Synthesis and X-Ray Crystal Structure of $[S_3N_5Me_2CO]AsF_5$, the First Carbon-containing Bicyclic Sulphur–Nitrogen Compound. A Bridged S_3-Ring

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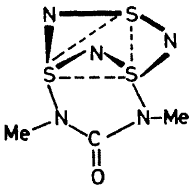
Summary An X-ray crystallographic study has shown that the new bicyclic cation $[S_3N_5Me_2CO]^+$ contains a three-membered ring of sulphur atoms, which is bridged by three nitrogen atoms and a urethane group; this compound was prepared by the reaction of $S_3N_3Cl_3$ with $Me_3SiNMeC(O)MeSiMe_3$ in CCl_4.

It is well known that main group elements having co-ordination number two can be stabilised when they form part of a ring system. Characteristic examples are phospha- and arsa-benzene.[1] We have now obtained the bicyclic cation $[S_3N_5Me_2CO]^+$ (**1**), which is analogous to the $S_4N_5^+$ cation reported by Chivers and Fielding,[2] and which provides an example of the stabilization of an unstable ring by incorporation into a bicyclic system.



(1)

Reaction of a stirred suspension of $S_3N_3Cl_3$ (41 mmol) in n-hexane (100 ml) with $(Me_3SiNMe)_2CO$ (41 mmol) for 12 h gave a yellow precipitate of $[S_3N_5Me_2CO]^+Cl^-$, which was recrystallized from CCl_4 (90% yield). The same product may also be obtained from the reaction of $S_4N_4Cl_2$[3] with $(Me_3SiNMe)_2CO$. Reaction of $[S_3N_5Me_2CO]^+Cl^-$ with an excess of AsF_5 in CCl_4 solution gave $[S_3N_5Me_2CO]^+AsF_6^-$, which was recrystallized from MeCN–CCl_4 (1:15) (89% yield). Analogous compounds may be obtained similarly with $SbCl_6^-$, $TiCl_5^-$, or $SnCl_5^-$ counter-ions.

Crystal data: $[S_3N_5Me_2CO]AsF_6$, orthorhombic, space group $P2_12_12_1$, $a = 21{\cdot}077(6)$, $b = 8{\cdot}574(2)$, $c = 6{\cdot}949(2)$ Å, $Z = 4$, $D_c = 2{\cdot}18$ g cm^{-3}. Data were collected on a Hilger and Watts automatic diffractometer using niobium-filtered Mo-K_α radiation. The structure was solved by direct methods and Fourier techniques to give an R-factor of 0·053 for 1840 observed reflections. Refinement is being continued.†

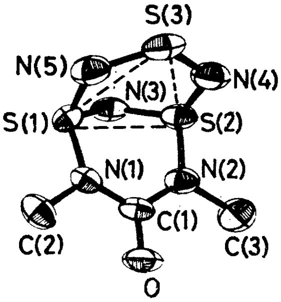


FIGURE. Structure of the bicyclic cation (**1**).

The Figure shows the structure of the $[S_3N_5Me_2CO]^+$ cation (**1**). It may be considered to consist of a three-membered ring of sulphur atoms, two sides of which are bridged by nitrogen atoms and the third side by a nitrogen atom and a urethane group. The S–S distances [S(1)–S(2) 2·703(2), S(1)–S(3) 2·802(2), and S(2)–S(3) 2·830(2) Å] are much shorter than the sum of the van der Waals' radii for sulphur (3·5 Å) indicating strong bonding interactions. Alternatively, the cation may be viewed as consisting of a six-membered 1,3,2,4,6-dithiatriaza-cyclic ketone, with the sulphur atoms bridged by a sulphur di-imide group.

Of special interest are the angles between the three different planes of the molecule, which differ considerably: ∠I and II 76·2, I and III 59·3, and II and III 45·3°. (I = plane with the ketone group, II = plane with the SN_2-five-membered ring, III = plane of the S_2N-skeleton).

This compound is the first example of a sulphur–nitrogen bicyclic derivative containing a carbon atom. Mass spectroscopy (70 eV) shows that the cation is quite stable, since the molecular ion is observed with 54% relative intensity. The ^1H n.m.r. spectrum in MeCN shows that the methyl groups are equivalent at room temperature: δ 3·15 (internal Me_4Si).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] A. J. Ashe, III, *Accounts Chem. Res.*, 1978, 153.
[2] T. Chivers and L. Fielding, *J.C.S. Chem. Comm.*, 1978, 212.
[3] L. Zbořilovà and L. Gebauer, *Z. Chem.*, 1979, **19**, 32.