Conversion of a 1,2,3-dithiazole into a 3*H*-pyrrole-3-thione and a 3*H*-pyrrol-3-ylidenephosphorane

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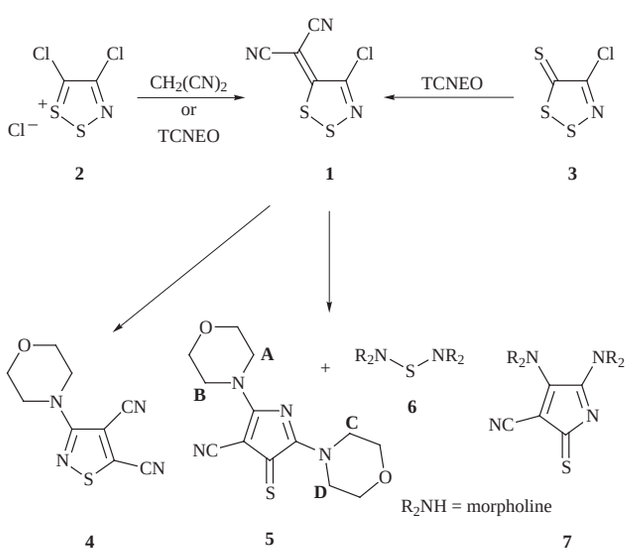
Treatment of the readily available dicyanomethylenedithiazole 1 with excess of morpholine or triphenylphosphine gives the 3-azacyclopentadienethione (3*H*-pyrrole-3-thione) 5 and the 3-azacyclopentadienylphosphorane (3*H*-pyrrol-3-ylidenephosphorane) 16 respectively. Both products are deeply coloured and highly stabilised by extensive electron delocalisation: ^{1}H and ^{13}C NMR spectra show that rotation of the morpholine groups in 5 is hindered. Structure 16, the first azacyclopentadienylphosphorane reported, is proved by X-ray crystallography. Mechanisms are reported for these transformations in which the initial step is considered to be opening of the dithiazole ring of 1 by nucleophilic attack by the amine or the phosphine at the central heteroatom.

We recently reported the synthesis of dicyanomethylenedithiazole **1** from 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt) **2** and malononitrile or tetracyanoethylene oxide (TCNEO), and from 4-chloro-5*H*-1,2,3-dithiazole-5-thione **3** and tetracyanoethylene oxide, together with the conversion of **1** into 4,5-dicyano-3-morpholinoisothiazole **4** with morpholine in boiling benzene.[1]

In an attempt to improve the yield of isothiazole **4**, in what could be a very direct and attractive route to this ring system, the dithiazole **1** was treated with an excess of morpholine (10 equiv.) in boiling toluene. A yellow precipitate was formed immediately, the reaction mixture rapidly darkened and within 10–15 min a new deep red product was formed together with an unidentified black precipitate. TLC also showed the presence of isothiazole **4**, dimorpholino sulfide **6** and sulfur, but these were not isolated. After chromatography and purification the red compound was shown to be 4-cyano-2,5-dimorpholino-3*H*-pyrrole-3-thione **5** (30%) as follows.

HRMS gave the formula $C_{13}H_{16}N_4O_2S$, the 16 hydrogens and two oxygens suggesting the presence of two morpholino substituents. The parent ion *m*/*z* 292 (100%) was by far the strongest in the mass spectrum, which revealed little else of value. The IR spectrum showed a nitrile stretch at 2197 cm^{-1} which, at this low wavenumber, indicated extensive electron delocalisation to the cyano group.



2 **1** **3**

4 **5** **7**

^{13}C NMR spectroscopy showed five low field and eight high field carbon resonances; the presence of the cyano group was supported by the carbon signal at 118 ppm and of a thiocarbonyl group by the low field signal at 197 ppm. The eight high field signals were attributed to the morpholine substituents, whose rotations must be restricted on the ^{13}C NMR timescale. The ^{1}H NMR spectrum supported this, with four groups of resonances in the ratio of 2:2:4:8 at 4.94, 3.92, 3.81–3.76 and 3.66–3.55 ppm; these signals were well resolved. Few structures agree with these data for the red compound; **5** and **7** retain the carbon and nitrogen connectivity of the starting material but only **5** retains the carbon, nitrogen and sulfur connectivity. The 3-thione structure **5** was assigned to the product on the basis of a more rational mechanism for its formation (see below) and by comparison with the related 4-cyano-3*H*-pyrrole **16** formed from **1** and triphenylphosphine, the structure of which was proved by X-ray crystallography (see below). The 3*H*-pyrrole-3-thione ring of the deep red product **5** is formally 4π anti-aromatic, but extensive electron release from the morpholino groups and electron withdrawal by the other three heteroatoms results in a highly delocalised structure, imparting the observed stability. The resulting iminium ion character of the morpholino nitrogen atoms also accounts for their hindered rotation.

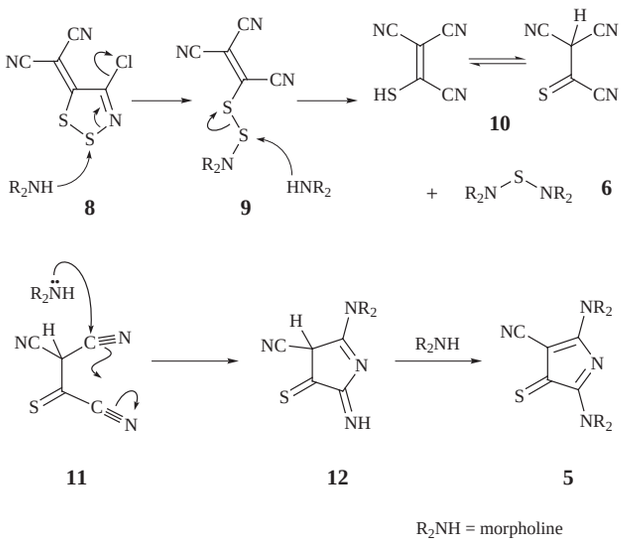
On the basis of structure **5**, the ^{1}H NMR spectrum can be assigned more completely. The environment of all the CH_2O protons will be very similar and they should have similar chemical shifts, close to the value for this methylene in morpholine itself (3.67 ppm). The multiplet at 3.66–3.55 ppm with the integral ratio of 8 is assigned to these protons. The remaining, CH_2N, proton resonances at 4.94, 3.92 and 3.81–3.76 ppm are strongly deshielded compared to the same protons in morpholine (2.87 ppm) because of the electron withdrawal mentioned above. The local environment of the CH_2N protons **A** and **C** is similar and they can be assigned to the multiplet at 3.81–3.76 ppm, with an integral ratio of 4. One of the two remaining CH_2N resonances (4.94) is shifted 1 ppm downfield from the other (3.92 ppm). This extra deshielding could arise from the local environment of the protons where the hindered rotation of the morpholine ring could bring the protons at **B** into the deshielding zone of the cyano group; the protons at **D** are assigned to the 3.92 ppm signal.

There are few reports in the literature on 3*H*-pyrrole-3-ones (3-azacyclopentadienones), the oxygen analogues of **5**, but only one example of a 3*H*-pyrrole-3-thione. 2,4,5-Tris(dimethyl-

amino)-3*H*-pyrrole-3-thione has been prepared in an entirely different way from pentachloro-2*H*-pyrrole, as deeply coloured crystals.[2]

Mechanism for the formation of 5

5-(*N*-Arylimino)-4-chloro-5*H*-1,2,3-dithiazoles **14** (see below) have been shown to undergo nucleophilic attack at S-1, S-2 and C-5, with S-2 being the usual electrophilic centre in intermolecular reactions.[3,4] Kim has shown that secondary aliphatic amines displace the 4-chlorine atom by a ring opening–ring closing mechanism initiated by attack at S-2.[4] In the reaction of the dicyanomethylenedithiazole **1** with morpholine it seems entirely reasonable that the first reaction (arrows in **8**) should be the same to give the disulfide **9** where the relatively weak S–N bond has been broken and a new cyano group formed (Scheme 1).



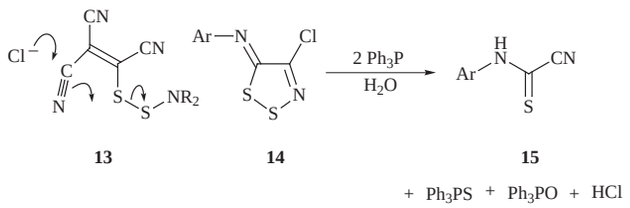
Scheme 1

The powerfully electron withdrawing tricyanovinyl group in **9** will activate the S–S bond to further nucleophilic attack by the excess of morpholine (arrows in **9**) to give the dimorpholino sulfide **6** and tricyanovinyl thiol **10**.† This last species, in equilibrium with the thione and possibly the ketenimine forms, could add morpholine and cyclise to the pyrrole derivative **12** (*cf*. ref. 6). Tautomerism and amine exchange with more morpholine would then give the product **5** isolated (Scheme 1).

For the earlier conversion of the dithiazole **1** into isothiazole **4** with one equivalent of morpholine in benzene,[1] we proposed that the first step could be addition of morpholine to a cyano group, followed by opening of the dithiazole ring by the amidine so formed to give **4**. In view of the mechanism of Scheme 1 and the evidence for ready nucleophilic attack at S-2 in the aryliminodithiazole compounds **14**,[3,4] we now consider that the first step for **1**→**4** is more likely to be the attack at S-2, as in **8**, to give the same intermediate **9** (Scheme 1). It is then possible that with only one equivalent of morpholine present, the chloride generated in this displacement competes effectively with morpholine in adding to **9**, as shown in **13**, to give 3-chloro-4,5-dicyanoisothiazole as we found before.[1] We also found that this chloro compound reacted in high yield (80%) with morpholine to give the 3-morpholinoisothiazole **4**.[1]

Reaction of dithiazole 1 with triphenylphosphine

Triphenylphosphine abstracts the 2-sulfur atom from aryliminodithiazoles **14** with the formation of a cyano group to give cyanothioformanilides **15** in high yield under very mild conditions.[7]



This reaction appears to involve initial nucleophilic attack by phosphorus at S-2, of the type described above (*cf*. **8**). It was therefore of interest to apply this reaction to the dicyanomethylenedithiazole **1**, to see if triphenylphosphine acted similarly to morpholine by a pathway analogous to **8**→**9**→**10** (Scheme 1) to generate the same tricyanovinyl thiol species.

Upon addition of triphenylphosphine (1 equiv.) to a toluene solution of **1** a black precipitate was formed which did not dissolve even at reflux. Chromatography gave triphenylphosphine oxide and sulfide and a very dark red crystalline compound (mp >250 °C) which dissolved readily in DCM to give a deep blue solution. The red compound was shown by single crystal X-ray analysis to be the ylide [4-cyano-5-tricyanovinyl-2-(triphenylphosphoranylideneamino)-3*H*-pyrrol-3-ylidene]-triphenylphosphorane **16** (24%), Fig. 1, the first 3*H*-pyrrol-3-ylidenephosphorane, as follows.

A UV absorption at λ_{max} 594 nm (log ε 4.41) indicated an extensive chromophore. The FAB (glycerol) mass spectrum showed a strong protonated molecular ion of *m*/*z* 729 (MH^+, 100%) and little other structural information. HRMS supported the molecular formula, $C_{46}H_{30}N_6P_2$, of a highly "unsaturated" molecule. The IR data showed aromatic C–H stretching at 3150 and 3060 cm^{-1}, strong ethene or imine stretching at 1515 cm^{-1} and a strong broad nitrile band at 2204 cm^{-1}. The ^1H NMR spectrum showed three complex aromatic multiplets of the triphenylphosphine groups. ^{31}P NMR showed two similar phosphorus environments at 15.4 and 13.3 ppm, in the range for phosphonium ylides, $Ph_3P{=}CR_2$, with no ^{31}P–^{31}P coupling. The proton decoupled ^{13}C NMR data was not clear; all the aromatic C–H resonances were assigned and confirmed by a C–H DEPT, with the ^{31}P–^{13}C coupling values. One of the aromatic quaternary carbons directly attached to phosphorus was not visible. The ^{31}P–^{13}C coupling values for such carbons are very large ($^1J_{PC}$ 80–100 Hz) and we could only identify one pair of doublets (128.8 ppm, $^1J_{PC}$ 101 Hz); we assume that both aromatic quaternary carbon signals overlap at this resonance. Two significantly higher field signals (121.1 and 120.7 ppm) gave the appearance of being coupled ($^1J_{PC}$ 94 Hz) but their assignment has not been confirmed. Four non-coupled carbon signals were in the nitrile region (117.2, 115.5, 114.5 and 113.1 ppm) and a signal at 71.2 ppm was typical for the central carbon in dicyanomethylene compounds. The remaining sp^2 carbon resonances were weak and complex signals, presumably caused by ^{31}P–^{13}C coupling between both phosphorus atoms and nearby carbon atoms.

The ylide nature of **16** is further demonstrated by the patterns of bonding in the molecule. The P(2)–C(3) linkage has clear partial double bond character [1.755(4) Å] though it is noticeably longer than that reported for triphenylphosphonium cyclopentadienylide [1.718(2) Å].[8] The bond lengths within the pyrrole ring indicate a pattern of delocalisation extending between P(2) and N(6) *via* N(1), the C(2)–C(3) bond having pronounced single bond character [1.440(6) Å]. This delocalisation also includes, to a lesser degree, the cyano carbon C(7) and the carbon atom C(8) of the tricyanoethylene group. The P=N double bond length is typical at 1.577(4) Å and the bond lies close to the plane of the pyrrole ring, the average torsion angle about the C(2)–N(6) bond being *ca*. 22°. The only intermolecular packing interaction of note is an edge-to-face

† Whilst this sulfur compound **10** appears to be unknown, its highly acidic oxygen analogue has been prepared in aqueous solution by hydrolysis of tetracyanoethylene and characterised as various salts.[5]

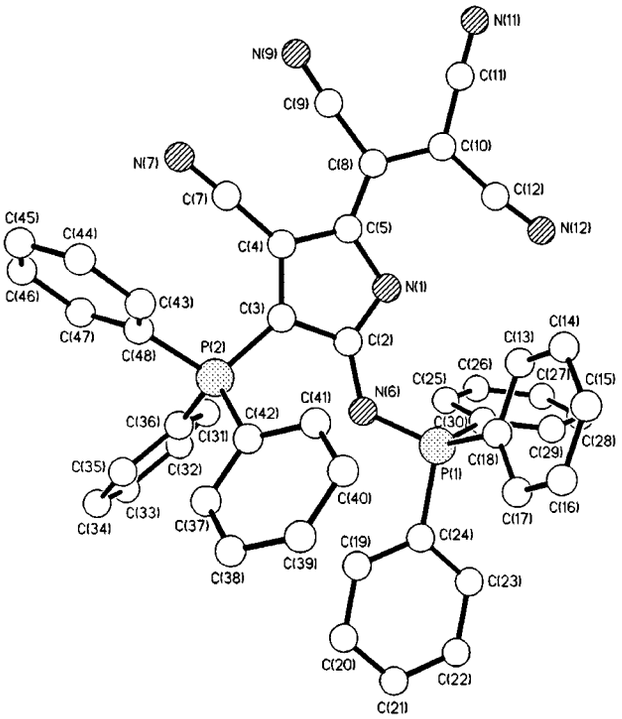
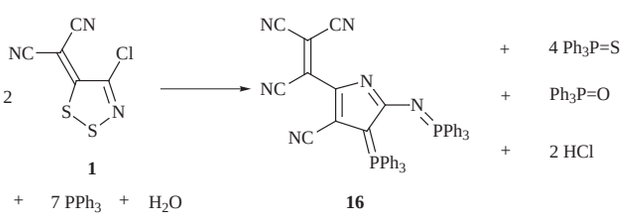


Fig. 1 The molecular structure of **16**. Selected bond lengths (Å) are: N(1)–C(2) 1.336(6), C(2)–C(3) 1.440(6), C(3)–C(4) 1.403(6), C(4)–C(5) 1.417(6), C(5)–N(1) 1.374(6), C(2)–N(6) 1.360(5), N(6)–P(1) 1.577(4), C(3)–P(2) 1.755(4), C(4)–C(7) 1.414(6), C(5)–C(8) 1.412(7).

C–H · · · π aromatic · · · aromatic interaction between one of the phenyl rings attached to P(1) in one molecule and one of the phenyl rings attached to P(2) in another [the H · · · π distance is 2.80 Å and the C–H · · · π angle is 170°].

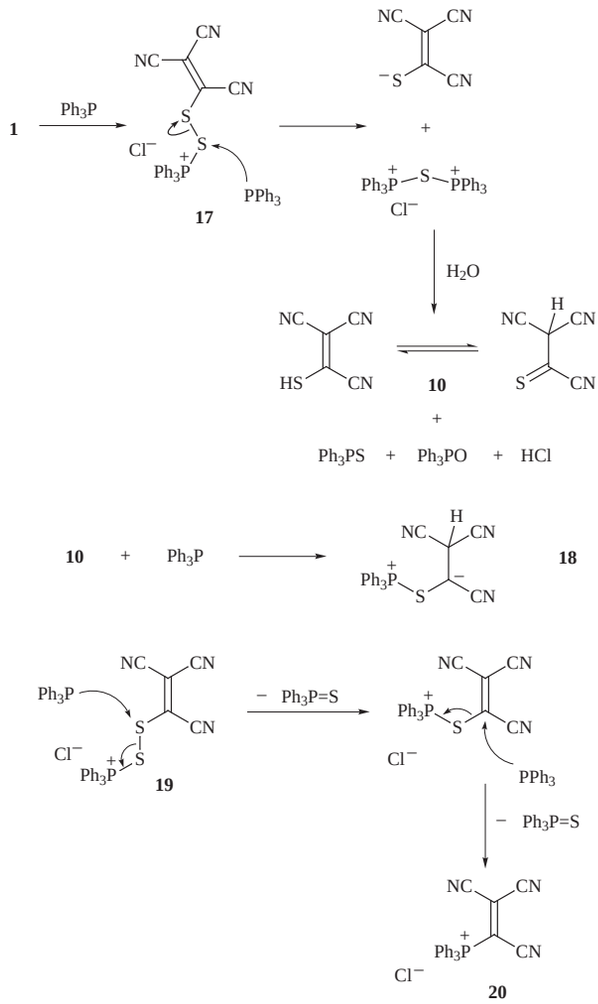
Mechanism for the formation of ylide 16

Although the structure of ylide **16** is somewhat analogous to that of **5**, the reaction of dithiazole **1** with triphenylphosphine is more complex than its reaction with morpholine. Two molecules of both starting materials are incorporated into the product and all the sulfur and chlorine atoms are removed as triphenylphosphine sulfide and, after chromatographic work up, triphenylphosphine oxide. The simplest overall stoichiometry is shown in Scheme 2, and the key problem is how the two dithiazole derived portions combine together.

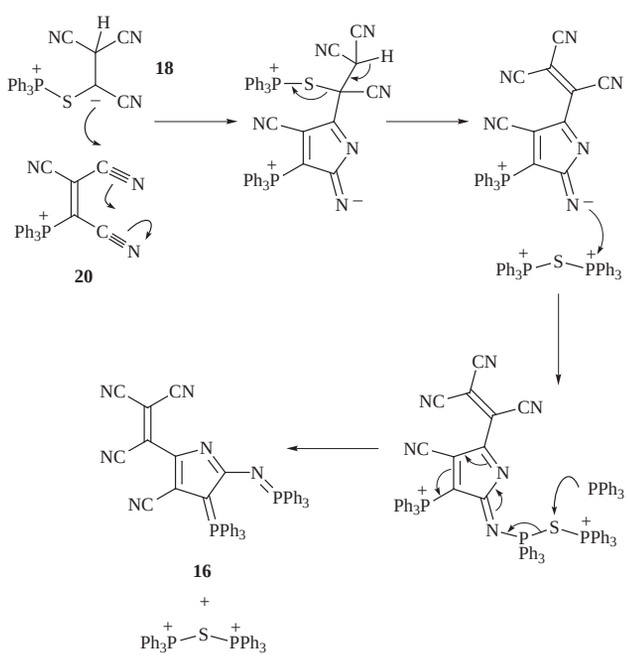


Scheme 2

We again assume that the reaction starts by attack of triphenylphosphine at S-2, with cleavage of the S–N bond to give **17** which is analogous to the intermediate **9** in the morpholine reaction. Then either sulfur atom of **17** could suffer further attack by triphenylphosphine (Scheme 3). Attack at the same sulfur as before would lead to the tricyanovinyl species **10**, exactly as described in Scheme 1; in its thiocarbonyl tautomer this could be attacked yet again by the phosphine to give the zwitterion **18**. Attack at the other sulfur atom in **17**, as shown in **19** could lead to the tricyanovinylphosphonium salt **20** with its *cis* cyano groups being susceptible to nucleophilic addition and cyclisation to a pyrrole derivative.[6] Such attack of **20** by the carbanionic centre of **18**, analogous to **11** in Scheme 1, could



Scheme 3



Scheme 4

lead to the highly delocalised product **16** isolated, as shown in Scheme 4.

In the reaction of the arylimino derivatives **14** with triphenylphosphine, the species analogous to the thione **10** are the thioamides **15** which are isolated in high yield. The thione is

expected to be more reactive than the thioamide and not surprisingly it reacts further with triphenylphosphine, as proposed in Scheme 3. Our suggested mechanism agrees with the stoichiometry of Scheme 2, where the small amount of water required is assumed to be introduced during work up and chromatography.

The very rare 3-azacyclopentadienethione **5** and the previously unknown 3-azacyclopentadienylphosphorane **16** systems are thus readily available from the dithiazole **1** in one step, and are worthy of further examination.

Experimental

Light petroleum refers to the fraction, bp 60–80 °C. Reactions and column eluents were monitored by TLC using aluminium backed thin layer chromatography plates (Merck Kieselgel 60 F_{254}) viewed under UV light at 254 and 350 nm. Dry flash chromatography on Sorbsil C60 M40 silica was used for separations. UV and IR spectra were measured on Perkin-Elmer Lambda II and Perkin-Elmer 1710FT spectrometers respectively. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on Bruker AM300WB and RX-400 machines. *J* Values are given in Hz. Mass spectra were recorded on VG micromass 7070E or Autospec "Q" machines. Microanalyses were carried out on a Perkin-Elmer 2400 CHN Analyser.

4-Cyano-2,5-dimorpholino-3*H*-pyrrole-3-thione 5

To a stirred solution of (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-propanedinitrile **1** (60 mg, 0.30 mmol) in toluene (8 ml) at 110 °C, morpholine (260 μl, 3 mmol) was added in one portion. The mixture rapidly gave a yellow precipitate and then became deep red. After 1 h a deep red product was observed (TLC) and the mixture was allowed to cool to *ca*. 20 °C. Filtration of the mixture gave a black precipitate (35 mg), which was apparently a mixture for which no good spectroscopic data could be obtained. Chromatography (DCM) of the filtrate gave the *title compound* **5** (27 mg, 31%) as deep red needles, mp 215–220 °C (from 1,2-dichloroethane–pentane); λ_{max}(DCM)/nm 256 (log ε 4.06), 359 (4.30), 372 (4.32), 391 inf (4.10), 526 (3.67); ν_{max}(Nujol)/cm^{-1} 2197m (CN), 1624m (C=N), 1574s (C=C), 1456s, 1403m, 1388m, 1371m, 1353s, 1330m, 1309s, 1276s, 1254s, 1225w, 1212w, 1154w, 1112s, 1086w, 1064m, 1043m, 1021m, 1007w, 954s, 918w, 894m, 853w, 741w, 715m, 699w, 666w, 652m, 634m, 613s; δ_H(300 MHz; $CDCl_3$) 4.94 (2H, t, *J* 4.8, CH_2N), 3.92 (2H, t, *J* 4.8, CH_2N), 3.81–3.76 (4H, m, CH_2N), 3.66–3.55 (8H, m, CH_2O); δ_C(76 MHz; $CDCl_3$) 196.84 (*C*=S), 174.79 (*C*=N), 159.94 (*C*–N), 117.97 (*C*N), 96.92 (*C*–CN), 67.24 (*C*H_2O), 66.75 (*C*H_2O), 66.72 (*C*H_2O), 66.62 (*C*H_2O), 48.99 (*C*H_2N), 48.31 (*C*H_2N), 48.26 (*C*H_2N), 45.91 (*C*H_2N); *m*/*z* (EI) 292 (M^+, 100%), 259 (M^+ − HS, 4), 249 (16), 235 (20), 222 (8), 191 (4), 178 (10), 162 (9), 151 (7), 122 (7), 94 (5), 56 (6), 43 (17) (Found: M^+, 292.0998. $C_{13}H_{16}N_4O_2S$ requires *M*, 292.0994).

[4-Cyano-5-tricyanovinyl-2-(triphenylphosphoranylideneamino)-3*H*-pyrrol-3-ylidene]triphenylphosphorane 16

To a stirred solution of (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-propanedinitrile **1** (50 mg, 0.25 mmol) in toluene (3 ml) at *ca*. 20 °C, triphenylphosphine (326 mg, 1.24 mmol) was added in one portion. A black precipitate formed and the mixture was then heated to reflux (110 °C). After 3 days at 110 °C no starting material remained (TLC) and the mixture was allowed to cool to *ca*. 20 °C. Chromatography (light petroleum–DCM, 1 : 1) gave triphenylphosphine (70 mg). Further elution gave triphenylphosphine sulfide (127 mg, 86%), identical with an authentic specimen. Further elution gave the *title compound* **16** (22 mg, 24%) as dark red needles, mp >250 °C (from 1,2-dichloroethane–pentane) (Found: C, 71.1; H, 4.3; N, 10.2. $C_{46}H_{30}N_6P_2\cdot C_2H_4Cl_2$ requires C, 69.7; H, 4.1; N, 10.2%); λ_{max}(DCM)/nm 229 (log ε 4.70), 268 (4.15), 322 (4.06), 387 (3.96), 594 (4.41); ν_{max}(DCM film)/cm^{-1} 3150w and 3060w (Ar CH), 2204s (CN), 1589w and 1575w (C=N), 1515s (C=C), 1483s, 1417s, 1333s, 1271s, 1228m, 1186s, 1163m, 1110s, 1070m, 1028w, 999m, 980s, 928w, 897m, 884m, 851w, 724s, 692s, 625s, 613s; δ_H(400 MHz; DCM-d_2) 7.79–7.69 (10H, m, Ar H), 7.57–7.47 (10H, m, Ar H), 7.42–7.30 (10H, m, Ar H); the following carbon resonances could be observed, δ_C(100 MHz; DCM-d_2) 164.23, 141.16 (d, J_{PC} 20.5 ?), 134.74 (d, J_{PC} 10.5, C-3), 134.36 (d, J_{PC} 2.4, C-4), 133.25 (d, J_{PC} 10.3, Ar C-3), 132.24 (d, J_{PC} 2.2, Ar C-4), 129.76 (d, J_{PC} 13.0, C-2), 128.81 (d, J_{PC} 101.3, C-1), 128.58 (6H, d, J_{PC} 12.7, Ar C-2), 121.14 (d, J_{PC} 93.7, ?), 117.16 (CN), 115.50 (CN), 114.49 (CN), 113.09 (CN), 109.80 (d, J_{PC} 14, ?), 96.81 (dd, J_{PC} 25.0, 110.8, C=P), 71.16 [C(CN)$_2$]; δ_P(109.4 MHz; DCM-d_2) 15.38, 13.33; *m*/*z* (FAB) 729 (MH^+, 100%), 290 (24), 150 (46), 135 (34), 120 (43), 105 (27), 90 (70), 77 ($C_6H_5^+$, 71), 65 (27) (Found: M^+, 728.2114. $C_{46}H_{30}N_6P_2$ requires *M*, 728.2007). A final elution (ethyl acetate) gave triphenylphosphine oxide (10 mg, 29%), identical with an authentic specimen.

Crystal structure determination

Crystal data for **16**.—$C_{46}H_{30}N_6P_2\cdot C_2H_5OH$, $M = 774.8$, monoclinic, space group $P2_1/n$ (no. 14), a =13.560(1), b =22.508(7), c = 13.934(1) Å, β = 91.83(1)°, V = 4251(1) Å^3, Z = 4, D_c = 1.211 g cm^{-3}, μ(Cu-Kα) = 12.7 cm^{-1}, F(000) = 1616, T = 293 K, red needles, 0.57 × 0.17 × 0.10 mm.

Data collection and processing.—Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. 6311 Independent reflections were measured [$2\theta \leqslant 120°$] of which 4203 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and an empirical absorption correction was applied; the maximum and minimum transmission factors were 0.64 and 0.16 respectively.

Structure analysis and refinement.—The structure was solved by direct methods and the pendant phenyl rings were refined as idealised rigid bodies. Disorder was found in the terminal C(CN)$_2$ unit and in one of the triphenylphosphine phenyl rings with, in both instances, two partial occupancy orientations being identified. In each case only the major occupancy non-hydrogen atoms were refined anisotropically. The included ethanol solvent molecule was found to be disordered over three partial occupancy sites with only the major occupancy non-hydrogen atoms being refined anisotropically. The remaining, full occupancy, non-hydrogen atoms were refined anisotropically and the C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, [U(H) = 1.2U_{eq}(C), U(H) = 1.5U_{eq}(C–Me)], and allowed to ride on their parent atoms. The O–H hydrogen atoms of the disordered ethanol molecule could not be located. Refinements were by full matrix least-squares based on F^2 to give $R_1 = 0.079$, $wR_2 = 0.213$ for the observed data and 553 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.44 and −0.35 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively. All computations were carried out using the SHELXTL PC program system.[9]

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web Pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/248.

Acknowledgements

We thank the EPSRC for a Research Studentship (P. A. K.), MDL Information Systems (UK) Ltd for financial support and the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medicinal Science at Imperial College.

References

1 K. Emayan, R. F. English, P. A. Koutentis and C. W. Rees, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 3345.
2 R. Gompper and M. Junius, *Tetrahedron Lett.*, 1980, **21**, 2883.
3 T. Besson, J. Guillard, C. W. Rees and V. Thiéry, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 889 and references therein.
4 H. Lee and K. Kim, *J. Org. Chem.*, 1993, **58**, 7001; H. Lee, K. Kim, D. Whang and K. Kim, *J. Org. Chem.*, 1994, **59**, 6179.
5 W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc.*, 1958, **80**, 2795.
6 J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 1952, 5000; M. P. Sammes and A. R. Katritzky, *Adv. Heterocycl. Chem.*, 1982, **32**, 248.
7 T. Besson, K. Emayan and C. W. Rees, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 2097.
8 H. L. Ammon, G. L. Wheeler and P. H. Watts, *J. Am. Chem. Soc.*, 1973, **95**, 6158.
9 SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.

Paper 8/04815K
Received 24*th June* 1998
Accepted 17*th July* 1998