Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O	0.3891 (2)	0.5614 (8)	0.5490 (2)	5.5 (2)
O5	0.1921 (2)	−0.0116 (8)	0.4194 (2)	4.6 (2)
N	0.4289 (3)	0.198 (1)	0.4336 (2)	4.5 (2)
C1	0.5015 (3)	−0.094 (1)	0.3361 (3)	4.9 (3)
C2	0.4817 (3)	−0.292 (1)	0.2814 (3)	5.1 (3)
C3	0.3914 (3)	−0.403 (1)	0.2668 (3)	5.0 (3)
C4	0.3208 (3)	−0.315 (1)	0.3081 (2)	4.5 (3)
C4A	0.3383 (3)	−0.111 (1)	0.3650 (2)	3.8 (2)
C4B	0.2852 (3)	0.033 (1)	0.4163 (2)	3.9 (2)
C6	0.1433 (3)	0.243 (1)	0.4423 (3)	4.5 (3)
C6A	0.1532 (3)	0.298 (1)	0.5237 (2)	4.5 (2)
C7	0.0757 (4)	0.284 (1)	0.5654 (3)	5.7 (3)
C8	0.0805 (4)	0.345 (2)	0.6398 (3)	6.6 (3)
C9	0.1644 (4)	0.422 (2)	0.6749 (3)	7.0 (4)
C10	0.2419 (4)	0.442 (1)	0.6348 (3)	5.9 (3)
C10A	0.2373 (3)	0.380 (1)	0.5598 (2)	4.5 (2)
C11	0.3258 (3)	0.402 (1)	0.5217 (2)	4.3 (2)
C11A	0.3409 (3)	0.219 (1)	0.4589 (2)	3.8 (2)
C12A	0.4290 (3)	−0.000 (1)	0.3781 (2)	4.0 (2)

Table 2. *Geometric parameters* ($\mathring{A}$, °)

O—C11	1.243 (5)	C4A—C12A	1.410 (5)
O5—C4B	1.364 (5)	C4B—C11A	1.370 (6)
O5—C6	1.435 (6)	C6—C6A	1.486 (6)
N—C11A	1.384 (5)	C6A—C7	1.392 (6)
N—C12A	1.348 (6)	C6A—C10A	1.390 (6)
C1—C2	1.353 (7)	C7—C8	1.368 (7)
C1—C12A	1.401 (6)	C8—C9	1.373 (8)
C2—C3	1.407 (7)	C9—C10	1.378 (7)
C3—C4	1.366 (6)	C10—C10A	1.379 (6)
C4—C4A	1.393 (6)	C10A—C11	1.496 (6)
C4A—C4B	1.405 (6)	C11—C11A	1.433 (6)
C4B—O5—C6	113.4 (4)	C6A—C7—C8	122.1 (5)
C11A—N—C12A	110.0 (4)	C7—C8—C9	119.2 (5)
C2—C1—C12A	118.0 (5)	C8—C9—C10	119.9 (5)
C1—C2—C3	121.6 (5)	C9—C10—C10A	121.0 (5)
C2—C3—C4	120.6 (5)	C6A—C10A—C10	119.8 (4)
C3—C4—C4A	119.6 (5)	C6A—C10A—C11	123.3 (4)
C4—C4A—C4B	135.8 (4)	C10—C10A—C11	116.9 (4)
C4—C4A—C12A	118.9 (4)	O—C11—C10A	119.0 (4)
C4B—C4A—C12A	105.3 (4)	O—C11—C11A	120.4 (4)
O5—C4B—C4A	122.7 (4)	C10A—C11—C11A	120.4 (4)
O5—C4B—C11A	127.7 (4)	N—C11A—C4B	106.7 (4)
C4A—C4B—C11A	109.6 (4)	N—C11A—C11	119.7 (4)
O5—C6—C6A	113.9 (4)	C4B—C11A—C11	133.5 (4)
C6—C6A—C7	120.0 (4)	N—C12A—C1	130.2 (4)
C6—C6A—C10A	122.0 (4)	N—C12A—C4A	108.5 (4)
C7—C6A—C10A	118.0 (4)	C1—C12A—C4A	121.4 (4)

We thank the SERC (UK) for funds towards the purchase of equipment, and the Wellcome Trust for support.

References

Ashcroft, W. R., Dalton, L., Beal, M. G., Humphrey, G. L. & Joule, J. A. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 2409–2412.

Beal, M. G., Ashcroft, W. R., Cooper, M. M. & Joule, J. A. (1982). *J. Chem. Soc. Perkin Trans.* 1, pp. 435–439.

Cooper, M. M., Hignett, G. J. & Joule, J. A. (1981) *J. Chem. Soc. Perkin Trans.* 1, pp. 3008–3011.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* 17, 781–782.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Mui, P. W., Jacober, S. P., Hargreave, K. D. & Adams, J. (1992). *J. Med. Chem.* 35, 201–202.

N,N',N''-Triphenyl-1,3,5-triaminobenzene and its σ Complex on Protonation: a Stable N,N',N''-Triphenyl-2,4,6-triaminocyclohexadienylium Cation

DANIEL T. GLATZHOFER* AND MASOOD A. KHAN

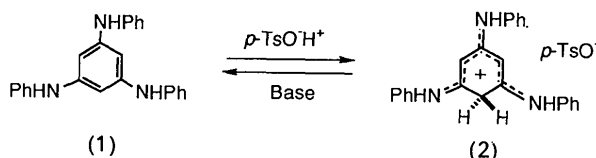*Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, Oklahoma 73019-0370, USA*

Abstract

Protonation of N,N',N''-triphenyl-1,3,5-triaminobenzene (N,N',N''-triphenyl-1,3,5-benzenetriamine) (1) by *p*-toluenesulfonic acid occurs at one of the C atoms of the central benzene ring, rather than at an N atom, to form the stable σ complex N,N',N''-triphenyl-2,4,6-triaminocyclohexadienylium *p*-toluenesulfonate (N,N',N''-triphenyl-2,4,6-triamino-1*H*-benzenium *p*-toluenesulfonate) (2). Changes in bond lengths clearly show the disruption of the aromaticity of the central ring in (1) on protonation and the stabilizing role of the N atoms in the delocalization of the positive charge. One of the outer benzene rings is probably involved in electronic stabilization since it approaches planarity with the central system. The other outer benzene rings do not show any obvious changes that would indicate a strong electronic contribution to the stability of (2), but are probably involved sterically.

Comment

Cationic σ complexes of arenes are of considerable importance as reactive intermediates in electrophilic

aromatic substitution reactions and have been extensively studied in solution (Kopytug, 1984). However, few have been stable enough to be isolated and characterized (Effenberger *et al.*, 1987). Of the arenium compounds characterized, X-ray structural data are available for systems based on hexamethylbenzene (Baenziger & Nelson, 1968; Borodkin, Nagi, Bagryanskaya & Gatilov, 1984) and 1,3,5-tripyrrolidinylbenzene (Effenberger *et al.*, 1987), but the refinements on these data were often poor, especially for protonated systems. We have discovered that *N,N',N''*-triphenyl-1,3,5-triaminobenzene (1) can be protonated by *p*-toluenesulfonic acid (p-TsO⁻H⁺) to form the stable crystalline σ complex *N,N',N''*-triphenyl-2,4,6-triaminocyclohexadienylium *p*-toluenesulfonate (2), as shown below (Glatzhofer, Allen & Taylor, 1990).

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (1) showing the atom- and ring-numbering systems.

Compound (1) is related to the 1,3,5-tripyrrolidinylbenzene system but the steric and electronic demands of forming the σ complex are considerably different. For example, the pK_a's of (2) and its analogs with substitutions on the outer rings exhibit a linear free-energy relationship, showing that the electronic structure of the molecules can be altered systematically (Glatzhofer *et al.*, 1990). The magnitude of the Hammet reaction parameter ($ρ = -6.14$) suggests that the electronic transmission of substituent effect is quite efficient and not inductive in nature. However, since the developing charge cannot interact directly with substituents by delocalization through the outer rings using simple resonance structures, the mechanism of transmission is not clear. Protonation of (1) and its analogues may represent a complex example of the poorly understood 'positive bridge effect' exhibited in certain cases by the enhanced transmission of electronic substituent effects through heteroatom-bridged diphenyl systems (Litvinenko, Popova & Popov, 1975). To investigate further the nature of σ complexes in general, the origin of the extreme stability of (2), and the structural/electronic effects that lead to the unusual structure–reactivity behavior of its analogs, we have determined the structures of (1) and (2).

ORTEP drawings and numbering schemes for (1) and (2) are shown in Figs. 1 and 2, respectively. Crystals of (2) consist of *p*-toluenesulfonate anions which are weakly hydrogen bonded [H(N4)⋯N(4) 1.04 (3), H(N4)⋯O(2) 1.82 (3), H(N6)⋯N(6) 0.91 (3),
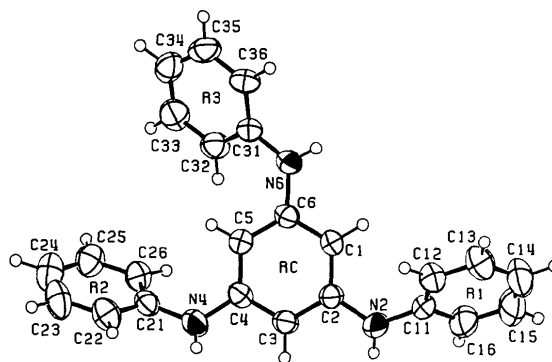
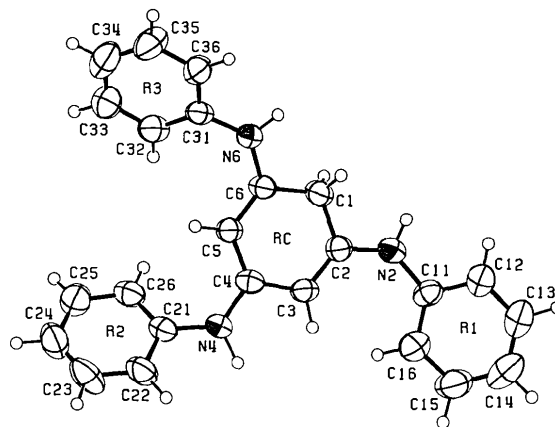

Fig. 2. *ORTEP* (Johnson, 1965) drawing of (2) showing the atom- and ring-numbering systems.

H(N6)⋯O(1) 2.07 (3) Å] to the *N,N',N''*-triphenyl-2,4,6-triaminocyclohexadienylium cations. The structure of (2) clearly shows that protonation occurs on C(1) [C(1)—H(1*A*) and C(1)—H(1*B*) are 0.96 (3) and 0.91 (3) Å, respectively] rather than on an N atom as usually occurs for amines. The central rings of the protonated tripyrrolidinylbenzene σ complexes were found to be essentially planar, with C(1) deviating less than 1° from the C(2)—C(3)—C(4)—C(5)—C(6) plane (Effenberger *et al.*, 1987). However, the central ring in (2) is only approximately planar, with C(1) being 0.080 (4) Å out of the C(2)—C(3)—C(4)—C(5)—C(6) plane and with a dihedral angle of 5.8 (10)° between the C(2)—C(1)—C(6) and C(2)—C(3)—C(4)—C(5)—C(6) planes. Although the H(1*A*)—C(1)—H(1*B*) bond angle in (2) is 109 (3)°, the deviation from planarity may result from relieving angle strain at sp^3 C(1), for which the C(2)—C(1)—C(6) bond angle is 117.1 (3)°.

Loss of aromaticity in the central ring of (1) on protonation is accompanied by significant changes in the bond lengths. The C(1)—C(2) and C(1)—C(6) distances in (1) alter from 1.391 (3) and 1.384 (3) Å to 1.480 (5) and 1.494 (5) Å in (2), reflecting an increase in localized C—C single-bond character. The C(2)—C(3) and C(5)—C(6) distances shorten from 1.381 (3) and 1.386 (3) Å to 1.356 (6) and 1.365 (5) Å, respectively, indicating the development of more C—C double-bond character. These changes are accompanied by a lengthening of the C(3)—C(4) and C(4)—C(5) distances to 1.422 (5) and 1.408 (5) Å in (2) from 1.383 (3) and 1.392 (3) Å in (1), respectively.

Perhaps the most striking of the changes on the protonation of (1) to (2) is the considerable shortening of the C(2)—N(2), C(4)—N(4) and C(6)—N(6) distances from 1.405 (3), 1.407 (3) and 1.411 (3) Å to 1.358 (5), 1.358 (5) and 1.350 (5) Å, respectively; an average decrease of 0.052 Å. This bond contraction reflects the role each N atom plays in stabilizing the positive charge on (2) and suggests considerable delocalization over the N(2)—C(2)—C(3)—C(4)—N(4)—C(5)—C(6)—N(6) system. These changes, which occur on protonation of (1), are accompanied by increases in the C(2)—N(2)—C(11), C(4)—N(4)—C(21) and C(6)—N(6)—C(31) angles between the central and outer rings from 126.4 (2), 125.5 (2) and 126.3 (2)° to 133.4 (3), 128.3 (3) and 130.3 (3)°, respectively. These changes possibly occur because of the increased steric interactions between the central and outer rings as they are brought closer together by the shortening of the inner C—N bonds.

Given the influence of outer-ring substituents on the protonation equilibria of N,N',N''-triphenyl-1,3,5-triaminobenzenes in solution (Glatzhofer et al., 1990), the relationship of the outer to inner rings in the structure of (2) is of particular interest. Unlike the dramatic changes in the central triaminobenzene moiety of (1) upon protonation, changes in the bond lengths and angles of the outer ring systems are subtle at best. The most obvious change is that, on protonation of (1), there is an increasing overall tendency for the dihedral angles between the planes of the outer rings and the inner rings (R1–RC, R2–RC and R3–RC) to be reduced [from 60.6 (2), 123.4 (2) and 43.1 (2)° to 10.7 (6), 135.5 (2) and 37.8 (3)°, respectively (average 75.7–61.3°)]. These changes are also reflected in the decreased torsional angles between the inner and outer aromatic rings in (2), such as C(1)—C(2)—N(2)—C(11), C(5)—C(4)—N(4)—C(21) and C(5)—C(6)—N(6)—C(31) [5.0 (4), 10.1 (6) and 10.1 (6)°, respectively], relative to those of (1) [20.7 (4), 13.8 (4) and 14.3 (4)°, respectively]. This tendency towards planarity in (2) is likely to arise in order to increase the overlap of the π systems and is largely manifested in the large

decrease in dihedral angle between the R1 and RC planes, which come close to being planar, while the corresponding values for the other two outer rings change relatively little from their values in (1). The increased R2–RC dihedral angle in (2) is possibly the result of increased steric interactions arising from the decrease of the R1–RC and R3–RC angles. Other changes occurring on protonation of (1) that might suggest strong electronic interactions with the outer rings, such as the slight shortening of the C(23)—C(24) bond, are of interest but it is difficult to judge their significance.

It has been suggested that N,N',N''-trisubstituted analogs of 1,3,5-triaminobenzene will not form stable σ complexes because they can easily deprotonate at the N atom to form non-benzenoid tautomeric imine species (Effenberger, 1989). The stability of (2) is the likely result of a mixture of electronic and steric effects. The results presented here suggest that the electronic stabilization of (2) and the substituent effects seen in the pK_a values for its substituted analogs largely occur through one outer ring (R1), which becomes more planar, although the pK_a values are measured in solution where the system is dynamic. The other outer rings in (2) then largely play a steric role in stabilizing the cation. Further experiments are needed to determine the crystal structures of the substituted analogs of (1) and (2) to help elucidate the nature of the strong outer-ring substituent effects.

There has been a report recently of the crystal structure of the N-phenyl-substituted analog of (1), N,N,N',N',N'',N''-hexaphenyl-1,3,5-triaminobenzene (3) (Yoshizawa et al., 1992). Our initial investigations have shown that (3) will protonate in the same way as (1), but with much more difficulty; we have not yet succeeded in isolating a protonated salt of (3). This difficulty in protonating (3) relative to (1) presumably results from steric hindrance to planarization of any of the outer rings, which would help in electronic stabilization of the positive charge.

Experimental

Compound (1)

Crystal data

$C_{24}H_{21}N_3$	$D_x = 1.240$ Mg m^{-3}
$M_r = 351.4$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71069$ Å
$P2_1/n$	Cell parameters from 25
$a = 23.513$ (6) Å	reflections
$b = 5.965$ (2) Å	$\theta = 12\text{–}16°$
$c = 13.433$ (4) Å	$\mu = 0.07$ mm^{-1}
$\beta = 92.05$ (3)°	$T = 295$ (2) K
$V = 1882.8$ Å^3	Needle
$Z = 4$	0.6 × 0.2 × 0.2 mm
	Colorless

Data collection

Enraf-Nonius CAD-4
  diffractometer
$\theta/2\theta$ scans
Absorption correction:
  none
3291 measured reflections
3291 independent reflections
1787 observed reflections
  $[I > 2\sigma(I)]$

$\theta_{max} = 25°$
$h = -27 \rightarrow 27$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 15$
3 standard reflections
  frequency: 120 min
  intensity variation: ±1%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.040$
$S = 1.4$
1787 reflections
328 parameters
All H-atom parameters
  refined isotropically

$w = [1/\sigma^2(F)]$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.11$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or
equivalent isotropic thermal parameters* (Å^2) *for* (1)

$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$; U_{iso} for H atoms.

	x	y	z	U_{eq}/U_{iso}
N(2)	0.48402 (8)	0.0997 (4)	0.1354 (1)	0.0612 (8)
N(4)	0.40601 (9)	0.5098 (4)	-0.1437 (1)	0.0623 (8)
N(6)	0.28884 (8)	0.3517 (4)	0.1411 (2)	0.0639 (8)
C(1)	0.38422 (9)	0.2120 (4)	0.1339 (2)	0.0480 (8)
C(2)	0.43628 (8)	0.2003 (4)	0.0880 (1)	0.0454 (8)
C(3)	0.44285 (9)	0.3030 (4)	-0.0029 (2)	0.0483 (8)
C(4)	0.39788 (9)	0.4162 (4)	-0.0492 (1)	0.0467 (8)
C(5)	0.3459 (1)	0.4301 (4)	-0.0031 (2)	0.0487 (8)
C(6)	0.33991 (8)	0.3331 (4)	0.0897 (1)	0.0462 (7)
C(11)	0.48351 (9)	-0.0535 (4)	0.2135 (2)	0.0491 (8)
C(12)	0.4467 (1)	-0.2348 (4)	0.2115 (2)	0.0563 (9)
C(13)	0.4487 (1)	-0.3900 (5)	0.2865 (2)	0.072 (1)
C(14)	0.4880 (1)	-0.3729 (6)	0.3630 (2)	0.088 (1)
C(15)	0.5249 (1)	-0.1963 (7)	0.3661 (2)	0.094 (1)
C(16)	0.5229 (1)	-0.0350 (5)	0.2918 (2)	0.070 (1)
C(21)	0.36916 (9)	0.6625 (4)	-0.1930 (2)	0.0492 (8)
C(22)	0.3551 (1)	0.6365 (5)	-0.2932 (2)	0.064 (1)
C(23)	0.3237 (1)	0.7980 (6)	-0.3440 (2)	0.078 (1)
C(24)	0.3042 (1)	0.9828 (6)	-0.2956 (2)	0.078 (1)
C(25)	0.3173 (1)	1.0087 (5)	-0.1961 (2)	0.068 (1)
C(26)	0.3501 (1)	0.8526 (4)	-0.1447 (2)	0.0573 (9)
C(31)	0.24420 (9)	0.5001 (4)	0.1190 (1)	0.0483 (8)
C(32)	0.2545 (1)	0.7157 (2)	0.0860 (2)	0.0586 (9)
C(33)	0.2098 (1)	0.8539 (5)	0.0587 (2)	0.070 (1)
C(34)	0.1546 (1)	0.7845 (6)	0.0671 (2)	0.073 (1)
C(35)	0.1440 (1)	0.5768 (6)	0.1056 (2)	0.066 (1)
C(36)	0.1884 (1)	0.4354 (5)	0.1318 (2)	0.0550 (9)
H(N2)	0.5153 (10)	0.1656 (39)	0.1249 (16)	0.060 (7)
H(N4)	0.4262 (10)	0.4308 (44)	-0.1798 (18)	0.075 (9)
H(N6)	0.2835 (8)	0.2559 (40)	0.1849 (16)	0.054 (7)
H(1)	0.3793 (7)	0.1494 (32)	0.1976 (14)	0.037 (5)
H(3)	0.4779 (9)	0.2970 (37)	-0.0341 (15)	0.057 (6)
H(5)	0.3160 (8)	0.4917 (35)	-0.0374 (14)	0.052 (6)

Table 2. *Geometric parameters* (Å, °) *for* (1)

N(2)—C(2)	1.405 (3)	C(13)—C(14)	1.363 (4)
N(2)—C(11)	1.392 (3)	C(14)—C(15)	1.364 (5)
N(4)—C(4)	1.407 (3)	C(15)—C(16)	1.385 (5)
N(4)—C(21)	1.406 (3)	C(21)—C(22)	1.383 (3)
N(6)—C(6)	1.411 (3)	C(21)—C(26)	1.388 (4)
N(6)—C(31)	1.397 (3)	C(22)—C(23)	1.380 (4)

C(1)—C(2)	1.391 (3)	C(23)—C(24)	1.367 (5)
C(1)—C(6)	1.384 (3)	C(24)—C(25)	1.369 (4)
C(2)—C(3)	1.381 (3)	C(25)—C(26)	1.379 (4)
C(3)—C(4)	1.383 (3)	C(31)—C(32)	1.384 (4)
C(4)—C(5)	1.392 (3)	C(31)—C(36)	1.385 (3)
C(5)—C(6)	1.386 (3)	C(32)—C(33)	1.375 (4)
C(11)—C(12)	1.384 (3)	C(33)—C(34)	1.371 (4)
C(11)—C(16)	1.381 (3)	C(34)—C(35)	1.369 (5)
C(12)—C(13)	1.368 (4)	C(35)—C(36)	1.378 (4)
C(2)—N(2)—C(11)	126.4 (2)	C(1)—C(6)—C(5)	120.3 (2)
C(4)—N(4)—C(21)	125.5 (2)	N(2)—C(11)—C(12)	121.4 (2)
C(6)—N(6)—C(31)	126.3 (2)	N(2)—C(11)—C(16)	119.9 (2)
C(2)—C(1)—C(6)	119.8 (2)	C(12)—C(11)—C(16)	118.6 (2)
N(2)—C(2)—C(1)	121.5 (2)	C(11)—C(12)—C(13)	120.7 (2)
N(2)—C(2)—C(3)	118.5 (2)	C(12)—C(13)—C(14)	120.6 (3)
C(1)—C(2)—C(3)	119.8 (2)	C(13)—C(14)—C(15)	119.6 (3)
C(2)—C(3)—C(4)	120.4 (2)	C(14)—C(15)—C(16)	120.6 (3)
N(4)—C(4)—C(3)	118.2 (2)	C(11)—C(16)—C(15)	119.9 (3)
N(4)—C(4)—C(5)	121.8 (2)	N(4)—C(21)—C(22)	120.4 (2)
C(3)—C(4)—C(5)	119.9 (2)	N(4)—C(21)—C(26)	120.9 (2)
C(4)—C(5)—C(6)	119.6 (2)	N(6)—C(31)—C(32)	121.2 (2)
N(6)—C(6)—C(1)	118.2 (2)	N(6)—C(31)—C(36)	120.4 (2)
N(6)—C(6)—C(5)	121.5 (2)		

C(1)—C(2)—N(2)—C(11)	20.7 (4)
C(1)—C(6)—N(6)—C(31)	166.6 (2)
C(2)—N(2)—C(11)—C(12)	46.6 (3)
C(2)—N(2)—C(11)—C(16)	-138.0 (2)
C(3)—C(2)—N(2)—C(11)	-164.0 (2)
C(3)—C(4)—N(4)—C(21)	-167.8 (2)
C(4)—N(4)—C(21)—C(22)	-136.0 (3)
C(4)—N(4)—C(21)—C(26)	49.7 (3)
C(5)—C(4)—N(4)—C(21)	13.8 (4)
C(5)—C(6)—N(6)—C(31)	-14.3 (4)
C(6)—N(6)—C(31)—C(32)	-36.9 (3)
C(6)—N(6)—C(31)—C(36)	144.6 (2)

Compound (2)

Crystal data

$C_{24}H_{22}N_3^+.C_7H_7O_3S^-$
$M_r = 523.6$
Monoclinic
$P2_1/n$
$a = 14.469$ (4) Å
$b = 19.264$ (6) Å
$c = 9.814$ (3) Å
$\beta = 98.15$ (3)°
$V = 2707.9$ Å^3
$Z = 4$
$D_x = 1.284$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25
  reflections
$\theta = 12-14°$
$\mu = 0.15$ mm^{-1}
$T = 295$ (2) K
Prism
0.4 × 0.3 × 0.3 mm
Dark red-orange

Data collection

Enraf-Nonius CAD-4
  diffractometer
$\theta/2\theta$ scans
Absorption correction:
  none
4747 measured reflections
4747 independent reflections
1745 observed reflections
  $[I>2\sigma(I)]$

$\theta_{max} = 25.0°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 11$
3 standard reflections
  frequency: 120 min
  intensity variation: ±2%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.037$
$S = 1.3$

$w = [1/\sigma^2(F)]$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

1742 reflections
Refined in two blocks with
    343 and 117 parameters
All H-atom parameters
    refined isotropically

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters ($\mathring{A}^2$) for (2)*

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j; \quad U_{iso} \text{ for H atoms.}$$

	x	y	z	U_{eq}/U_{iso}
C(25)	−0.2372 (3)	0.2675 (2)	0.2324 (6)	0.072 (2)
C(26)	−0.1694 (3)	0.2304 (2)	0.3146 (4)	0.060 (2)
C(31)	−0.2752 (3)	0.1109 (2)	0.7229 (4)	0.047 (2)
C(32)	−0.3001 (3)	0.1727 (2)	0.6561 (4)	0.060 (2)
C(33)	−0.3907 (4)	0.1969 (2)	0.6448 (5)	0.075 (2)
C(34)	−0.4571 (3)	0.1602 (3)	0.7009 (6)	0.089 (3)
C(35)	−0.4331 (3)	0.0994 (3)	0.7685 (5)	0.079 (2)
C(36)	−0.3427 (3)	0.0746 (2)	0.7795 (4)	0.062 (2)
C(41)	0.2641 (2)	0.1232 (2)	0.1402 (4)	0.048 (2)
C(42)	0.3278 (3)	0.1196 (2)	0.0499 (4)	0.065 (2)
C(43)	0.4147 (3)	0.1501 (3)	0.0825 (5)	0.075 (2)
C(44)	0.4395 (3)	0.1841 (2)	0.2044 (6)	0.071 (2)
C(45)	0.3776 (4)	0.1835 (3)	0.2959 (5)	0.092 (3)
C(46)	0.2901 (3)	0.1548 (3)	0.2635 (5)	0.079 (2)
C(47)	0.5322 (3)	0.2221 (3)	0.2365 (7)	0.118 (3)
S(1)	0.14840 (7)	0.09205 (6)	0.0932 (1)	0.0529 (4)
O(1)	0.1560 (2)	0.0222 (1)	0.0367 (2)	0.054 (1)
O(2)	0.1075 (2)	0.0903 (1)	0.2200 (3)	0.073 (1)
O(3)	0.1035 (2)	0.1405 (1)	−0.0071 (3)	0.072 (1)
N(2)	0.1357 (2)	0.0349 (2)	0.7266 (3)	0.056 (1)
N(4)	−0.0470 (2)	0.1413 (2)	0.3377 (3)	0.054 (1)
N(6)	−0.1829 (2)	0.0853 (2)	0.7455 (3)	0.053 (1)
C(1)	−0.0210 (3)	0.0667 (2)	0.7400 (4)	0.054 (2)
C(2)	0.0569 (3)	0.0635 (2)	0.6574 (4)	0.046 (2)
C(3)	0.0447 (3)	0.0884 (2)	0.5268 (4)	0.050 (2)
C(4)	−0.0426 (3)	0.1170 (2)	0.4684 (4)	0.046 (2)
C(5)	−0.1209 (2)	0.1180 (2)	0.5385 (4)	0.048 (2)
C(6)	−0.1129 (2)	0.0920 (2)	0.6691 (4)	0.045 (1)
C(11)	0.2231 (3)	0.0171 (2)	0.6888 (4)	0.052 (2)
C(12)	0.2795 (3)	−0.0240 (2)	0.7796 (5)	0.076 (2)
C(13)	0.3649 (4)	−0.0452 (3)	0.7508 (6)	0.106 (3)
C(14)	0.3961 (4)	−0.0269 (3)	0.6317 (7)	0.096 (3)
C(15)	0.3417 (4)	0.0145 (3)	0.5432 (5)	0.090 (2)
C(16)	0.2551 (3)	0.0362 (3)	0.5690 (5)	0.084 (2)
C(21)	−0.1200 (3)	0.1791 (2)	0.2596 (4)	0.050 (2)
C(22)	−0.1379 (3)	0.1663 (2)	0.1203 (5)	0.069 (2)
C(23)	−0.2059 (4)	0.2050 (3)	0.0411 (5)	0.085 (2)
C(24)	−0.2563 (3)	0.2537 (3)	0.0959 (6)	0.082 (2)
H(N2)	0.1320 (15)	0.0269 (12)	0.8122 (25)	0.038 (7)
H(N4)	0.0096 (22)	0.1314 (17)	0.2868 (36)	0.104 (12)
H(N6)	−0.1682 (20)	0.0570 (15)	0.8191 (31)	0.077 (10)
H(1A)	−0.0303 (18)	0.0221 (14)	0.7793 (29)	0.064 (11)
H(1B)	−0.0010 (21)	0.0969 (16)	0.8089 (34)	0.097 (11)
H(3)	0.0893 (17)	0.0895 (13)	0.4645 (26)	0.050 (8)
H(5)	−0.1794 (16)	0.1295 (13)	0.4936 (26)	0.048 (8)

Table 4. *Geometric parameters ($\mathring{A}$, °) for (2)*

N(2)—C(2)	1.358 (5)	C(11)—C(16)	1.374 (7)
N(2)—C(11)	1.410 (5)	C(12)—C(13)	1.369 (7)
N(4)—C(4)	1.358 (5)	C(13)—C(14)	1.359 (9)
N(4)—C(21)	1.415 (5)	C(14)—C(15)	1.348 (8)
N(6)—C(6)	1.350 (5)	C(15)—C(16)	1.377 (7)
N(6)—C(31)	1.411 (5)	C(21)—C(22)	1.377 (6)
C(1)—C(2)	1.480 (5)	C(21)—C(26)	1.374 (6)
C(1)—C(6)	1.494 (5)	C(22)—C(23)	1.383 (7)
C(1)—H(1A)	0.96 (3)	C(23)—C(24)	1.346 (8)
C(1)—H(1B)	0.91 (3)	C(24)—C(25)	1.355 (8)
C(2)—C(3)	1.356 (6)	C(25)—C(26)	1.378 (6)
C(3)—C(4)	1.422 (5)	C(31)—C(32)	1.383 (6)
C(3)—H(3)	0.95 (3)	C(31)—C(36)	1.381 (6)
C(4)—C(5)	1.408 (5)	C(32)—C(33)	1.381 (7)
C(5)—C(6)	1.365 (5)	C(33)—C(34)	1.369 (7)
C(5)—H(5)	0.92 (2)	C(34)—C(35)	1.367 (8)
C(11)—C(12)	1.370 (6)	C(35)—C(36)	1.383 (6)

C(2)—N(2)—C(11)	133.4 (3)	N(6)—C(6)—C(5)	125.9 (3)
C(4)—N(4)—C(21)	128.3 (3)	C(1)—C(6)—C(5)	120.6 (3)
C(6)—N(6)—C(31)	130.3 (3)	N(2)—C(11)—C(12)	116.3 (4)
C(2)—C(1)—C(6)	117.1 (3)	N(2)—C(11)—C(16)	125.8 (4)
H(1A)—C(1)—H(1B)	109 (3)	C(12)—C(11)—C(16)	118.0 (4)
N(2)—C(2)—C(1)	113.1 (3)	C(11)—C(12)—C(13)	120.7 (5)
N(2)—C(2)—C(3)	127.2 (4)	C(12)—C(13)—C(14)	121.3 (5)
C(1)—C(2)—C(3)	119.7 (3)	C(13)—C(14)—C(15)	118.2 (5)
C(2)—C(3)—C(4)	120.5 (4)	C(14)—C(15)—C(16)	121.6 (5)
N(4)—C(4)—C(3)	115.8 (3)	C(11)—C(16)—C(15)	120.2 (4)
N(4)—C(4)—C(5)	121.6 (3)	N(4)—C(21)—C(22)	117.8 (4)
C(3)—C(4)—C(5)	122.6 (3)	N(4)—C(21)—C(26)	123.2 (4)
C(4)—C(5)—C(6)	119.2 (3)	N(6)—C(31)—C(32)	123.6 (4)
N(6)—C(6)—C(1)	113.5 (3)	N(6)—C(31)—C(36)	117.8 (4)

C(1)—C(2)—N(2)—C(11)	175.0 (4)
C(1)—C(6)—N(6)—C(31)	170.7 (4)
C(2)—N(2)—C(11)—C(12)	−167.2 (4)
C(2)—N(2)—C(11)—C(16)	11.6 (7)
C(3)—C(2)—N(2)—C(11)	−5.5 (7)
C(3)—C(4)—N(4)—C(21)	−172.3 (4)
C(4)—N(4)—C(21)—C(22)	−144.3 (4)
C(4)—N(4)—C(21)—C(26)	39.8 (6)
C(5)—C(4)—N(4)—C(21)	10.1 (6)
C(5)—C(6)—N(6)—C(31)	−10.1 (6)
C(6)—N(6)—C(31)—C(32)	−32.1 (6)
C(6)—N(6)—C(31)—C(36)	152.7 (4)

Crystals of (1) were grown by slow cooling of a hot saturated absolute ethanol solution. Crystals of (2) were grown by the rapid addition of a 54 mg (0.28 mmol) solution of *p*-toluenesulfonic acid monohydrate in *ca* 5 ml of acetone to a 100 mg (0.28 mmol) solution of (1) in *ca* 5 ml of acetone, followed by leaving the undisturbed solution overnight in a capped vial at room temperature. *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *ORTEP* (Johnson, 1965) and some locally written programs were used for both (1) and (2).

References

Baenziger, N. C. & Nelson, A. D. (1968). *J. Am. Chem. Soc.* **90**, 6602–6607.

Borodkin, G. I., Nagi, S. M., Bagryanskaya, I. Y. & Gatilov, Y. V. (1984). *Zh. Stukt. Khim. (Engl. Transl.)* **25**, 440–445.

Effenberger, F., Reisinger, F., Schönwalder, K. H., Bäuerle, P., Stezowski, J. R., Jogun, K. H., Schöllkopf, K. & Stohrer, W. D. (1987). *J. Am. Chem. Soc.* **109**, 882–892.

Effenberger, F. (1989). *Acc. Chem. Res.* **22**, 27–35.

Glatzhofer, D. T., Allen, D. & Taylor, R. W. (1990). *J. Org. Chem.* **55**, 6229–6231.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kopytug, V. A. (1984). *Top. Curr. Chem.* **122**, 1–245.

Litvinenko, L. M., Popova, R. S. & Popov, A. F. (1975). *Russ. Chem. Rev.* **44**, 718–732.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Yoshizawa, K., Chano, A., Ito, A., Tanaka, K., Yamabe, T., Fujita, H., Yamauchi, J. & Shiro, M. (1992). *J. Am. Chem. Soc.* **114**, 5994–5998.

Acta Cryst. (1993). C49, 2133–2134

Tetrathiooxalsäure-Dimethylester

IRINA SENS

Fachbereich Chemie der Universität, Hans-Meerwein-Strasse, D-35032 Marburg, Deutschland

ULRICH MÜLLER

Fachbereich Biologie/Chemie der Universität, Heinrich-Plett-Strasse 40, D-34109 Kassel, Deutschland

Abstract

Dimethyl tetrathiooxalate molecules occupy centrosymmetric positions and in addition fulfil the point symmetry $2/m$ in excellent approximation, *i.e.* the molecules are planar and have *trans* conformation. The C—C bond length corresponds to a single bond and there are three significantly different C—S bond lengths.

Kommentar

Die Dithio- und Trithiooxalat-Ionen $[O_2C\text{-}CS_2]^{2-}$, $[OSC\text{-}CSO]^{2-}$ bzw. $[OSC\text{-}CS_2]^{2-}$ sind nicht planar; die Konformationswinkel zwischen den Carboxylat- bzw. Thiocarboxylatgruppen liegen nahe bei 90°. Dagegen sind die Molekülgerüste der S,S'-Diester der Di- und Trithiooxalsäure sowie diejenigen der Salze der Thiooxalsäure-S-monoester exakt oder annähernd planar (Kiel, Dräger & Reuter, 1974; Niemer & Mattes, 1978; Niemer, Mennemann & Mattes, 1978).

Beim Tetrathiooxalat-Ion $[S_2C\text{-}CS_2]^{2-}$ sind die beiden CS_2-Gruppen ebenfalls gegenseitig um 90° verdreht (Lund, Hoyer & Hazell, 1982; Bacher, Sens & Müller, 1992). Der auffällige Unterschied zur Struktur des entsprechenden Esters zeigt sich auch in diesem Falle: der Tetrathiooxalsäure-dimethylester hat innerhalb der Fehlergrenzen ein planares Molekülgerüst (Fig. 1). Die Abweichung der Methyl-C-Atome von der Ebene durch die übrigen Atome beträgt nur 0,015(4) Å. Die Bindungswinkel und -abstände weichen kaum nennenswert von den entsprechenden Werten im S,S'-Dithiooxalsäure-diethylester (Kiel, Dräger & Reuter,

1974) und Trithiooxalsäure-dimethylester (Niemer, Mennemann & Mattes, 1978) ab. Die C—C-Bindungslänge entspricht einer Einfachbindung, während sich die drei Sorten von C—S-Bindungen deutlich voneinader unterscheiden (Tabelle 2). Am längsten ist die Bindung H_3C—S [1,790(4) Å].

Im Kristall sind die Moleküle zu Säulen in Richtung a gestapelt, wobei die Molekülebene um 68,6° gegen a geneigt ist (Fig. 2). Es sind keine auffällig kurzen intermolekularen Kontakte vorhanden. $C_2S_4(CH_3)_2$ kristallisiert nicht isotyp zum Oxalsäure-dimethylester, obwohl die Packungen für beide Verbindungen ähnlich sind (Dougill & Jeffrey, 1953).
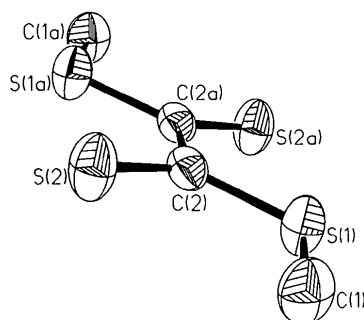

Fig. 1. Das Molekül des Tetrathiooxalsäure-dimethylesters mit Ellipsoiden der thermischen Schwingung (ohne H-Atome; 50% Aufenthaltswahrscheinlichkeit).
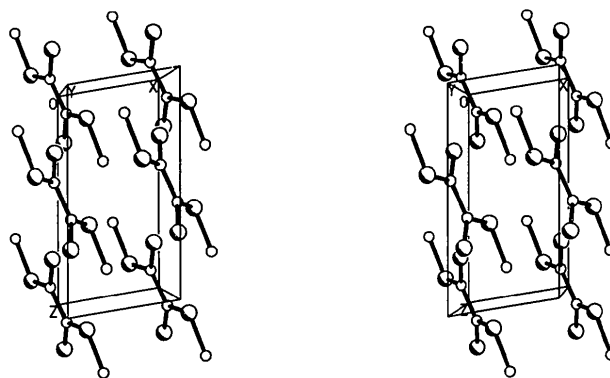

Fig. 2. Stereoskopische Ansicht der Elementarzelle.

Experimentelles

Kristalldaten

$C_4H_6S_4$	$D_x = 1{,}606$ Mg m^{-3}
$M_r = 182{,}3$	Mo $K\alpha$ Strahlung
Monoklin	$\lambda = 0{,}7107$ Å
$P2_1/c$	Gitterparameter aus 24 Reflexen
$a = 3{,}986$ (3) Å	$\theta = 7\text{--}18°$
$b = 11{,}753$ (4) Å	$\mu = 1{,}16$ mm^{-1}
$c = 8{,}154$ (2) Å	$T = 293$ K
$\beta = 99{,}20$ (3)°	Prisma