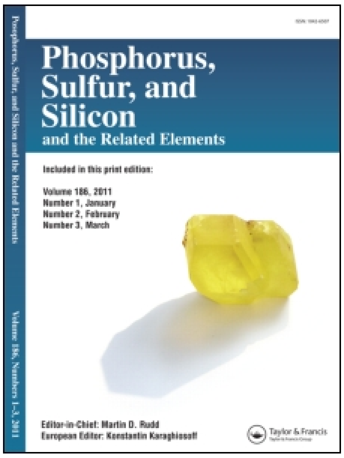

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SYNTHESIS AND CRYSTAL STRUCTURE OF TETRACYANO-FORMYLPENTADIENYLIDENE PHOSPHORANE. TRANSFORMATION INTO TETRACYANOBENZENE

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Addition of triphenylphosphine to 2,3,5,6-tetracyano-7-oxabicyclo-[2.2.1]hepta-2,5-diene yielded blue crystals of 1,2,4,5-tetracyano-5-formylpenta-2,4-dienylidenetriphenylphosphorane (**9**), the structure of which was elucidated by X-ray crystallography. The unique molecular packing in the unit cell provides ready explanation for the transformation of **9** in the solid state into 1,2,4,5-tetracyanobenzene (**12**).

Key words: X-Ray; crystal data; Wittig-reaction; cyanocarbons; phosphorane; solid state reaction.

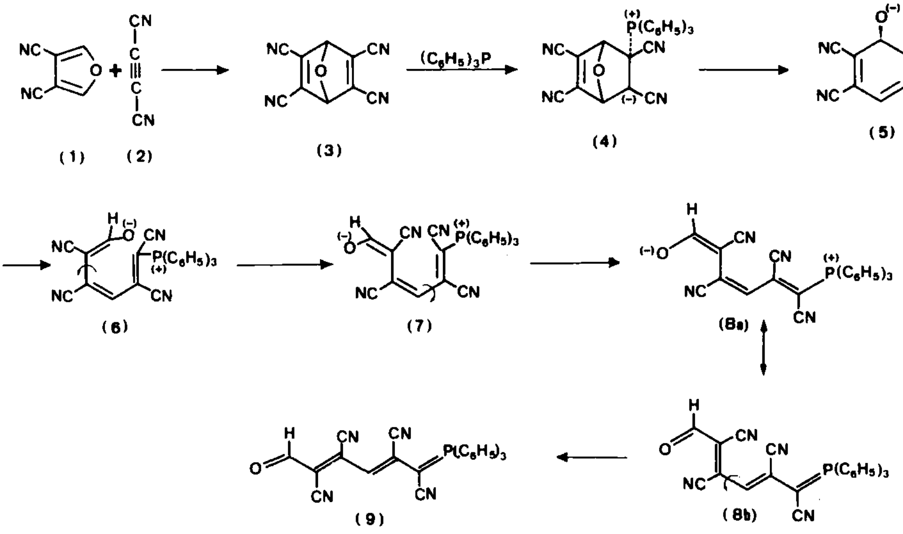
INTRODUCTION

The addition of dicyanoacetylene (**2**) to 3,4-dicyanofuran (**1**) was reported[1] to yield the Diels–Alder adduct (**3**) (Scheme 1), the structure of which was confirmed by its infrared and nmr data. A suspension of the adduct (**3**) in acetonitrile reacted with triphenylphosphine at room temperature to form a dark blue, yet sparingly soluble compound the structure of which was supposed to be best represented by the formula of the betaine (**5**). Attempts to elucidate and to confirm the betaine structure by nmr were, at the time of its synthesis,[1] frustrated due to the low solubility in suitable solvents. Thus, the structural argument favoring (**5**) rested upon its thermal transformation occurring at 190°C yielding only 1,2,4,5-tetracyanobenzene (**12**) and triphenylphosphine oxide accompanied by concomitant disappearance of its blue color.

RESULTS AND DISCUSSION

We present an X-ray structural determination of the blue crystals showing that the correct structure is indicated by (**9**), and further evidence for a unique molecular arrangement of (**9**) in the crystalline state.

The molecular stereochemistry of (**9**) is shown in Figure 1 as PLUTO-plot[2] with the atom numbering system. The final atomic coordinates are listed in Table I. Compound (**9**) possesses the linear structure of a tetracyano-formylpentadiene having a triphenylphosphorane moiety attached to the carbon atom (C-1) at one end of the carbon atom chain, and thus representing a thoroughly conjugated π-system with four conjugated double bonds. The C=C bond distances with



SCHEME 1

1.38 Å agree well with the data for conjugated C=C double bonds (Table II). The carbon–nitrogen bonds with 1.133 – 1.148 Å are typical of nitrile groups. The substituents on the phosphorus atom are in a tetrahedral environment, the P-C7 distance is shorter (1.768 Å) than the other P—C bonds (1.789 – 1.803 Å)[3]. The atoms O-2, C-16, C-14, C-12, C-11, C-9, C-7, P-1 and C-29 are almost coplanar.

Molecular packing is provided by Van der Waals distances. Figure 2 shows two molecules of a unit cell projected along the *a*-axis. The intramolecular P—O distance (P-1, O-2) is 8.885 Å, and the shorter intermolecular distance is 4.408 Å as indicated in Figure 2.

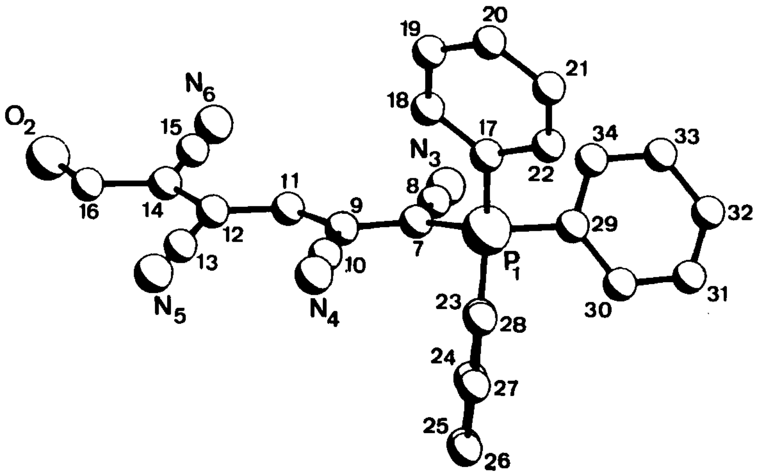


FIGURE 1 Perspective view of the molecule with atom numbering scheme.

TABLE I

Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*
P1	0.16358(6)	0.13922(5)	0.22770(5)
O2	0.3723(2)	0.7005(2)	0.8150(2)
N3	0.4702(2)	0.1502(2)	0.4388(2)
N4	0.0396(3)	0.4408(2)	0.2809(2)
N5	0.1265(3)	0.6737(2)	0.4652(2)
N6	0.4973(3)	0.4201(2)	0.7514(2)
C7	0.2634(2)	0.2323(2)	0.3423(2)
C8	0.3761(3)	0.1836(2)	0.3947(2)
C9	0.2324(2)	0.3484(2)	0.3905(2)
C10	0.1254(3)	0.4022(2)	0.3299(2)
C11	0.2959(2)	0.4056(2)	0.4912(2)
C12	0.2761(2)	0.5186(2)	0.5506(2)
C13	0.1910(3)	0.6039(2)	0.5019(2)
C14	0.3372(3)	0.5563(2)	0.6565(2)
C15	0.4260(3)	0.4797(2)	0.7091(2)
C16	0.3190(3)	0.6711(2)	0.7216(2)
C17	−0.0149(3)	0.0573(2)	0.2660(2)
C18	−0.0716(3)	0.0909(2)	0.3641(2)
C19	−0.2120(3)	0.0265(3)	0.3893(3)
C20	−0.2913(3)	−0.0705(3)	0.3175(3)
C21	−0.2344(3)	−0.1063(3)	0.2214(3)
C22	−0.0957(3)	−0.0426(3)	0.1941(2)
C23	0.1544(2)	0.2444(2)	0.1130(2)
C24	0.2818(3)	0.3272(2)	0.0805(2)
C25	0.2783(3)	0.4105(3)	−0.0061(3)
C26	0.1484(3)	0.4129(3)	−0.0623(3)
C27	0.0223(3)	0.3318(3)	−0.0295(3)
C28	0.0234(3)	0.2480(2)	0.0576(2)
C29	0.2490(2)	0.0096(2)	0.1852(2)
C30	0.2973(3)	0.0045(2)	0.0782(2)
C31	0.3511(3)	−0.1042(3)	0.0446(2)
C32	0.3573(3)	−0.2019(3)	0.1180(3)
C33	0.3103(3)	−0.1964(3)	0.2244(3)
C34	0.2519(3)	−0.0911(2)	0.2588(2)
H35	0.353(4)	0.354(3)	0.540(3)
H36	0.261(4)	0.727(3)	0.679(3)
H37	−0.009(4)	0.148(3)	0.427(3)
H38	−0.251(4)	0.044(3)	0.468(3)
H39	−0.383(4)	−0.114(3)	0.338(3)
H40	−0.287(4)	−0.171(3)	0.167(3)
H41	−0.057(4)	−0.065(3)	0.119(3)
H42	0.359(4)	0.326(3)	0.126(3)
H43	0.366(4)	0.470(3)	−0.034(3)
H44	0.149(4)	0.469(3)	−0.132(3)
H45	−0.066(4)	0.335(3)	−0.072(3)
H46	−0.066(4)	0.193(3)	0.087(3)
H47	0.288(4)	0.071(3)	0.022(3)
H48	0.364(4)	−0.110(3)	−0.035(3)
H49	0.397(4)	−0.280(3)	0.088(3)
H50	0.310(4)	−0.266(3)	0.285(3)
H51	0.222(4)	−0.086(3)	0.341(3)

TABLE II

Selected bond distances in Å

Atom 1	Atom 2	Distance
P1	C7	1.768(2)
P1	C17	1.802(2)
P1	C23	1.789(2)
P1	C29	1.803(3)
O2	C16	1.210(3)
N3	C8	1.148(4)
N4	C10	1.139(4)
N5	C13	1.139(4)
N6	C15	1.133(4)
C7	C8	1.419(3)
C7	C9	1.423(3)
C9	C10	1.450(4)
C9	C11	1.382(3)
C11	C12	1.413(3)
C11	H35	1.02(4)
C12	C13	1.451(4)
C12	C14	1.381(3)
C14	C15	1.428(4)
C14	C16	1.459(4)
C16	H36	1.02(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

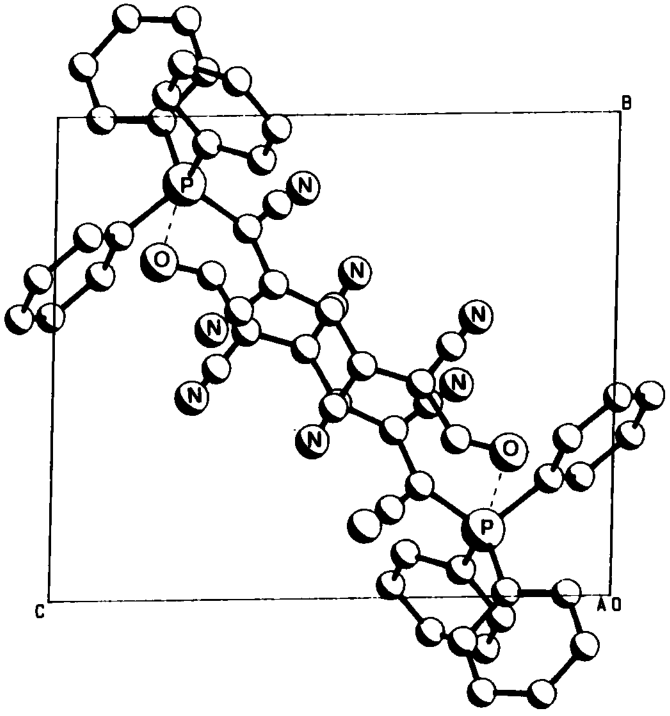


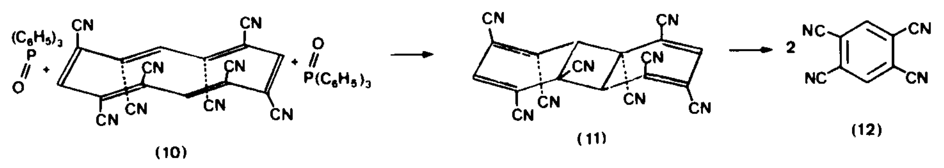
FIGURE 2 Packing diagram viewed down the *a*-axis.

The structure of the linear conjugated π-system of (**9**) is in agreement with the blue color of its crystals. It has been recognized that conjugated electroactive polymer chains may exhibit nonlinear optical activity (NLO).[4,5] The availability of polyenes and in particular synthons of facile synthetic accessibility having such polar substituents as formyl- and nitrile groups,[6] respectively, may enhance the possibility for constructing electrooptical devices which can be built using molecular optical materials.

The formation of (**9**) may be envisaged as an initial addition of triphenylphosphine to the nitrile substituted double bond of (**3**) to yield (**4**), followed by ring opening of the epoxy moiety to provide (**5**), having the two ionic centers placed in trans positions to each other as otherwise a spontaneous formation of triphenylphosphine oxide and tetracyanobenzene would be expected to occur. The all-trans structure of (**9**) suggested a disrotatory ring opening of (**5**) leading to (**6**) which is followed by rotation around the bonds as indicated by the sequence (**6**)→(**7**)→(**8a, b**) to furnish (**9**), having the carbonyl group and the phosphine moiety, respectively, each placed at one of the ends of the 2,4-pentadienal molecule.

Consideration of the linear structure of (**9**) would not necessarily indicate a facile cyclization and transformation, respectively, into 1,2,4,5-tetracyanobenzene. However, inspection of the unique molecular packing in the unit cell in the solid state as indicated in Figure 2 shows that two molecules of (**9**) are situated inversely above one another, e.g. each oxygen atom of an aldehyde group is placed next to the phosphorus atom of a second molecule (P—O distance 4.408 Å), however, both are well outside their respective Van der Waals radii. Thermal vibrations of the crystalline lattice will bring both phosphorus and oxygen atoms into close contact, and then initiate the double cyclization reaction with the extrusion of two molecules of triphenylphosphine oxide, and the formation of two moles of 1,2,4,5-tetracyanobenzene.

A tentative mechanism explaining this reorganization might involve (Scheme 2) a cyclododecahexaen structure (**10**), which, via the intermediate cyclobutane derivative (**11**), underwent fragmentation yielding two moles of tetracyanobenzene (**12**).



SCHEME 2

EXPERIMENTAL

2,3,5,6-Tetracyano-7-oxabicyclo[2.2.1]hepta-2,5-diene (**3**) was prepared as reported earlier,[1] $\delta_C[(CD_3)_2SO]$139.395(C-2), 111.088(CN), 86.717(C-4).

1,2,4,5-Tetracyano-5-formylpenta-2,4-dienylidenetriphenylphosphorane (**9**) was prepared from **3** and triphenylphosphine as reported,[1] $\lambda_{max}(CH_3CN)$ 549 nm (ϵ: 57800 dm^3 mol^{-1} cm^{-1}).

Crystal structure analysis of (**9**). Crystal data: Compound **9** was prepared as reported.[1] $C_{28}H_{17}N_4OP$, triclinic, space group PI, $a = 9.529(1)$ Å, $b = 10.416(1)$ Å, $c = 11.965(1)$ Å, $\alpha = 91.42°$, $\beta = 94.40(2)°$,

$\gamma = 103.36°$, $Z = 2$, $D_{calcd} = 1.31$ g/cm^3, crystal size $0.50 \times 0.13 \times 0.003$ mm. A NONIUS CAD4 automatic diffractometer was used for data collection with CuKα radiation and graphite monochromator. The intensities of 4973 independent reflections with $\theta < 67°$ were measured, of which 4516 were classified as observed with $I > 2\sigma(I)$.

The structure was solved by direct methods (MULTAN 80).[7] All hydrogen atoms were found from a difference Fourier map. The structure was refined by full matrix least squares calculations with anisotropic (fixed for hydrogen atoms) thermal parameters to a final R value of 0.055.

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