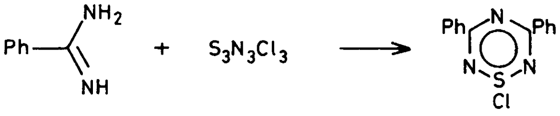
Preparation and Molecular Structure of 1-Chloro-3,5-diphenyl-1,2,4,6-thiatriazine; Reduction of $Ph_2C_2N_3SCl$ and the E.S.R. Spectrum of the $(Ph_2C_2N_3S)^\cdot$ Radical

A. Wallace Cordes,[a] Patrick J. Hayes,[b] P. David Josephy,[b] Hans Koenig,[b] Richard T. Oakley,*[b] and William T. Pennington[a]

[a] *Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, 72701, U.S.A.*
[b] *Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*

The reaction of benzamidine with $S_3N_3Cl_3$ yields 1-chloro-3,5-diphenyl-1,2,4,6-thiatriazine, whose molecular structure has been determined by *X*-ray crystallography; reduction of $Ph_2C_2N_3SCl$ with triphenylantimony yields the radical species $(Ph_2C_2N_3S)^\cdot$ characterized by its e.s.r. spectrum.

The preparation and characterization of a variety of novel heterocyclic thiazyl derivatives have recently been reported.[1–5] These molecules combine the structural stability of carbocyclic π-systems with the more unusual electronic properties of conjugated sulphur–nitrogen linkages. As a continuation of our work[1,2] in this area we report herein that the reaction of benzamidine with $S_3N_3Cl_3$ provides a convenient synthetic route to 1-chloro-3,5-diphenyl-1,2,4,6-thiatriazine (**1**) [equation (1)].



(1)

(**1**)

Compound (**1**) was prepared by heating a mixture of benzamidine (46.9 mmol) and $S_3N_3Cl_3$ (18.7 mmol) at reflux in acetonitrile (115 ml) for 16 h. Subsequent hot filtration and cooling of the filtrate afforded a yellow crystalline solid from which a small quantity of S_4N_4 was removed by sublimation *in vacuo*. Extraction of the residual material (which contains $PhCN_2S_2Cl$)[6] with hot carbon tetrachloride, removal of the solvent by evaporation, and recrystallization from acetonitrile

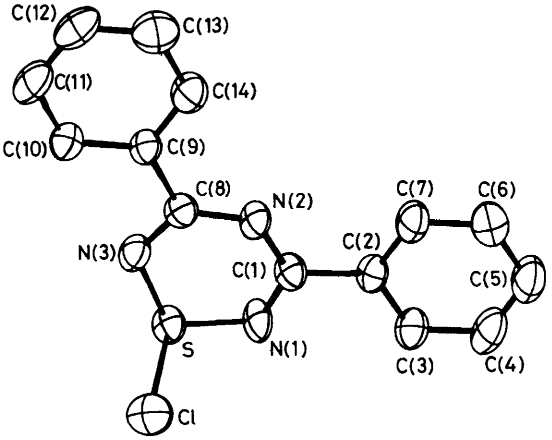


Figure 1. ORTEP Drawing (50% probability ellipsoids) of $Ph_2C_2N_3SCl$ (**1**). Selected bond lengths (in Å) and bond angles (in °) are: S–Cl 2.283(1), S–N(1) 1.590(3), S–N(3) 1.583(3), N(1)–C(1) 1.332(4), N(2)–C(1) 1.348(4), N(2)–C(8) 1.332(4), N(3)–C(8) 1.348(4), C(1)–C(2) 1.468(4), C(8)–C(9) 1.464(5); Cl–S–N(1) 100.5(1), Cl–S–N(3) 101.9(1), N(1)–S–N(3) 117.6(2), C(1)–N(2)–C(8) 119.8(3), S–N(3)–C(8) 117.7(2), N(1)–C(1)–N(2) 126.2(3), N(2)–C(8)–N(3) 125.9(3), S–N(1)–C(1) 117.6(2).

yielded yellow transparent needles of $Ph_2C_2N_3SCl$ (**1**) (7.9 mmol), m.p. 162—167 °C.†

The crystal structure of (**1**) was determined by *X*-ray crystallography.‡ An ORTEP drawing of the molecule and pertinent structural information are provided in Figure 1. The six-membered C_2N_3S ring of (**1**) adopts a shallow boat-like conformation, with the sulphur and N(3) nitrogen atoms lying 0.24 and 0.05 Å respectively away from the mean plane of the other four atoms. The CN bond lengths are similar to those observed in other thiatriazine structures, but the SN distances are considerably shorter,[7] reflecting the different extents of π-donation from exocyclic amino and chloro groups bound to sulphur into antibonding acceptor orbitals distributed over the S–N linkages.

The reduction of (**1**) with triphenylantimony in methylene dichloride yielded a brown solution which exhibited a strong and persistent e.s.r. signal (Figure 2, g = 2.0059) whose appearance is consistent with that expected for the free radical $(Ph_2C_2N_3S)^{\bullet}$ (**2**), in which hyperfine coupling constants to all three nitrogen atoms are equal (a_N = 0.397 mT). When the reduction was performed in acetonitrile solution a dark brown microcrystalline precipitate (m.p. 178—181 °C) was formed. This latter material is diamagnetic, but dissolves in methylene dichloride to give yellow–orange solutions which exhibit the e.s.r. spectrum assigned to (**2**). We suggest that in the solid state (**2**) exists in a dimeric form possessing a sulphur–sulphur bond, *e.g.* (**3**).† The dissociation (**3**) ⇌ (**2**) [equation (2)] is then reminiscent of the well known $S_2O_4^{2-}$ ⇌ $SO_2^{\bullet -}$ equilibrium.[8] Oxidation of solutions of (**2**) with sulphuryl chloride regenerated the starting material (**1**).

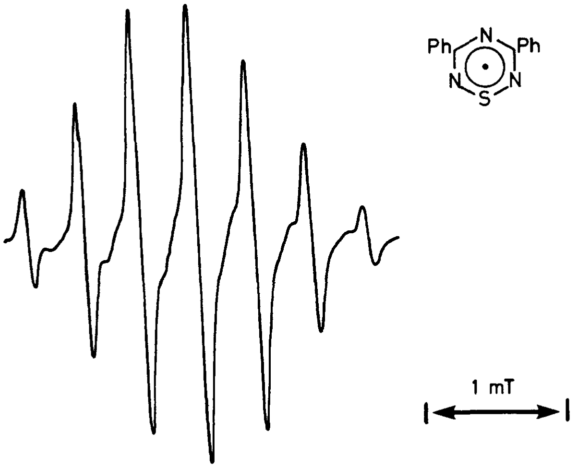
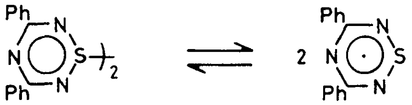


Figure 2. E.s.r. spectrum of $(Ph_2C_2N_3S)^{\bullet}$ (**2**) in methylene dichloride.



(2)

(**3**) (**2**)

We note that the reduction of (**1**) with retention of the cyclic structure is in contrast to the reduction of the related $Ph_4P_2N_3SCl$ ring, which results in the cleavage of one of the S–N bonds and dimerization to a twelve-membered $P_4N_6S_2$ ring.[9]

We thank the Natural Sciences and Engineering Research Council of Canada (R. T. O., P. D. J.), the Research Corporation (R. T. O.), The National Science Foundation (A. W. C.), the State of Arkansas (A. W. C.), and the National Cancer Institute of Canada (P. D. J.) for financial support.

Received, 9th April 1984; Com. 510

References

1 H. Koenig and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1983, 73.
2 P. W. Codding, H. Koenig, and R. T. Oakley, *Can. J. Chem.*, 1983, **61**, 1562.
3 G. K. Maclean, J. Passmore, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1983, 807.
4 S. T. A. K. Daley, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 55, 57.
5 A. Vegas, A. Perez-Salazar, A. J. Banister, and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812.
6 H-U. Hofs, R. Mews, W. Clegg, M. Noltemeyer, M. Schmidt, and G. M. Sheldrick, *Chem. Ber.*, 1983, **116**, 416.
7 A. Kalman, Gy. Argay, E. Fischer, and G. Rembauz, *Acta Crystallogr., Sect. B*, 1979, **35**, 860; A. Kalman, Gy. Argay, E. Fischer, G. Rembauz, and G. Voss, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1322.
8 R. G. Rinker, T. P. Gordon, D. M. Mason, and W. H. Corcoran, *J. Phys. Chem.*, 1959, **63**, 302.
9 T. Chivers, M. N. S. Rao, and J. F. Richardson, *J. Chem. Soc., Chem. Commun.*, 1982, 186.

---

† The elemental compositions of (**1**) and (**3**) were confirmed by chemical analyses and mass spectrometry. The mass spectrum of each shows the monomeric ion $Ph_2C_2N_3S^+$ (*m/z* 252) as the highest mass fragment.

‡ *Crystal data:* $C_{14}H_{10}SN_3Cl$, M = 287.8, orthorhombic, space group $P2_12_12_1$, a = 6.773(2), b = 11.114(2), c = 17.571(2) Å, U = 1323 Å^3, Z = 4, D_c = 1.45 g cm^{-3}. Data were collected on an Enraf-Nonius CAD-4 automated diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω–2θ scans (θ_{max} of 25°), and were corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares to an R value of 0.044 for 1142 independent reflections ($I > 3\sigma_I$) and 172 parameters (all non-hydrogen atoms were anisotropic: H atoms were included in calculated positions with fixed isotropic temperature factors).

The atomic co-ordinates 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.