reflections, 1 723 independent reflections with $2.0 \leqslant \theta \leqslant 23.0$°. Hydrogen atoms were taken from a ΔF map and refined isotropically. Convergence was reached at R = 0.044, R_w = 0.042 {230 variables, $w = 1/[\sigma^2(F_o) + (0.02F_o)^2]$}. The maximum shift/error ratio at this point was 0.12.

(**4**): crystal size 0.50 × 0.40 × 0.36 mm. R_{int} = 0.016 for averaged symmetrically equivalent reflections; 2 711 independent reflections with $2.0 \leqslant \theta \leqslant 23.5$°, no intensity loss for three monitoring reflections. Hydrogen atoms were calculated and refined isotropically. R = 0.0426, R_w = 0.0402 (326 variables, $w = 1/[\sigma^2(F_o) + 0.022F_o)^2]$); $\Delta_{max.}/\sigma$ = 0.00.

The anisotropic temperature factors and details for the least-squares planes for (**3**) and (**4**) have been deposited in Supplementary Publication No. 56315 (18 pp.).*

Discussion

The final parameters for (**3**) are given in Table 1 and those for (**4**) in Table 2. Stereoplots of both compounds are depicted in Figure 1 and bond distances and angles appear in Figures 2 and 3. The dication ether salt (**3**) has crystallographic C_2 symmetry, with the ether oxygen lying on the two-fold axis. Both compounds have a bent-perpendicular conformation around the ether bonds, which is, however, different from structure (**1B**), where one R_2C^+ unit is coplanar with the C–O–C plane. In (**3**) and (**4**), the two acridine rings are tilted against the C–O–C plane in opposite directions (Table 3). In the neutral ether (**4**), the angles between the acridine rings and the C–O–C plane are larger than in (**3**) by 5—11°; on the other hand, the C–O–C valence angle in (**4**) is smaller than in (**3**) by 5.3°. The shortest non-bonding contacts between the *peri*-hydrogens of one ring and atoms of the second ring are equal within error limits in both structures: In (**3**), one finds C(12)–H(1′) 2.52(3) Å, in (**4**) C(9)–H(8′) 2.52(3) Å and C(9′)–H(1) 2.55(3) Å. These facts may be taken as a hint to the balance of steric interactions which is established by the interplay between the bond angle at oxygen and the molecular conformation. The structural data of the related salt (**5**)[9] support this view. The interplanar angles between the acridine rings and the central C–N–C unit are 19.0

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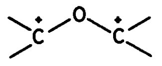
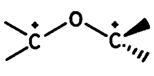
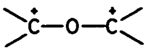
* For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.



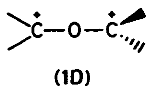
(1A)



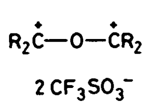
(1B)



(1C)



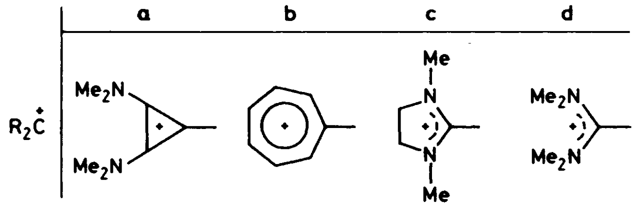
(1D)

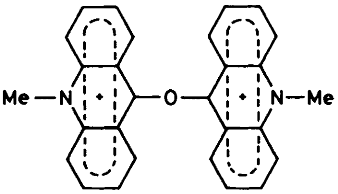


$$\overset{+}{R_2C}—O—\overset{+}{CR_2}$$

$$2\,CF_3SO_3^-$$

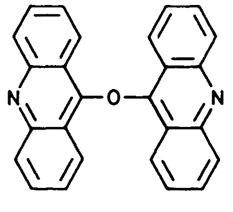
(2)



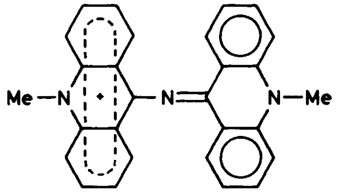


$2\,BF_4^-$

(3)

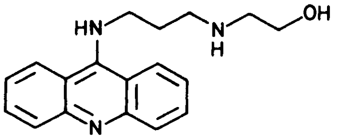


(4)

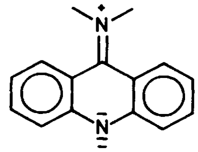


ClO_4^-

(5)



(6)



(7)

Table 1. Positional and isotropic thermal parameters for all atoms of (**3**)

Atom	x	y	z	$B/\text{Å}^{2\,a}$
F(1)	0.407 7(1)	0.521 4(6)	0.459 2(2)	8.02(9)
F(2)	0.349 4(1)	0.330 6(7)	0.372 7(2)	8.3(1)
F(3)	0.321 2(1)	0.396 9(6)	0.479 3(2)	8.20(9)
F(4)	0.325 3(1)	0.688 7(6)	0.402 8(2)	7.44(8)
O	1.000	0.032 3(7)	0.250	3.08(9)
N	0.862 5(1)	−0.287 8(6)	0.115 4(2)	3.32(8)
C(1)	1.023 9(2)	−0.332 8(8)	0.151 0(2)	3.3(1)
C(2)	1.031 8(2)	−0.513 0(9)	0.107 3(2)	3.7(1)
C(3)	0.982 9(2)	−0.631 7(8)	0.070 2(2)	4.3(1)
C(4)	0.927 7(2)	−0.564 7(8)	0.072 5(2)	3.8(1)
C(5)	0.917 7(2)	−0.371 0(8)	0.115 3(2)	3.07(9)
C(6)	0.852 4(2)	−0.099 9(8)	0.155 8(2)	3.22(9)
C(7)	0.795 4(2)	−0.007 7(9)	0.154 5(2)	4.1(1)
C(8)	0.788 3(2)	0.177 8(9)	0.196 2(3)	4.6(1)
C(9)	0.834 8(2)	0.285 1(9)	0.241 7(2)	4.4(1)
C(10)	0.889 3(2)	0.202 7(8)	0.244 1(2)	3.8(1)
C(11)	0.900 1(2)	0.007 8(8)	0.202 2(2)	2.90(9)
C(12)	0.955 8(2)	−0.081 3(7)	0.203 9(2)	2.68(8)
C(13)	0.966 9(2)	−0.260 4(7)	0.158 5(2)	2.86(9)
C(14)	0.812 1(2)	−0.402(1)	0.067 2(3)	5.0(1)
B	0.351 1(2)	0.485(1)	0.428 5(3)	4.7(1)
H(1)	1.057(1)	−0.249(6)	0.175(2)	3.0(8)
H(2)	1.072(1)	−0.557(7)	0.100(2)	3.9(9)
H(3)	0.990(1)	−0.758(7)	0.041(2)	3.6(9)
H(4)	0.896(1)	−0.655(7)	0.047(2)	3.8(9)
H(7)	0.763(2)	−0.085(7)	0.124(2)	5(1)
H(8)	0.7[illegible]9(2)	0.239(8)	0.193(2)	5(1)
H(9)	0.828(2)	0.422(7)	0.267(2)	4(1)
H(10)	0.921(1)	0.264(7)	0.276(2)	3.9(9)
H(14A)	0.780(2)	−0.347(9)	0.085(2)	7(1)
H(14B)	0.816(2)	−0.37(1)	0.013(3)	11(2)
H(14C)	0.814(2)	−0.57(1)	0.075(3)	10(2)

[a] B_{eq} for non-hydrogen atoms. $B_{eq} = 4/3\ \Sigma_i\Sigma_j\ \beta_{ij}\ a_i{\cdot}a_j$.

and 52.9°, and the valence angle at the bridging nitrogen is 137°. Thus, opening up this latter angle allows a more coplanar arrangement between the C–N–C plane and one of the acridine rings, as required for a 9-iminoacridinium unit.

Steric interactions between both acridine rings also lead to a distortion of the ideal sp^2 geometry at C(12) in (**3**) and C(9), C(9′) in (**4**). In both structures, the exocyclic angle O–C–C, which is closer to the *peri*-hydrogen having the shorter intramolecular contact to the opposite acridine ring, is markedly larger than 120°, the other exocyclic angles being correspondingly smaller. Furthermore, the same steric interactions may account for the lengthening of the C–O bonds in both structures, as compared with reference compounds. The C–O distance in (**4**) is much larger than the usual value found in diaryl ethers (1.38 Å), and also larger than that for dialkyl ethers (1.43 Å).[5] Also, the ether linkage in (**3**) is significantly longer than in the other known dication ether structures (1.345—1.368 Å).

The conformation of (**3**) and (**4**), a so-called twist conformation,[10] is apparently quite uncommon in diaryl ethers. In the structures known so far, in which, however, one or more *ortho*-substituted phenyl rings are present most often, one usually finds a large (50—80°) and a small ($\leqslant$*ca.* 20°) twisting angle between aryl ring and C–O–C plane.[10–12] The interplanar angles in (**3**) (Table 3), taken together, are larger than in all other dication ethers studied so far. For an sp^3-hybridised oxygen atom, the lone-pair directions form an angle of ±55° with the C–O–C plane. Therefore, an angle of 35° between the C–O–C plane and an acridine ring would allow maximum overlap between such a lone pair on oxygen and the aromatic π-system. The conformation found in (**3**) is sufficiently close to the geometry for ideal overlap of both π-systems, each with a different lone-pair of an sp^3 oxygen; in (**4**), the geometry around C–O–C is somewhat less favourable. Whether or not such an interaction is the decisive factor for the conformation in the crystalline state may be debated. Inspection of the interplanar angles around the C–O–C unit of the dication ethers investigated up to now [(**1a**) 41.3, 17.1°; (**1b**) 33.5, 33.5°; (**1c**) 47.2, 42.4°; (**1d**) 39.4, 36.1°; (**3**) 46.3, 46.3°] shows that in all cases except (**1a**)

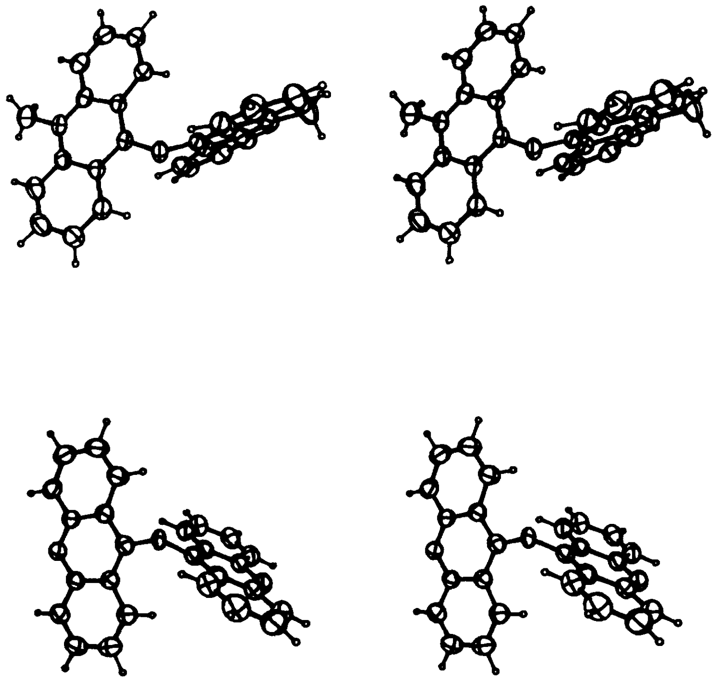
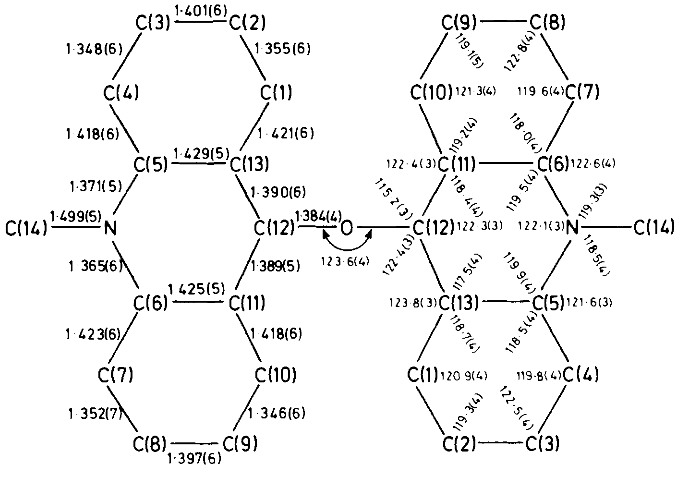


Figure 1. Stereoplot of (3) (top) and (4) (bottom)



Anion

B-F(1)	1·356(6) Å
B-F(2)	1·367(7)
B-F(3)	1·370(7)
B-F(4)	1·368(7)

F(1)-B-F(2)	108·8(5)°
F(1)-B-F(3)	109·6(4)
F(1)-B-F(4)	110·3(5)
F(2)-B-F(3)	110·0(5)
F(2)-B-F(4)	109·7(4)
F(3)-B-F(4)	108·5(4)

Figure 2. Bond distances (Å) and bond angles (°) in (3). The molecule has crystallographic C_2 symmetry

effective overlap of the π-systems of both positively charged parts of the dication with the lone pairs of an sp^3 oxygen could be realised.

Depending on the particular substituents, the hybridisation state of ethers seems to be a quite variable model. Based on the bond geometry, the oxygen in diaryl ethers and alkyl aryl ethers is generally assumed to be sp^2-hybridised, but an sp^3-hybridisation is considered for dialkyl ethers.[5] A recent survey[13] of crystal structures of sterically unhindered cyclic ethers, in which the oxygen acts as hydrogen-bond acceptor, reveals a directionality of the hydrogen-bond donors which comes close to the expected region of the sp^3 lone pairs.* On the other hand, both MO calculations[14,15] and photoelectron spectral data[15] of dimethyl ether indicate an energy difference between both lone pairs, one of which has pure p-character.

The bond distances in the neutral ether (**4**) are quite similar to those in acridine itself, the latter structure having been refined only isotropically, however.[16] This indicates that the conjugation in the heteroaromatic ring remains essentially unaffected by the oxygen substituent. In contrast, bond distances in the central ring of the 9-(alkylamino)acridine (**6**) deviate significantly from those in (**4**),[17] giving rise to a bond pattern which can easily be explained by an increased contribution from resonance structure (**7**).

Methylation of the nitrogen atoms [compound (**3**)] results only in significant changes of the endocyclic angles in the central ring and in a lengthening of the endocyclic C–N distances by 0.02—0.03 Å, as far as the acridine part is concerned. At the

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* The proton-donor density is, however, almost continous between the assumed directions of the lone pairs above and below the C–O–C plane.

Table 2. Positional parameters and temperature factors for (**4**)

Atom	x	y	z	B/Å$^{2\,a}$
O	0.671 8(1)	0.082 3(2)	0.357 1(2)	3.68(4)
N	1.024 1(2)	0.081 5(2)	0.381 2(2)	3.51(5)
N′	0.452 5(2)	−0.169 4(2)	0.371 7(2)	3.90(5)
C(1)	0.793 7(2)	−0.046 4(3)	0.198 5(3)	4.15(7)
C(1′)	0.494 6(3)	0.052 0(3)	0.182 7(3)	4.47(7)
C(2)	0.854 1(3)	−0.095 5(3)	0.123 9(3)	4.98(8)
C(2′)	0.405 8(3)	0.038 5(3)	0.101 8(3)	5.22(8)
C(3)	0.971 3(3)	−0.085 7(3)	0.134 4(3)	4.98(8)
C(3′)	0.333 4(3)	−0.044 9(3)	0.108 9(3)	5.33(8)
C(4)	1.024 6(2)	−0.028 6(2)	0.219 8(3)	4.26(7)
C(4′)	0.349 2(3)	−0.112 1(3)	0.197 4(3)	4.52(7)
C(4A)	0.965 2(2)	0.024 2(2)	0.300 6(2)	3.27(6)
C(4A′)	0.441 2(2)	−0.100 8(2)	0.285 5(3)	3.76(6)
C(5)	1.031 0(3)	0.194 3(2)	0.541 5(3)	4.06(7)
C(5′)	0.544 7(2)	−0.226 5(2)	0.551 2(3)	4.17(7)
C(6)	0.979 6(3)	0.250 7(3)	0.617 5(3)	4.87(8)
C(6′)	0.626 4(3)	−0.218 6(2)	0.639 8(3)	4.40(7)
C(7)	0.862 7(3)	0.252 0(3)	0.611 2(3)	5.19(8)
C(7′)	0.708 5(3)	−0.142 2(3)	0.639 3(3)	4.38(7)
C(8)	0.799 1(3)	0.195 8(2)	0.531 0(3)	4.36(7)
C(8′)	0.704 5(2)	−0.074 2(2)	0.550 9(3)	3.90(7)
C(8A)	0.850 2(2)	0.135 0(2)	0.450 1(2)	3.24(6)
C(8A′)	0.618 9(2)	−0.078 1(2)	0.456 0(2)	3.33(6)
C(9)	0.791 2(2)	0.072 2(2)	0.367 6(2)	3.23(6)
C(9′)	0.605 7(2)	−0.008 8(2)	0.363 8(2)	3.36(6)
C(9A)	0.846 7(2)	0.015 3(2)	0.289 5(2)	3.13(6)
C(9A′)	0.515 4(2)	−0.017 1(2)	0.277 4(2)	3.54(6)
C(10A)	0.968 4(2)	0.135 1(2)	0.454 6(2)	3.26(6)
C(10A′)	0.537 6(2)	−0.157 7(2)	0.455 9(3)	3.54(6)
H(1)	0.712(2)	−0.053(2)	0.192(2)	4.8(7)
H(1′)	0.546(2)	0.109(2)	0.180(2)	5.0(7)
H(2)	0.814(3)	−0.139(3)	0.057(3)	7.1(9)
H(2′)	0.390(3)	0.086(2)	0.038(3)	6.7(8)
H(3)	1.013(2)	−0.124(2)	0.080(3)	6.0(8)
H(3′)	0.270(2)	−0.056(2)	0.047(3)	6.0(8)
H(4)	1.106(2)	−0.023(2)	0.230(2)	4.9(7)
H(4′)	0.301(2)	−0.176(2)	0.203(2)	5.2(7)
H(5)	1.114(2)	0.192(2)	0.544(2)	4.8(7)
H(5′)	0.487(2)	−0.281(2)	0.547(2)	5.7(8)
H(6)	1.027(2)	0.292(2)	0.679(3)	6.1(8)
H(6′)	0.631(2)	−0.266(2)	0.707(2)	5.2(7)
H(7)	0.827(2)	0.292(2)	0.668(3)	5.9(8)
H(7′)	0.767(2)	−0.136(2)	0.709(3)	6.2(8)
H(8)	0.717(2)	0.194(2)	0.530(2)	5.6(8)
H(8′)	0.760(2)	−0.021(2)	0.552(2)	5.0(7)

[a] B_{eq} for non-hydrogen atoms. $B_{eq} = 4/3\ \Sigma_i \Sigma_j\ \beta_{ij}\ a_i a_j$.

same time, the C–O bonds become shorter by 0.06 Å and the C–O–C angle increases by 5.3°. These findings seem to indicate that resonance structures analogous to (**5**) (O^+ instead of N), in which the oxygen atom becomes positively charged, contribute to the bond state of the dication ether (**3**). The further consequences of such an altered bond order, shortening of the C(6)–C(11) bond and lengthening of the C(11)–C(12) bond (and their equivalents in the pyridine ring), are, however, not observed. When 9-aminoacridines are quaternized at the ring nitrogen, the geometrical changes in the pyridine ring are even smaller than for the pair (**3**) and (**4**). In 9-aminoacridinium chloride monohydrate,[18] the exocyclic C–N distance is shorter by 0.02 Å than in (**6**), but no significant bond-length changes in the pyridine ring itself occur.* This comes as no surprise, however, as the resonance structure (**7**) plays a significant role already in the neutral aminoacridine (**6**).

Table 3. Angles (°) between least-squares planes in (**3**) and (**4**)

Plane		$\Delta_{max.}{}^{a}$/Å	Angle with plane		
			a	b	c
	in (**3**)				
a	C(12)–O–C(12′)			46.3	46.3
b	acridine system 1[b]	0.128[c]			76.3
c	acridine system 2[b]	0.128[c]			
	in (**4**)				
a	C(9)–O–C(9′)			57.4	51.1
b	ring with C(9)....	0.055			96.7
c	ring with C(9′)....				

[a] Maximum deviation of an atom from the plane. [b] Both acridine ring systems are related by symmetry. [c] Maximum deviation shown by C(12). The outer rings of the heterocyclic system form angles of 5.6 and 1.6°, respectively, with the least-squares plane of the central ring.

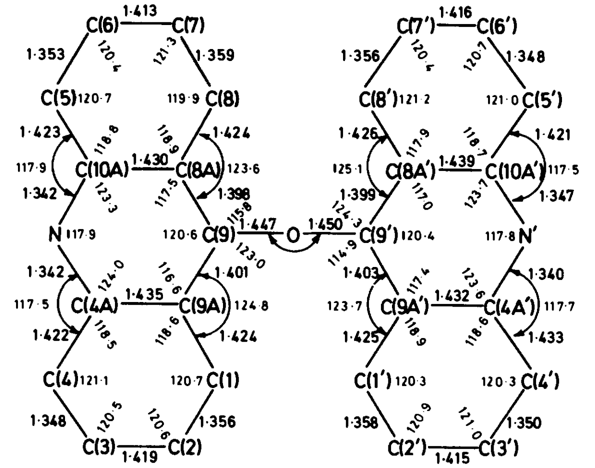

Figure 3. Bond distances (Å) and bond angles (°) in (**4**). E.s.d.s: ±0.003 Å for C–O, ±0.004—0.005 Å for all other bond lengths, ±0.2—0.3° for bond angles

The u.v. spectrum of (**3**) gives no hint to a perturbation of the aromatic conjugation typical for the acridine system by the oxygen substituent, a fact which also rules out a significant contribution from resonance structures analogous to (**7**).[20] Steric interactions between the acridine rings in both (**3**) and (**4**) being quite similar, one may conclude that the shortening of the C–O bond by 0.06 Å in the dication ether is mainly due to the ability of oxygen to donate electrons to a neighbouring electron-deficient centre irrespective of the particular geometry around the C–O bond. This phenomenon was also observed in the structures of diaryl ethers with electron-withdrawing substituents on one phenyl ring.[21,22]

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* In 9-aminoacridinium chloride dihydrate, all bonds in the central ring are, on the average, shortened by 0.01—0.02 Å as compared with the neutral amine (**6**). Furthermore, the exocyclic C–N distance is 0.04 Å less than in (**6**).[19] Because of the insufficient level of refinement, this structure was, however, not considered further.

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