# Polyfluoroarenes. Part XI.[1] Reactions of Tetrafluorophthalonitrile with Nucleophilic Reagents

By **J. M. Birchall, R. N. Haszeldine,*** and **J. O. Morley,** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Dimethylformamide, sodium 1-naphtholate, aniline, *N*-methylaniline, and ammonia readily effect nucleophilic displacement of fluoride ion from the 4-position in tetrafluorophthalonitrile to give high yields of monosubstituted products. Diethylphosphine, sodium benzenethiolate, lithium chloride, and lithium bromide give mainly 4,5-di- and 3,4,5,6-tetra-substituted products under the conditions described. The reaction with lithium chloride has also been applied to tetrafluorohydroquinone, and gives tetrachlorohydroquinone in high yield. Tetrafluorophthalonitrile reacts with arylamines and with polynuclear aromatic hydrocarbons in solvents of low polarity to give stable, crystalline molecular complexes.

The limited number of nucleophilic substitution reactions of pentafluorobenzonitrile which have been reported are sufficient to show that the cyano-group can exert a powerful activating influence on this type of reaction. For example, pentafluorobenzonitrile reacts in acetone with the weak base, sodium pentafluorophenoxide, to give 4-cyanononafluorodiphenyl ether in good yield,[2] and the reaction of the nitrile with sodium methoxide in methanol is $10^5$ times faster than the corresponding reaction of hexafluorobenzene.[3] The reactions of tetrafluorophthalonitrile with certain metal carbonyl anions have also been described;[4] this compound would be expected to be highly reactive towards nucleophilic reagents.

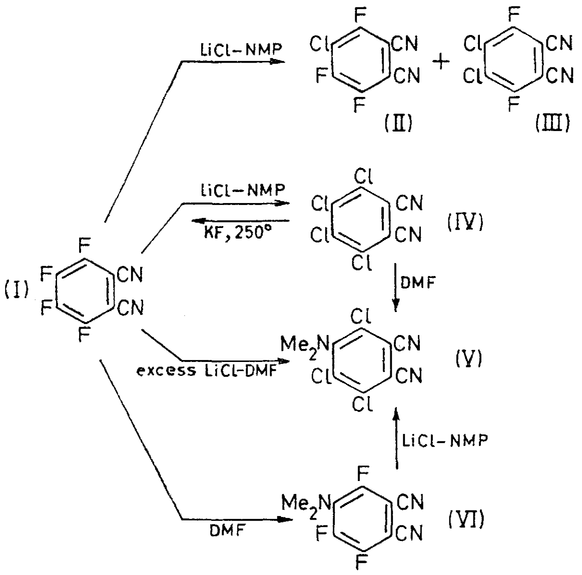
Tetrafluorophthalonitrile (I) may be prepared either by the reaction[5] of tetrachlorophthalonitrile (IV) with an excess of anhydrous potassium fluoride at 250° or from 1,2-dibromotetrafluorobenzene and copper(I) cyanide in dimethylformamide.[6] We used the former route; the tetrafluoro-compound was consistently obtained in 65—70% yield.

*Reactions with Lithium Halides*.—Although iodide ion has been used as a nucleophile with pentafluoropyridine,[7] there is little published information on the reactions of either bromide or chloride ion with polyfluoroarenes. Lithium bromide and lithium chloride were selected for study with tetrafluorophthalonitrile because they are soluble in polar organic solvents whereas lithium fluoride is insoluble, so that the equilibrium

$$\mathrm{ArF} + \mathrm{LiX} \rightleftharpoons \mathrm{ArX} + \mathrm{LiF}$$

should move continuously to the right as lithium fluoride is precipitated from solution. Aprotic solvents, such as *NN*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) were selected in order to limit the degree of solvation of the halide ions.

The reaction of tetrafluorophthalonitrile with lithium chloride (8 mol.) in refluxing NMP gives tetrachlorophthalonitrile (IV) in 73% yield. However, a 1 : 1 mole ratio of reactants leads to 85% conversion into two products, 4-chloro-3,5,6-trifluorophthalonitrile (II) (47% yield) and 4,5-dichloro-3,6-difluorophthalonitrile (III) (17% yield). The structures of the nitriles (II) and (III) are deduced from their $^{19}$F n.m.r. spectra (see later).



The reaction of tetrafluorophthalonitrile with an excess of lithium chloride in refluxing DMF during 3 hr. is complicated by direct participation of the solvent in the reaction, and yields 3,5,6-trichloro-4-dimethylaminophthalonitrile (V) (72%). The same compound (78% yield) is obtained from the reaction of tetrachlorophthalonitrile (IV) with DMF alone during 10 hr., but conversion is incomplete after only 3 hr. The structure of the trichloro-compound (V) is confirmed by a further synthesis from 4-dimethylamino-3,5,6-trifluorophthalonitrile (VI) and lithium chloride in NMP (83% yield). The trifluoro-compound (VI) is obtained (72%) by the reaction of tetrafluorophthalonitrile (I) with refluxing DMF during 3 hr., and its structure is deduced by $^1$H and $^{19}$F n.m.r. spectroscopy. The relative rates of these reactions indicate that formation of the trichloro-

---

[1] Part X, J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, preceding paper.

[2] R. J. De Pasquale and C. Tamborski, *J. Org. Chem.*, 1968, **33**, 1658.

[3] K. C. Ho and J. Miller, *Austral. J. Chem.*, 1966, **19**, 423.

[4] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1837.

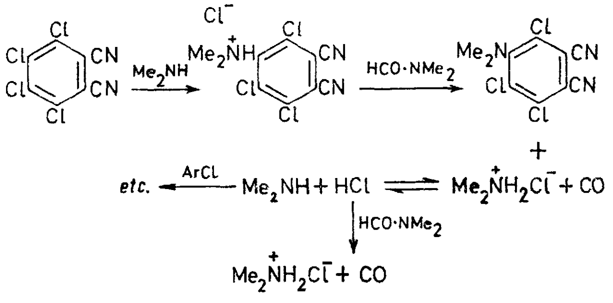
[5] R. N. Haszeldine, B.P. 1,026,290/1966 (*Chem. Abs.*, 1966, **64**, 19,507).

[6] L. J. Belf, M. W. Buxton, and G. Fuller, *J. Chem. Soc.*, 1965, 3372.

[7] R. E. Banks, R. N. Haszeldine, E. Phillips, and I. M. Young, *J. Chem. Soc.* (*C*), 1967, 2091.

compound (V) from tetrafluorophthalonitrile proceeds mainly *via* the initial replacement of fluorine by the dimethylamino-group, rather than by initial formation of the tetrachloro-compound (IV).

Dimethylamination by DMF has been observed before in the polyfluoroarene field and elsewhere. Refluxing DMF reacts with pentafluorobenzonitrile to give 4-dimethylaminotetrafluorobenzonitrile,[8] with 2,5-dichlorobenzimidazole to give 5-chloro-2-dimethylaminobenzimidazole,[9] with 4-chloronitrobenzene to give 4-dimethylaminonitrobenzene,[10] and with acid chlorides and anhydrides to yield the corresponding *NN*-dimethylamides.[11] It has been suggested that DMF itself can serve as the nucleophile in this type of reaction,[9] but it seems more probable that the attacking entity is dimethylamine, produced with carbon monoxide by the decomposition of DMF.[8,12] However, carbon monoxide formation cannot be detected when DMF is heated under reflux for 10 hr., but a rapid evolution follows the addition of 5% of concentrated hydrochloric acid to the refluxing solvent. The reactions with polyhalogenoarenes could be initiated by traces of free dimethylamine, which are usually present in DMF,[12] and further decomposition would be catalysed by the acid liberated during the reaction *e.g.* Scheme. In agreement with this suggestion is the observation that the maximum rate of carbon monoxide evolution during the reaction of tetrachlorophthalonitrile with a large excess of DMF is reached only after about 75 min. under reflux (Figure). The decline in rate after about two moles of carbon monoxide per mole of substrate have been evolved may be attributed to gradual neutralisation by dimethylamine of the hydrogen chloride liberated from the arene.

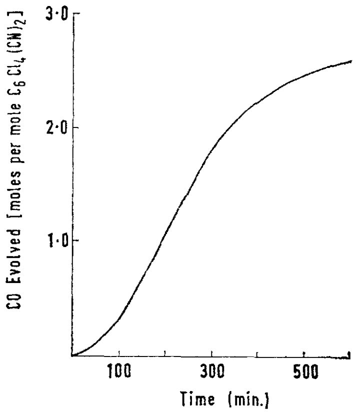


Scheme

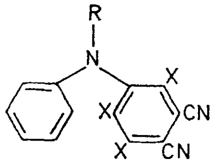
Tetrafluorophthalonitrile reacts with an excess of lithium bromide in NMP to give 4,5-dibromo-3,6-difluorophthalonitrile and tetrabromophthalonitrile, in yields depending on the molar ratio of the reactants. Lithium bromide and chloride may also be used to convert other fluoroaromatic compounds into their bromo- or chloro-carbon analogues, *e.g.* tetrafluorohydroquinone reacts readily with lithium chloride (8 mol.) in NMP to give tetrachlorohydroquinone (75%).

As a result of these studies, it has been shown that many chloro- and fluoro-aromatic compounds are interconvertible, the direction of the reaction depending on the conditions employed.

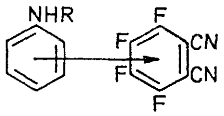
*Reactions with Arylamines.*—Tetrafluorophthalonitrile reacts with aniline under reflux in either NMP or aqueous ethanol to give 3,4-dicyano-2,5,6-trifluorodiphenylamine (VII), m.p. 159—160°, in high yield, whereas either a 1 : 1 or a 1 : 2 mixture of the same reactants in boiling light petroleum gives a crystalline 1 : 1 molecular complex or addition compound (X), m.p. 113—114°. The complex (X) breaks down in hot aqueous ethanol to to give the substitution product (VII) in 75% yield.



Carbon monoxide evolution during the reaction of tetrachlorophthalonitrile with DMF



(VII) R = H, X = F
(VIII) R = H, X = Cl
(IX) R = Me, X = F



(X) R = H
(XI) R = Me

3,4-Dicyano-2,5,6-trifluorodiphenylamine (VII) reacts readily with an excess of lithium chloride in NMP to give 2,5,6-trichloro-3,4-dicyanodiphenylamine (VIII) in 79% yield. The same compound is obtained (64%) from the reaction of tetrachlorophthalonitrile with aniline in the same solvent.

The reaction of *N*-methylaniline with tetrafluorophthalonitrile in NMP also results in substitution, to give 3,4-dicyano-2,5,6-trifluoro-*N*-methyldiphenylamine (IX) (79%), m.p. 129°, whereas the same reactants yield the 1 : 1 complex (XI), m.p. 81°, in either light petroleum or *aqueous ethanol*. The *N*-methylaniline complex (XI) is

---

[8] E. Felstead, H. C. Fielding, and B. J. Wakefield, *J. Chem. Soc.* (*C*), 1966, 708.

[9] L. Joseph and A. H. Albert, *J. Heterocyclic Chem.*, 1966, **3**, 107.

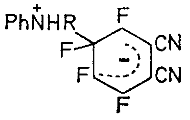
[10] R. S. Asquith, W. M. Lord, A. T. Peters, and F. Wallace, *J. Chem. Soc.* (*C*), 1966, 95.

[11] G. M. Coppinger, *J. Amer. Chem. Soc.*, 1954, **76**, 1372.

[12] A. B. Thomas and E. G. Rochow, *J. Amer. Chem. Soc.*, 1957, **79**, 1843.

thus more stable in protic media than its aniline counterpart (X).

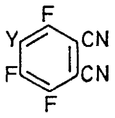
Evidence for the complexes [(X) and (XI)] is based exclusively on elemental analysis and m.p. data. U.v. spectroscopic analysis of both complexes in either hexane or ethanol indicates that they dissociate in solution into a mixture of the arylamine and tetrafluorophthalonitrile. The effects of changes in electron-donor concentration on the n.m.r. spectra of the complexes[13] were not examined. Although it is possible that the complexes are σ-bonded structures of the Meisenheimer type (XII), a considerable number of which are now known to exist as reasonably stable entities,[14] the π-bonded structures [(X) and (XI)] seem more likely for the complexes described here. There is little doubt, however, that decomposition of the anilino-complex (X) to the substitution product (VII) proceeds through a complex of type (XII).[3,15,16]



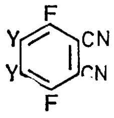
(XII)

The formation of π-complexes between polyfluoroarenes and aromatic hydrocarbons has been observed previously,[13,17] and the ability of tetrafluorophthalonitrile to form complexes of this type is confirmed by the isolation in almost quantitative yield of complexes with naphthalene, 1-chloronaphthalene, and phenanthrene. These products are crystalline solids, which may be recovered from boiling light petroleum (b.p. 80—100°) or aqueous ethanol.

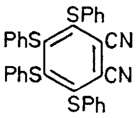
*Reactions with Other Nucleophiles.*—Tetrafluorophthalonitrile readily reacts with an equimolar quantity of sodium 1-naphtholate in aqueous methanol, to give 3,5,6-trifluoro-4-(1-naphthoxy)phthalonitrile (XIII) in 71% yield, and with two molecular proportions of diethylphosphine in dioxan, to give 4,5-bisdiethylphosphino-3,6-difluorophthalonitrile (XV) (64%). Treatment of tetrafluorophthalonitrile with an excess of aqueous ammonia in dioxan leads to the monosubstituted product, 4-amino-3,5,6-trifluorophthalonitrile (XIV) (79%), but the tetrafluoro-compound reacts with an equimolar quantity of sodium benzenethiolate in methanol to give 3,6-difluoro-4,5-bisphenylthiophthalonitrile (XVI) [62% based on $C_6F_4(CN)_2$ transformed] and tetrakisphenylthiophthalonitrile (XVII) (8%), 44% of the tetrafluorophthalonitrile being recovered. The results of the last two experiments are consistent with the previously observed deactivating influence of the amino-group on further nucleophilic substitution[18] and the pronounced activating effect of the phenylthio-group.[15,19] The tetrakisphenylthio-compound (XVII) may be prepared in high yield by the reaction of tetrachlorophthalonitrile with four moles of potassium benzenethiolate.



(XIII) $Y = 1\text{-}C_{10}H_7O$
(XIV) $Y = NH_2$



(XV) $Y = Et_2P$
(XVI) $Y = PhS$



(XVII)

*Product Orientation.*—The presence of absorption in the 4·40—4·50 μm. region of the i.r. spectra of all the compounds described here confirms the presence of at least one cyano-group, and no products resulting from the attack of a nucleophile at a cyano-group have been isolated from any of the reactions. The orientation of the substituents round the benzene ring is deduced from analysis of the $^{19}F$ n.m.r. chemical shifts and coupling constants.

The replacement of a fluorine atom in hexafluorobenzene by another substituent causes changes in the chemical shifts of the other $^{19}F$ nuclei, the magnitudes of which are well established for most of the substituents involved here. For example, chloropentafluorobenzene shows resonances at −21·6 (*ortho* $^{19}F$ nuclei), −1·0 (*meta* $^{19}F$ nuclei), and −6·2 (*para* $^{19}F$ nucleus) p.p.m. relative to hexafluorobenzene.[20] Tetrafluorophthalonitrile shows absorption bands at 51·1 and 66·3 p.p.m.,* which are assigned to the $^{19}F$ nuclei at the 3,6- and 4,5-positions, respectively. The predicted spectrum for 4,5-dichloro-3,6-difluorophthalonitrile (III), therefore, should consist of a singlet at 28·5 p.p.m., whilst that for 3,6-dichloro-4,5-difluorophthalonitrile would be a singlet at 43·7 p.p.m. Less symmetrical orientations would give rise to at least two bands. In fact, the spectrum of the compound obtained from tetrafluorophthalonitrile and lithium chloride consists of a singlet at 28·8 p.p.m. and is consistent only with the structure presented earlier (III).

Similarly, the observed spectrum of the monochlorotrifluorophthalonitrile obtained from tetrafluorophthalonitrile and lithium chloride is an ABX system with bands at 30·9, 45·5, and 53·1 p.p.m. (Table). The predicted spectrum for the 4-chloro-compound (II) would contain bands at 29·5, 44·7, and 50·1 p.p.m. for the 3-, 5-, and 6-$^{19}F$ nuclei, respectively, whereas 3-chloro-4,5,6-trifluorophthalonitrile would have chemical shifts of 44·7, 65·3, and 44·9 p.p.m. The observed

---

* All $^{19}F$ chemical shifts reported are relative to external trifluoroacetic acid unless otherwise stated and are to high field of the reference.

[13] N. M. D. Brown, R. Foster, and C. A. Fyfe, *J. Chem. Soc.* (*B*), 1967, 406.

[14] R. Foster and C. A. Fyfe, *Rev. Pure and Appl. Chem.*, 1966, **16**, 61.

[15] J. M. Birchall, M. Green, R. N. Haszeldine, and A. D. Pitts, *Chem. Comm.*, 1967, 338.

[16] J. Burdon, *Tetrahedron*, 1965, **21**, 3373.

[17] C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021; J. M. Birchall, R. N. Haszeldine, R. Hazard, and A. W. Wakalski, *J. Chem. Soc.* (*C*), 1967, 47.

[18] J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 6329.

[19] P. Robson, T. A. Smith, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 3692; J. Burdon, V. A. Damodaran, and J. C. Tatlow, *ibid.*, 1964, 763.

[20] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459.

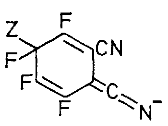
$^{19}$F N.m.r. spectra of 4-substituted 3,5,6-trifluorophthalonitriles

| Compound | Substituent | Chemical shifts (p.p.m.) | | | Coupling constants (moduli; in Hz) | | | |
|---|---|---|---|---|---|---|---|---|
| | | $F_3$ | $F_5$ | $F_6$ | $J_{3,5}$ | $J_{3,6}$ | $J_{5.6}$ | $J_{HF}$ |
| (II) | Cl | 30·9 | 45·5 | 53·1 | 6·49 | 11·0 | 20·3 | |
| (VI) | $Me_2N$ | 39·8 | 60·9 | 56·4 | 19·6 | 8·05 | 18·5 | 3·25 |
| (VII) | PhNH | 40·5 | 58·6 | 55·8 | 15·7 | 8·54 | 19·3 | |
| (IX) | PhMeN | 33·7 | 51·4 | 54·2 | 10·7 | 10·5 | 19·5 | 1·50 |
| (XIII) | 1-$C_{10}H_7O$ | 43·4 | 59·5 | 52·2 | 9·32 | 10·2 | 19·8 | 1·30 |
| (XIV) | $H_2N$ | 50·9 | 70·6 | 57·4 | 22·0 | 8·16 | 19·6 | |

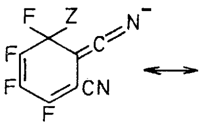
spectrum therefore provides powerful evidence in favour of substitution at the 4-position.

The $^{19}$F n.m.r. spectra of the other compounds described are consistent with spectra predicted in a similar way, and there seems little doubt that all the nucleophiles involved attack tetrafluorophthalonitrile at the 4- and 5-positions. This conclusion is reinforced by a study of the long-range H–F coupling observed in the spectra of the 4-dimethylamino-, 4-(*N*-methylanilino)-, and 4-(1-naphthoxy)-compounds [(VI), (IX), and (XIII)]. The $^1$H spectrum of the first of these compounds (VI) consists of a triplet (at +4·1 p.p.m. relative to external benzene) owing to equal coupling to the two $^{19}$F nuclei in the 3- and 5-positions; this is confirmed by the splitting of the bands in the $^{19}$F spectrum at 39·8 and 60·9 p.p.m. (Table). Coupling of this type is common with *ortho*-fluorine atoms, but does not occur with fluorine atoms further from the dimethylamino-substituent,[21] and the coupling constant of 3·25 Hz is consistent with previous observations (*e.g.* $C_6F_5{\cdot}NMe_2$ has $|J_{HF}|$ 1·9 Hz [21]). The methyl protons in the *N*-methylanilino-compound (IX) also couple to the 3- and 5-$^{19}$F nuclei and the bands at 43·4 and 59·5 p.p.m. in the $^{19}$F spectrum of the 1-naphthoxy-compound (XIII) exhibit equal coupling to a proton in the naphthalene ring. In the last case, it is not possible to identify the proton(s) involved in the coupling, nor to decide whether the same proton is coupling to each $^{19}$F nucleus, owing to the complexity of the $^1$H spectrum. Molecular models indicate that the hydrogen atoms at the β- and *peri*-positions of the naphthalene ring are roughly equidistant from the 3- and 5-fluorine atoms.

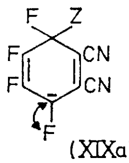
The susceptibility of tetrafluorophthalonitrile to attack by conventional nucleophiles at the 4- and 5-, rather than the 3- and 6-positions, is in accord with the observations on the related organometallic compounds,[4]



(XVIII)



(XIX)



(XIXa)

and may be attributed partly to the importance of carbanion-stabilising canonical forms of the intermediate of type (XVIII) (Z = attacking nucleophile); corresponding structures involving a cyano-group *ortho* to the site of attack [*e.g.* (XIX)] would be expected to have a smaller influence on the stability of the intermediate and first transition state in the reaction.[16] Furthermore, the absence of the carbanion-destabilising $I_\pi$ repulsion of a *para*-fluorine atom from the intermediate for attack at the 4-position (XVIII) and its presence in the alternative intermediate (XIXa) also favour formation of the former. A similar pattern of nucleophilic substitution has been observed with the related perfluoro-*o*-xylene [*o*-$C_6F_4(CF_3)_2$].[22]

## EXPERIMENTAL

All 'anhydrous' solvents were initially distilled, dried ($MgSO_4$ or $CaSO_4$), and finally stored over Union Carbide Molecular Sieve (4Å) for 24 hr., to give a water content of <20 p.p.m. The lithium halides used were dried by heating the reagent-grade materials at 250° *in vacuo* for 24 hr. I.r. spectra (mulls in Nujol and in hexachlorobutadiene) were recorded with a Perkin–Elmer Model 21 spectrophotometer, and n.m.r. spectra were recorded for solutions in acetone with a Perkin–Elmer R10 instrument, operating at 60·00 MHz for $^1$H spectra and at 54·46 MHz for $^{19}$F spectra. Unless otherwise stated, molecular weights were determined by mass spectrometry with an A.E.I. MS/2H instrument; figures for compounds containing chlorine or bromine are calculated for the $^{35}$Cl or $^{79}$Br isotope.

*Tetrachlorophthalonitrile.*—Tetrafluorophthalonitrile (5·01 g., 25 mmoles) [5] and lithium chloride (8·48 g., 200 mmoles) were heated under reflux in anhydrous NMP (50 ml.) for 20 min. The brown solution was cooled and poured on crushed ice (300 g.), and the resulting precipitate was collected and washed with water. Fluoride ion was detected in the aqueous filtrate (zirconium nitrate–Alizarin reagent). The brown solid was dried at 100° and sublimed *in vacuo* at 200°, to yield tetrachlorophthalonitrile (4·83 g., 73%) (Found: C, 36·3; Cl, 53·4; N, 10·5. Calc. for $C_8Cl_4N_2$: C, 36·1; Cl, 53·3; N, 10·5%), m.p. 245° (lit.,[23] 244°), identified by i.r. spectroscopy.

*Chlorotrifluoro- and Dichlorodifluoro-phthalonitrile.*—Tetrafluorophthalonitrile (5·02 g., 25 mmoles) and lithium chloride (1·06 g., 25 mmoles) were heated under reflux in anhydrous NMP (50 ml.) for 20 min. The precipitate, which separated when the mixture was poured on ice, was mixed with an equal bulk of activated charcoal and boiled in acetone (100 ml.). Filtration then yielded a clear filtrate, which was evaporated down to 10 ml., then analysed and separated by g.l.c. [Pye series 105 instrument at 200°; column (3 m. × 5 mm. internal diameter) packed with 30% w/w of Silicone MS550 on Celite; carrier gas, nitrogen]. The products collected were tetrafluorophthalonitrile (0·75 g., 15% recovery), m.p. 86° (lit.,[5] 88—89°), identified by i.r. spectroscopy; *4-chloro*-3,5,6-*trifluorophthalonitrile* [2·17 g., 47% based on $C_6F_4(CN)_2$ transformed] (Found: C, 44·1; Cl, 16·6; N, 12·8%; *M*, 216. $C_8ClF_3N_2$ requires C, 44·3; Cl, 16·4; N, 12·9%; *M*, 216), m.p. 106° (from aqueous ethanol); and 4,5-*dichloro*-3,6-*difluorophthalonitrile* (0·87 g., 17%) (Found: C, 40·9; Cl, 30·9; N, 11·9%; *M*, 232. $C_8Cl_2F_2N_2$ requires C, 41·0; Cl, 30·7; N, 12·0%;

---

[21] J. Burdon, *Tetrahedron*, 1965, **21**, 1101.

[22] E. V. Aroskar, M. T. Chaudhry, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1964, 2975.

[23] A. Haga and S. Saito, B.P. 982,892/1965 (*Chem. Abs.*, 1965, **62**, 16,151).

*M*, 232), m.p. 148—149° (from ethanol). The monochloro-compound shows cyano-group absorption at 4·44 μm. and the dichloro-compound at 4·45 μm.

4-*Dimethylamino*-3,5,6-*trifluorophthalonitrile*.— Tetrafluorophthalonitrile (5·00 g., 25 mmoles) was heated at 150° with anhydrous DMF (50 ml.) for 3 hr., during which time carbon monoxide (11 mmoles), identified by i.r. spectroscopy, was evolved. The pale yellow solution was cooled and added to crushed ice (300 g.), and the resulting precipitate was recrystallised from ethanol and then from light petroleum (b.p. 60—80°) to yield white needles of 4-*dimethylamino*-3,5,6-*trifluorophthalonitrile* (4·05 g., 72%) (Found: C, 53·5; H, 2·8; F, 25·8; N, 19·0%; *M*, 225. $C_{10}H_6F_3N_3$ requires C, 53·4; H, 2·7;, F, 25·2; N, 18·7%; *M*, 225), m.p. 76°; this compound shows C–H absorption at 3·37 μm. and $C\equiv N$ absorption at 4·45 μm.

3,5,6-*Trichloro*-4-*dimethylaminophthalonitrile*.—(a) *From the trifluoro-compound*. 4-Dimethylamino-3,5,6-trifluorophthalonitrile (2·25 g., 10 mmoles) and lithium chloride (2·54 g., 60 mmoles) were heated under reflux in anhydrous NMP (25 ml.) for 30 min. The brown solution was cooled and poured on crushed ice (100 g.), and the resulting precipitate was dried ($P_4O_{10}$ *in vacuo*) and sublimed at 100° *in vacuo*. The bright yellow sublimate was recrystallised from aqueous ethanol to give yellow crystals of 3,5,6-*trichloro*-4-*dimethylaminophthalonitrile* (2·24 g., 83%) (Found: C, 43·9; H, 2·3; Cl, 38·6; N, 15·4%; *M*, 273. $C_{10}H_6Cl_3N_3$ requires C, 43·7; H, 2·2; Cl, 38·8; N, 15·3%; *M*, 273), m.p. 118—119°; its i.r. spectrum shows C–H absorption at 3·30 μm. and $C\equiv N$ absorption at 4·50 μm.

(b) *From tetrafluorophthalonitrile*. The nitrile (5·01 g., 25 mmoles) and lithium chloride (8·48 g., 200 mmoles) were heated under reflux in anhydrous DMF (50 ml.) for 3 hr. The yellow solution was cooled and poured onto crushed ice (300 g.) and the resulting precipitate was dried, sublimed, and recrystallised to give 3,5,6-trichloro-4-dimethylaminophthalonitrile (4·94 g., 72%), m.p. and mixed m.p. 119°, identified by i.r. spectroscopy.

(c) *From tetrachlorophthalonitrile*. The tetrachloro-compound (5·01 g., 18·8 mmoles) and anhydrous DMF (50 ml.) were heated under reflux for 10 hr. The product was isolated as before and shown to be the trichloro(dimethylamino)-compound (4·04 g., 78%), m.p. and mixed m.p. 116°, by i.r. spectroscopy. An experiment on the same scale, but with heating for only 3 hr., gave tetrachlorophthalonitrile (1·76 g., 35% recovery) and the dimethylamino-compound [2·75 g., 82% based on $C_6Cl_4(CN)_2$ transformed].

The data on carbon monoxide formation shown in the Figure were obtained when tetrachlorophthalonitrile (4·432 g., 16·7 mmoles) was added in one portion to anhydrous DMF (100 g., 1408 mmoles), already refluxing at a steady rate.

*Tetrabromo- and Dibromodifluoro-phthalonitrile*.—Tetrafluorophthalonitrile (5·03 g., 25 mmoles) and lithium bromide (8·11 g., 100 mmoles) were heated under reflux in anhydrous NMP (50 ml.) for 20 min. The brown solution was cooled and poured onto crushed ice (200 g.), and the resulting precipitate was dried at 100°, finely powdered, and boiled in acetone (250 ml.) for 20 min. The cold suspension was filtered through a bed of activated charcoal (*ca*. 6 mm. thick), held on a glass sinter; the filtrate (A) was collected. The charcoal bed was then extracted with boiling 1-chloronaphthalene (3 × 50 ml.), and the filtrate was poured into light petroleum (b.p. 100—120°; 300 ml.). The resulting precipitate was washed with light petroleum (b.p. 40—60°; 50 ml.), dried, and sublimed at 260° *in vacuo*; the white sublimate was dissolved in the minimum quantity of hot dioxan and reprecipitated with light petroleum (b.p. 100—120°) to give *tetrabromophthalonitrile* (1·95 g., 18%) (Found: C, 21·8; Br, 72·2; N, 6·3%; *M*, 440. $C_8Br_4N_2$ requires C, 21·6; Br, 72·1; N, 6·3%; *M*, 440), m.p. 320—324°, showing $C\equiv N$ absorption at 4·49 μm. The original acetone filtrate (A) was evaporated down to 50 ml. and cooled in ice. Filtration removed traces of tetrabromophthalonitrile, and the filtrate was evaporated to dryness. The residue was sublimed at 150° *in vacuo*, and the white sublimate was recrystallised from aqueous ethanol to give 4,5-*dibromo*-3,6-*difluorophthalonitrile* (3·21 g., 40%) (Found: C, 29·7; Br, 50·0; N, 8·9%; *M*, 320. $C_8Br_2F_2N_2$ requires C, 29·8; Br, 49·7; N, 8·7%; *M*, 320), m.p. 158·5;° its i.r. spectrum shows $C\equiv N$ absorption at 4·50 μm. and its $^{19}F$ n.m.r. spectrum a singlet at +18·0 p.p.m. (from trifluoroacetic acid).

An experiment under the same conditions with tetrafluorophthalonitrile (5·03 g., 25 mmoles) and twice the quantity of lithium bromide (17·4 g., 200 mmoles) yielded tetrabromophthalonitrile (4·85 g., 44%) and 4,5-dibromo-3,6-difluorophthalonitrile (0·75 g., 9%).

*Tetrachlorohydroquinone*. Tetrafluorohydroquinone (2·51 g., 13·8 mmoles) (Imperial Smelting Corporation Ltd.) and lithium chloride (4·68 g., 110 mmoles) were heated and stirred at 145° for 15 min. in anhydrous NMP (40 ml.). The precipitate, which formed when the mixture was poured into water, was filtered off and dissolved in aqueous 10% sodium hydroxide. The alkaline solution was filtered, the filtrate was acidified with dilute hydrochloric acid, and the resulting precipitate was recrystallised from aqueous ethanol to give tetrachlorohydroquinone (2·49 g., 75%) (Found: Cl, 57·0. Calc. for $C_6H_2Cl_4O_2$: Cl, 57·2%), m.p. 229° (lit.,[24] 232°), identified by i.r. spectroscopy.

3,4-*Dicyano*-2,5,6-*trifluorodiphenylamine*.— Tetrafluorophthalonitrile (2·50 g., 12·5 mmoles) and redistilled aniline (2·33 g., 25 mmoles) were heated under reflux in NMP (30 ml.) for 10 min.; the solution was poured onto crushed ice (150 g.) and the resulting suspension was filtered. The filtrate was shown to contain fluoride ion. The residue was dried ($P_4O_{10}$ *in vacuo*) and sublimed at 150° *in vacuo*; the sublimate was recrystallised from aqueous ethanol to give pale yellow crystals of 3,4-*dicyano*-2,5,6-*trifluorodiphenylamine* (2·10 g., 61%) (Found: C, 61·7; H, 2·2; N, 15·6%; *M*, 273. $C_{14}H_6F_3N_3$ requires C, 61·5; H, 2·2; N, 15·4%; *M*, 273), m.p. 159—160°. Its i.r. spectrum shows $C\equiv N$ absorption at 4·49 μm. and N–H stretching at 3·00 μm.

The same compound (3·21 g., 94%), m.p. 157°, was obtained when tetrafluorophthalonitrile (2·50 g., 12·5 mmoles) and aniline (2·33 g., 25 mmoles) were heated under reflux in aqueous 80% ethanol (30 ml.) for 10 min.; the product was identified by i.r. spectroscopy. Equimolar quantities of the reactants in aqueous ethanol gave the diphenylamine (73%).

2,5,6-*Trichloro*-3,4-*dicyanodiphenylamine*.—(a) *From the trifluoro-compound*. 3,4-Dicyano-2,5,6-trifluorodiphenylamine (3·01 g., 11 mmoles) and lithium chloride (2·80 g., 66 mmoles) were heated under reflux in anhydrous NMP (30 ml.) for 30 min. The solution was cooled and poured

---

[24] J. Sutkowski, *Ber.*, 1886, **19**, 2314.

onto crushed ice (150 g.), and the resulting precipitate was sublimed at 200° *in vacuo* and then recrystallised from benzene, to give yellow crystals of 2,5,6-*trichloro*-3,4-*dicyanodiphenylamine* (2·81 g., 79%) (Found: C, 52·2; H, 2·1; N, 12·9%; *M*, 321. $C_{14}H_6Cl_3N_3$ requires C, 52·1; H, 1·9; N, 13·0%; *M*, 321), m.p. 219—221°. This compound shows C≡N absorption at 4·50 μm. and N–H absorption at 3·00 μm.

(b) *From tetrachlorophthalonitrile.* The nitrile (5·01 g., 18·8 mmoles) and redistilled aniline (3·50 g., 37·6 mmoles) were heated under reflux in NMP (50 ml.) for 90 min. The solution was poured into water (200 ml.), and the resulting precipitate was washed with boiling ether, dried at 100°, and sublimed at 210° *in vacuo* to give trichlorodicyanodiphenylamine (3·91 g., 64%), m.p. and mixed m.p. 219—221°, identified by i.r. spectroscopy.

3,4-*Dicyano*-2,5,6-*trifluoro*-N-*methyldiphenylamine*.—Tetrafluorophthalonitrile (3·01 g., 15 mmoles) and *N*-methylaniline (3·22 g., 30 mmoles) were heated under reflux in NMP (30 ml.) for 30 min. The solution was cooled and poured into cold water (100 ml.). After 3 hr., filtration yielded a filtrate which contained fluoride ion, and a black residue. Sublimation at 130° *in vacuo* followed by recrystallisation from aqueous ethanol yielded yellow crystals of 3,4-*dicyano*-2,5,6-*trifluoro*-N-*methyldiphenylamine* (3·41 g., 79%) (Found: C, 62·8; H, 2·8; N, 14·4%; *M*, 287. $C_{15}H_8F_3N_3$ requires C, 62·8; H, 2·8; N, 14·6%; *M*, 287), m.p. 129°, showing C≡N absorption at 4·45 μm.

*Molecular Complexes of Tetrafluorophthalonitrile.*—(a) *With aniline.* Tetrafluorophthalonitrile (2·49 g., 12·5 mmoles) and redistilled aniline (2·33 g., 25 mmoles) were heated under reflux in light petroleum (b.p. 100—120°; 40 ml.) for 10 min. The cold solution deposited yellow needles, and the mother liquor was distilled to yield aniline (1·11 g.), identified by i.r. spectroscopy. The yellow needles were recrystallised from light petroleum (b.p. 100—120°) to give the 1 : 1 *complex* (3·30 g., 90%) (Found: C, 57·6; H, 2·5; N, 14·2. $C_{14}H_7F_4N_3$ requires C, 57·4; H, 2·4; N, 14·3%), m.p. 113—114°. Recrystallisation of the complex (1·01 g.) from aqueous ethanol afforded 3,4-dicyano-2,5,6-trifluorodiphenylamine (0·74 g., 75%), m.p. 156°, identified by i.r. spectroscopy; fluoride ion was detected in the aqueous filtrate.

The 1 : 1 complex (3·21 g., 87%), m.p. 112°, was similarly obtained when equimolar quantities of the nitrile (2·49 g.) and aniline (1·16 g.) were heated in light petroleum (b.p. 80—100°; 40 ml.) for 10 min.

(b) *With* N-*methylaniline.* The nitrile (3·01 g., 15 mmoles) and redistilled *N*-methylaniline (3·22 g., 33 mmoles) were heated under reflux in aqueous 80% ethanol (30 ml.) for 90 min. The mixture was cooled and diluted with cold water (50 ml.) and the solid product was recrystallised from light petroleum (b.p. 60—80°) to give yellow crystals of the 1 : 1 *complex* (3·92 g., 85%) (Found: C, 59·0; H, 3·1; N, 13·8. $C_{15}H_9F_4N_3$ requires C, 58·7; H, 3·0; N, 13·7%), m.p. 80·5—81°.

This complex (4·21 g., 91%), m.p. 79°, was also obtained when equimolar quantities of the nitrile (3·02 g.) and *N*-methylaniline (1·61 g.) were heated in light petroleum (b.p. 80—100°; 40 ml.) for 10 min.

(c) *With polynuclear compounds.* The nitrile (3·00 g., 15 mmoles) and the polynuclear compound (15 mmoles) were dissolved in the minimum quantity of hot aqueous 80% ethanol and the solution was boiled for 5 min. and then allowed to cool slowly. The solid product was recrystallised from aqueous ethanol. In this way were obtained: the 1 : 1 *complex of tetrafluorophthalonitrile and naphthalene* (4·80 g., 99%) (Found: C, 65·5; H, 2·4; N, 8·8. $C_{18}H_8F_4N_2$ requires C, 65·8; H, 2·4; N, 8·5%), m.p. 146°; the 1 : 1 *complex of tetrafluorophthalonitrile and* 1-*chloronaphthalene* (5·36 g., 99%) (Found: C, 59·7; H, 2·0; Cl, 10·1; F, 21·1; N, 7·6. $C_{18}H_7ClF_4N_2$ requires C, 59·6; H, 1·9; Cl, 9·8; F, 21·0; N, 7·7%), m.p. 128°; and the 1 : 1 *complex of tetrafluorophthalonitrile and phenanthrene* (5·38 g., 95%) (Found: C, 69·8; H, 2·9; N, 7·6. $C_{22}H_{10}F_4N_2$ requires C, 69·8; H, 2·6; N, 7·4%), m.p. 146°.

3,5,6-*Trifluoro*-4-(1-*naphthoxy*)*phthalonitrile*.—Sodium 1-naphtholate (2·08 g., 12·5 mmoles) in water (20 ml.) was added to tetrafluorophthalonitrile (2·51 g., 12·5 mmoles) in methanol (40 ml.). The mixture was stirred at room temperature for 30 min., then evaporated down to 20 ml. and diluted with cold water (100 ml.). The resulting tarry solid was recrystallised from ethanol (charcoal) to give off-white crystals of 3,5,6-*trifluoro*-4-(1-*naphthoxy*)*phthalonitrile* (2·91 g., 71%) (Found: C, 66·4; H, 2·3; N, 8·8%; *M*, 325. $C_{18}H_7F_3N_2O$ requires C, 66·7; H, 2·2; N, 8·6%; *M*, 325), m.p. 145—146°, showing C≡N absorption at 4·45 μm.

4,5-*Bisdiethylphosphino*-3,6-*difluorophthalonitrile*.—Diethylphosphine (3·30 g., 36·6 mmoles) in dioxan (20 ml.) was added under nitrogen to tetrafluorophthalonitrile (3·71 g., 18 mmoles) in dioxan (40 ml.), and the mixture was heated under reflux for 1 hr. and then poured onto crushed ice. The red precipitate was dried and recrystallised from ethanol (charcoal) to yield pale orange crystals of 4,5-*bisdiethylphosphino*-3,6-*difluorophthalonitrile* (4·05 g., 64%) [Found: C, 56·7; H, 5·8; N, 8·3%; *M* (vapour pressure osmometry in ethanol), 328. $C_{16}H_{20}F_2N_2P_2$ requires C, 56·6; H, 5·9; N, 8·4%; *M*, 340], m.p. 97°. This compound shows C≡N absorption at 4·45 μm. and C–H absorption at 3·35, 3·40, and 3·46 μm.; its $^{19}F$ n.m.r. spectrum shows a singlet at 23·2 p.p.m.

4-*Amino*-3,5,6-*trifluorophthalonitrile*.—Concentrated ammonium hydroxide (*d* 0·88; 3·1 ml., *ca.* 45 mmoles) in dioxan (10 ml.) was added to tetrafluorophthalonitrile (3·01 g., 15 mmoles) in refluxing dioxan (25 ml.) during 30 min. The solution was heated under reflux for a further 90 min., cooled, and poured onto crushed ice (100 g.). The pink precipitate was dried ($P_4O_{10}$ *in vacuo*) and sublimed at 170° *in vacuo*, and the sublimate (2·70 g.) was recrystallised from aqueous ethanol to yield white crystals of 4-*amino*-3,5,6-*trifluorophthalonitrile* (2·40 g., 79%) (Found: C, 48·7; H, 1·2; N, 21·6%; *M*, 197. $C_8H_2F_3N_3$ requires C, 48·8; H, 1·0; N, 21·3%; *M*, 197), m.p. 179—180°; its i.r. spectrum shows C≡N absorption at 4·48 μm. and N–H absorption at 2·92 and 3·00 μm.

*Difluorobisphenylthio- and Tetrakisphenylthio-phthalonitrile.*—Sodium benzenethiolate in methanol [from sodium (0·35 g., 15 mg. atom) and benzenethiol (1·65 g., 15 mmoles) in methanol (10 ml.)] was added to tetrafluorophthalonitrile (3·02 g., 15 mmoles) in methanol (40 ml.), and the mixture was heated under reflux for 15 min. The mixture was cooled and filtered, and the yellow residue, which did not sublime at 150° *in vacuo*, was recrystallised from benzene–light petroleum (b.p. 80—100°) (charcoal) to yield yellow needles of 3,6-*difluoro*-4,5-*bisphenylthiophthalonitrile* [2·01 g., 62% based on $C_6F_4(CN)_2$ transformed] [Found: C, 62·8; H, 2·5; N, 7·5; S, 16·7%; *M* (vapour pressure osmometry in benzene), 374. $C_{20}H_{10}F_2N_2S_2$ requires C, 63·1; H, 2·6; N, 7·4; S, 16·9%; *M*, 380], m.p. 178°; its i.r. spectrum shows C≡N absorption at 4·46 *µm. and its* $^{19}F$ n.m.r. spectrum a singlet at 21·3 p.p.m. The original methanolic filtrate was evaporated to dryness, the residue was sublimed at 75° *in vacuo*, and the sublimate was recrystallised from light petroleum (b.p. 80—100°) to yield tetrafluorophthalonitrile (1·31 g., 44%), m.p. 86°, identified by i.r. spectroscopy. The residue from the sublimation was recrystallised from benzene–light petroleum (b.p. 80—100°) (charcoal) to yield fine yellow crystals of *tetrakisphenylthiophthalonitrile* (0·40 g., 8%) [Found: C, 68·7; H, 3·5; N, 5·3; S, 22·7%; *M* (vapour pressure osmometry in toluene), 542. $C_{32}H_{20}N_2S_4$ requires C, 68·5; H, 3·6; N, 5·0; S, 22·9%; *M*, 560], m.p. 152—153°, showing C≡N absorption at 4·50 µm.

*Tetrakisphenylthiophthalonitrile*.—Aqueous potassium benzenethiolate [from benzenethiol (8·31 g., 75 mmoles) and potassium hydroxide (4·21 g., 75 mmoles) in water (20 ml.)] and tetrachlorophthalonitrile (5·02 g., 18·8 mmoles) in acetone (100 ml.) were heated under reflux for 30 min. The solvents were removed and the residue was boiled with benzene and filtered hot to remove potassium chloride. The filtrate was evaporated to dryness, and recrystallisation of the resulting solid from benzene–light petroleum (b.p. 80—100°) (charcoal) gave tetrakisphenylthiophthalonitrile (7·95 g., 76%), m.p. 153°, identified by i.r. spectroscopy.

We thank I. I. O. Allinson and M. G. Barlow for assistance in the interpretation of n.m.r. spectra; we also thank the S.R.C. for a maintenance grant (to J. O. M.)

[9/1246 *Received, July 23rd*, 1969]