$S = 1.859$
768 reflections
53 parameters
H-atom parameters not refined

$\Delta\rho_{max} = 0.10$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.4964	0.5289 (1)	−0.0532	0.0453 (5)
N2	0.4712 (8)	0.6205 (1)	0.0040 (4)	0.0600 (6)
N3	0.4630 (8)	0.5991 (2)	0.1298 (4)	0.0613 (6)
N4	0.4815 (7)	0.4946 (2)	0.1559 (4)	0.0511 (5)
C1	0.5011 (8)	0.4519 (2)	0.0399 (4)	0.0425 (5)
C2	0.525 (1)	0.3401 (2)	0.0148 (5)	0.0662 (7)

Table 2. *Selected geometric parameters (Å, °)*

N1—N2	1.342 (3)	N3—N4	1.358 (3)
N1—C1	1.333 (2)	N4—C1	1.316 (3)
N2—N3	1.285 (3)	C1—C2	1.473 (3)
N2—N1—C1	109.4 (2)	N4—C1—N4	107.4 (2)
N1—N2—N3	106.2 (2)	N1—C1—C2	125.2 (2)
N2—N3—N4	110.6 (2)	N4—C1—C2	127.4 (2)
N3—N4—C1	106.5 (2)		
N1—N2—N3—N4	−0.1 (2)	N2—N3—N4—C1	−0.1 (3)
N1—C1—N4—N3	0.3 (2)	N3—N2—N1—C1	0.3 (2)
N2—N1—C1—N4	−0.4 (2)	N3—N4—C1—C2	−179.9 (2)
N2—N1—C1—C2	179.8 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H4···N4^i	0.87	1.94	2.811 (3)	173.4

Symmetry code: (i) $x, 1 - y, z - \frac{1}{2}$.

Table 4. *Bond lengths in 1H-tetrazole (1HT), 1-methyltetrazole (1MT) and 5-methyltetrazole (5MT) (Å)*

	1HT	1MT	5MT
N1—N2	1.332 (2)	1.344 (2)	1.342 (3)
N2—N3	1.295 (3)	1.299 (2)	1.285 (3)
N3—N4	1.346 (3)	1.360 (2)	1.358 (3)
N4—C1	1.315 (2)	1.315 (2)	1.316 (3)
C1—N1	1.308 (2)	1.331 (2)	1.332 (2)
N1—C		1.455 (2)	
C1—C2			1.473 (3)

The structure was solved by direct methods and difference Fourier synthesis and refined by full-matrix least-squares methods, with anisotropic displacement parameters for all non-H atoms. H atoms were located using a difference electron-density map and were included in the structure factor calculation but not refined.

Data collection: *CRYSTAN-GM* (Mackay *et al.*, 1995). Cell refinement: *CRYSTAN-GM*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Crystallographic evidence for the electronic distribution in (2,4-cyclopentadien-1-yl-idenehydrazono)triphenylphosphorane

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Abstract

The title compound, $C_{23}H_{19}N_2P$, can be graphically represented by several canonical forms. Its crystal structure analysis shows a clear bond alternation in the cyclopentadiene ring, which continues in the azo substructure, indicating that the resonance form containing the non-aromatic neutral cyclopentadienylidene moiety describes the actual hybrid form better than other 'inner ionic' resonance forms containing the aromatic anionic cyclopentadienylic portion. The preference for an *s-transoid*

(*E*) geometry for the P1—N1—N2—C1 substructure was also confirmed over the other possible *s-cisoid* (*Z*) conformer.

Comment

The synthetic utility of phosphazines (R_3P=N—N=CR_2) has been recognized for many years (Bestmann & Göthlich, 1962; Singh & Zimmer, 1967), and many investigations have been carried out to elucidate their electronic distribution and geometric conformation, utilizing UV and IR spectroscopy (Ramirez & Levy, 1958; Bock *et al.*, 1969), as well as ^{13}C-, ^{31}P- and ^{15}N-NMR techniques (Albright *et al.*, 1976; Duthaler *et al.*, 1978). Curiosity about the electronic structure of this class of molecules is driven by the difficulty in describing them with a single chemical structure, since several canonical forms appear almost equally likely to represent their true electronic distribution. Besides, there is very little structural information published on these kinds of azafulvenes (Fink & Regitz, 1986; Husebye *et al.*, 1985; Piniella *et al.*, 1991). An X-ray structure analysis of the title compound, (1), which belongs to the chemical class of phosphazines, was undertaken in order to further clarify its geometric and electronic properties. The most important canonical forms for (1) are shown below [(1a) and (1b)].

(1a)   (1b)

(1c)
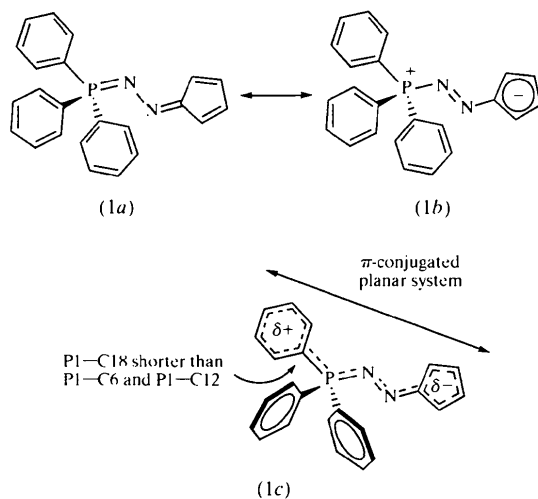
The rigid conformation around the C1—N2 bond is confirmed by ^{1}H-NMR analysis of (1), which shows four distinct signals for the four cyclopentadienylic protons (see *Experimental*), indicating a magnetic non-equivalence for them and a strong preference in acetonitrile for one conformer, which at 296 K does not interconvert rapidly on the NMR time scale. The X-ray structure (Fig. 1) confirms that the *s-transoid* (*E*) geometry, with a torsion angle of 174.5 (1)° for P1—N1—N2—C1, is the only one present in the crystal. A generic preference for *s-transoid* over *s-cisoid* geometry

in phosphazines had already been proposed based upon a comparison of calculated and measured dipole moments of a phosphazine closely related to the title compound (Lumbroso *et al.*, 1978).
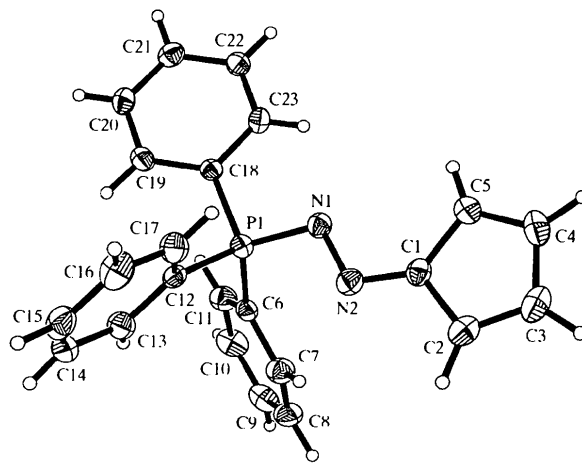

Fig. 1. *SHELXTL* (Sheldrick, 1995) plot showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms.

Curiously, conjugation extended from the cyclopentadienyl ring to the edge of a phenyl ring on the other side of the molecule. In fact, one of the three phenyl rings attached to the P atom, ring C18–C23, is almost coplanar with the cyclopentadiene ring C1—C5 [interplanar angle 14.4 (1)°], indicating the geometrical possibility of an active participation in π-conjugation with the planar system P1—N1—N2—Cp through a *d*-orbital of P1 [see hybrid structure (1c)]. This is supported by the comparison of the three bond lengths between the P and the quaternary C atoms of the phenyl substituents. The P1—C18 bond is 1.791 (2) Å. The other bonds, P1—C6 and P1—C12, are slightly but significantly longer [1.802 (2) and 1.803 (2) Å, respectively], suggesting that there is more double-bond character in the P1—C18 bond, due to a partial *d*π–*p*π overlap between phosphorus and carbon.

When compared with typical reference bond lengths (*International Tables for Crystallography*, Vol. C), several bond lengths support the prevalence of one resonance over the other [(1a) *versus* (1b)]. First of all, the lengths of the five bonds of the Cp ring are not all equal. Bonds C2—C3 and C4—C5 have values [1.344 (3) and 1.341 (3) Å] typical for a double bond, while bonds C1—C2, C1—C5 and C3—C4 are longer, showing lengths [1.447 (2), 1.444 (2) and 1.448 (3) Å] which are much closer to typical single bonds between two sp^2-hybridized C atoms. Moreover, the C1—N2 bond presents a 1.310 (2) Å length, which is close to the reference value for a double bond between Nsp^2 and Csp^2 atoms. The bond between the two N atoms, N1—N2, is 1.366 (2) Å, which is longer than a typical N=N.

For example, the mean bond length in *trans* diazo compounds is 1.222 (6) Å. Finally, the P1—N1 bond length shows a value [1.622 (1) Å] which compares favorably with a typical P=N [1.597 (16) Å], consistent with an efficient $d\pi$–$p\pi$ overlap between P1 and N1. All these observations indicate a higher contribution of the resonance form (1a) to the actual electronic distribution and geometry of the title compound. Additional support for this conclusion comes from ^{1}H NMR (see *Experimental*), which shows larger coupling constants for H2—H3 and H4—H5 (5.1 and 5.3 Hz, respectively), than for H3—H4 (1.8 Hz), confirming a single-bond character for C3—C4 as in (1a).

Nevertheless, a certain dipole character of (1), due to a partial charge separation similar to the one shown in the hybrid structure (1c), is revealed by the molecular arrangement in the crystal. Rings with like partial charges (positive in the C18–C23 phenyl ring and negative in the cyclopentadiene ring) are packed in alternating planes normal to the crystallographic *a* axis.

Experimental

Compound (1) was prepared according to a previously reported method (Weil & Cais, 1963). ^{1}H NMR (500 MHz, CD$_3$CN): δ (p.p.m.) 7.73–7.66 (*m*, 9H, *ortho* and *para* Ph$_3$P), 7.59–7.44 (*m*, 6H, *meta* Ph$_3$P), 6.60 (*dt*, 1H, H5, J_{H4H5} = 5.3, J_{H2H5} and J_{H3H5} = 1.6 Hz), 6.45 (*dt*, 1H, H4, J_{H4H5} = 5.3, J_{H3H4} and J_{H2H4} = 1.8 Hz), 6.42 (*ddt*, 1H, H2, J_{H2H3} = 5.1, J_{P1H2} = 2.2, J_{H2H4} and J_{H2H5} = 1.4 Hz), 6.09 (*dt*, 1H, H3, J_{H2H3} = 5.1, J_{H3H4} and J_{H3H5} = 1.8 Hz).

Crystals were grown from diethyl ether. The crystal was mounted using oil (paratone-N, Exxon) on a thin glass fiber with the (00$\bar{1}$) scattering planes roughly normal to the spindle axis.

Crystal data

$C_{23}H_{19}N_2P$	Mo $K\alpha$ radiation
$M_r = 354.37$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 2699
$P2_1/c$	reflections
$a = 11.1445$ (7) Å	$\theta = 4$–$25°$
$b = 11.7843$ (7) Å	$\mu = 0.158$ mm^{-1}
$c = 14.0877$ (9) Å	$T = 198$ (2) K
$\beta = 95.819$ (1)°	Columnar
$V = 1840.6$ (2) Å^3	$0.58 \times 0.11 \times 0.07$ mm
$Z = 4$	Orange
$D_x = 1.279$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens Platform/CCD diffractometer	$R_{int} = 0.043$
ω scans	$\theta_{max} = 25°$
Absorption correction: none	$h = -11 \rightarrow 14$
9638 measured reflections	$k = -15 \rightarrow 9$
3240 independent reflections	$l = -18 \rightarrow 18$
2112 reflections with	160 standard reflections
$I > 2\sigma(I)$	frequency: 360 min
	intensity decay: 2.0%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
$wR(F^2) = 0.073$	Extinction correction:
$S = 0.901$	*SHELXL*93 (Sheldrick,
3232 reflections	1993)
312 parameters	Extinction coefficient:
All H-atom parameters	0.0041 (7)
refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$	*International Tables for*
where $P = (F_o^2 + 2F_c^2)/3$	*Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} = 0.001$	

Systematic conditions suggested the unambiguous space group. The structure was solved by Patterson methods (Sheldrick, 1990). H-atom parameters were independently refined [range C—H = 0.89 (2)–1.01 (2) Å; range U_{iso} = 0.031 (5)–0.065 (7) Å^2]. The space-group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2 (*SHELXL*93; Sheldrick, 1993). The highest peaks in the final difference Fourier map were in the vicinity of atom P1; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed dependence on amplitude.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINT* (Siemens, 1994b). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1182). Services for accessing these data are described at the back of the journal.
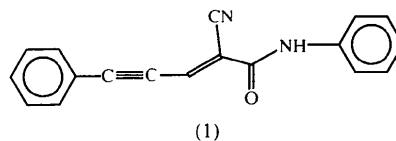
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The *N*-phenylamide of 2-cyano-5-phenyl-pent-2-en-4-ynoic acid

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Abstract

The central 2-cyanocarboxyaminoprop-2-enylic fragment of the title compound, 2-cyano-5,*N*-diphenylpent-2-en-4-ynamide, $C_{18}H_{12}N_2O$, is planar. The phenyl rings are rotated with respect to this plane. Molecules are linked by N—H···O hydrogen bonds and form stacks by translation along the crystallographic *c* axis.

Comment

In continuation of systematic study of the structure and reactivity of derivatives of 2-cyano-pentadien-2,4-oic acid (Borbulevych *et al.*, 1998; Golding *et al.*, 1999; Khrustalev *et al.*, 1996), we performed an X-ray study of a similar compound, (1), that contains a triple C≡C bond in an aliphatic chain. The interest in such compounds is explained by their ability to undergo anionic polymerization and copolymerization under mild conditions. In addition, topochemical reactions can occur in these compounds.

(1)

Bond lengths in molecule (1) do not differ from other derivatives of 2-cyanopentadien-2,4-oic acid (Borbulevych *et al.*, 1998; Golding *et al.*, 1999).

The 2-cyanocarboxyaminoprop-2-enylic fragment (N2/C1/O1/C2/C3/C6/N1) in (1) is planar despite the shortened intramolecular contacts H2···C6 2.44 (2) Å (van der Waals radii sum is 2.87 Å; Zefirov & Zorky, 1989) and O1···H3 2.40 (2) Å. The maximum deviations from the least-squares mean plane passing through all non-H atoms of this fragment is 0.038 (1) Å for O1 atom. The C13···C18 and C7···C12 phenyl rings are twisted with respect to 2-cyanocarboxyaminoprop-2-enylic fragment [angles between planes of these fragments are −40.55 (8) and 25.73 (9)°, respectively]. For the C13–C18 ring, this may be linked to short intramolecular contacts O1···C14 2.887 (2) and C1···H14 2.81 (2) Å.

In the crystal phase, molecules of (1) are linked by N2—H2···O1[i] hydrogen bonds [symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$]. Thus, molecules of (1) do not form centrosymmetric dimers in the crystal due to intermolecular hydrogen bonds unlike previously investigated related compounds (Borbulevych *et al.*, 1998; Golding *et al.*, 1999), but form stacks along the crystallographic *c* axis.
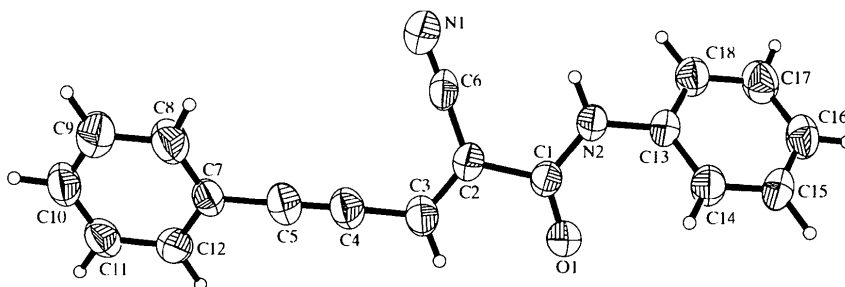

Fig. 1. View of the title compound (1). The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small circles of an arbitrary radius for clarity.