Acta Cryst. (1966). **21**, 957

The Crystal Structure of Phenylethynyl(trimethylphosphine)copper(I)

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(*Received* 18 *June* 1966)

Phenylethynyl(trimethylphosphine)copper(I), $C_6H_5C{\equiv}CCuP(CH_3)_3$, crystallizes in an orthorhombic cell with $a=12\cdot69$, $b=27\cdot25$, $c=21\cdot39$ Å, $Z=16$, space group *Pbca*. The structure was determined by the heavy-atom method and was refined by least-squares techniques to an R value of 0·074 for the 1451 observed reflexions. The molecule is a tetramer, with the four copper atoms forming a zigzag chain. It is centrosymmetric and is nearly flat apart from atoms of the phosphine groups. The terminal copper atoms are bound to two phosphorus atoms and to two ethynyl groups in a distorted tetrahedral arrangement. The inner copper atoms are attached to three ethynyl groups in an approximately trigonal arrangement. In addition, the separation between copper atoms in the two environments is only 2·45 Å. The metal–carbon interactions involve normal σ- and π-bonds together with oblique π-bonds similar to those in phenylethynyl(trimethylphosphine)silver(I).

Introduction

The acetylides of copper, of the formula $RC{\equiv}CCu$, are generally prepared as fine powders and are regarded as coordination polymers with strong π-bonding between the metal and the acetylenes (Blake, Calvin & Coates, 1959). In agreement with this, the ethynyl stretching frequencies are 270–300 cm^{-1} lower than in the disubstituted acetylenes (2200–2250 cm^{-1}). The polymeric structure is partly broken down by reaction with suitable donor molecules such as the tertiary phosphines. The monophosphine complexes have degrees of association of 2·5–3·5 in benzene and stretching frequencies about 100 cm^{-1} greater than in the uncomplexed compounds, indicating less intense copper–ethynyl interactions.

Phenylethynyl(trimethylphosphine)copper(I) has a degree of association of 2·6–2·8 in benzene (0·9–6·4 wt.%). It shows two stretching frequencies (potassium bromide disc) of 2019 and 2045 cm^{-1}, compared with values of 1933 cm^{-1} for phenylethynylcopper(I) and 2149 cm^{-1} for diphenylmercury(II). The lower values for the copper compounds demonstrate some substantial electronic effect additional to that present in the compound of mercury (Coates & Parkin, 1961). In phenylethynyl(trimethylphosphine)silver(I) (Corfield & Shearer, 1966) the silver atoms are bound to acetylene by π-bonds of a weak and unsymmetrical nature.

Experimental

The compound was crystallized from toluene as yellow needles elongated along **a**. Roughly cylindrical specimens about 0·2–0·3 mm. in diameter were used in the analysis. During the exposure the crystals became coated with a layer of decomposition material which appeared to protect the remainder, as there was no noticeable effect on the intensities of the reflexions. The unit-cell dimensions were measured from precession photographs, taken with Zr-filtered Mo radiation.

Crystal data

$C_6H_5C{\equiv}CCuP(CH_3)_3$, $C_{11}H_{14}CuP$ M.W. 240·8
Orthorhombic, $a=12\cdot69\pm0\cdot02$, $b=17\cdot25\pm0\cdot03$,
$c=21\cdot39\pm0\cdot03$ Å, $U=4682$ Å^3, $D_m=1\cdot34$, $Z=16$,
$D_x=1\cdot366$ g.cm^{-3}.
Absorption coefficient for Mo $K\alpha$ radiation,
$\lambda=0\cdot7107$ Å, $\mu=20$ cm^{-1}.

The $hk0$ reflexions were observed when $h=2n$, the $0kl$ when $k=2n$ and the $h0l$ with $l=2n$.

The space group is thus *Pbca* (D_{2h}^{15}).

Partial three-dimensional data were recorded photographically with Zr-filtered Mo radiation. The precession method was used for the layers $0kl$–$2kl$, $h0l$–$h4l$ and $hk0$, and the equi-inclination Weissenberg technique for the layers $3kl$–$7kl$. The intensities were estimated visually by comparison with a calibrated scale and corrected for the usual Lorentz and polarization factors. Empirical length corrections were also applied in the case of the Weissenberg data. The structure factors were placed on the same relative scale by a least-squares treatment of the common reflexions (Rollett & Sparks, 1960). 1451 independent reflexions were observed, 396 of them on two layers and 4 on three.

Structure determination

The positions of the two copper atoms in the asymmetric unit were found by inspection of the Patterson function in projection along the a and b axes. Calculation of the three-dimensional Patterson function confirmed these positions and, with the aid of superposition methods, revealed the positions of the two phosphorus atoms attached to Cu(2). For the heavy atoms alone, the reliability index R was 0·32.

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Calculation of two successive F_o syntheses allowed coordinates to be assigned to all the carbon atoms except the methyl carbon atoms bonded to P(2). A further F_o synthesis and an $F_o - F_c$ synthesis, in which F_c represented the contributions of the other atoms, confirmed that the positions of these methyl carbons were disordered. The electron density distribution could be interpreted by having two sets of carbon atoms, each with a weight of one half, attached to P(2). On this basis R was 0·17.

The refinement

The atomic parameters were refined by least-squares methods, first with isotropic temperature parameters to an R value of 0·13 and finally with anisotropic temperature parameters for all the atoms (including the disordered ones) to an R value of 0·074, calculated on the observed reflexions. In the final cycle the mean coordinate shift for all the atoms, except the methyl carbon atoms on P(2), was 0·0016 Å with a maximum shift of 0·0076 Å. No parameter shift was more than one half of the corresponding standard deviation.

During the last stages of refinement a second $F_o - F_c$ synthesis, based on the contributions of the ordered atoms alone, was calculated in the region of the disordered carbon atoms as a check on their arrangement. Two disordered atoms, which had come close together in the refinement, gave rise to a single peak in the difference map and the remaining four disordered atoms to smaller peaks on a semicircular ridge of electron density, in agreement with there being two alternative sets of positions. The variation in electron density appeared to rule out the possibility of free rotation about the Cu(2)–P(2) bond. On the basis of the values of the peak heights and of the temperature factors obtained during the previous refinement, one set of atoms C(20), C(21), C(22) was given a weight of 3/5 and the other set C(23), C(24), C(25) a weight of 2/5 in the last two cycles of refinement.

The structure factor least-squares calculations were carried out on a Pegasus computer with the program devised by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). In the final cycle the weighting was of the form

$$w = 1/\{a + k|F_o| + c(k|F_o|)^2\}$$

with $a = 15$, $c = 0·0085$ and $k = 1·11$. These weights were halved for planes with $\sin\theta/\lambda$ less than 0·1.

The final values of the atomic coordinates and their estimated standard deviations are shown in Table 1 and the temperature parameters in Table 2. The observed and calculated structure factors are listed in Table 3. The unobserved reflexions were given zero weight in the refinement but few have calculated values greater than the minimum observable values. The scattering factors for copper were those issued in the Leeds library of form factors, for phosphorus those listed in *International Tables for X-ray Crystallography* (1962) and for carbon those due to Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Table 1. *Atomic coordinates* (Å) *and their standard deviations* (10^3 Å)

	x	*y*	*z*
Cu(1)	−0·093 (2)	0·888 (2)	1·008 (2)
Cu(2)	1·972 (2)	2·199 (2)	0·857 (2)
P(1)	3·594 (4)	1·167 (4)	2·003 (5)
P(2)	2·222 (6)	4·174 (5)	−0·130 (6)
C(1)	0·281 (17)	2·315 (15)	2·295 (17)
C(2)	0·361 (15)	3·165 (15)	3·163 (17)
C(3)	0·429 (16)	4·185 (13)	4·189 (15)
C(4)	−0·727 (17)	4·488 (15)	4·927 (16)
C(5)	−0·638 (20)	5·471 (19)	5·928 (18)
C(6)	0·522 (20)	6·118 (16)	6·161 (18)
C(7)	1·668 (18)	5·845 (16)	5·421 (17)
C(8)	1·627 (15)	4·861 (17)	4·451 (17)
C(9)	1·347 (15)	0·688 (13)	−0·470 (15)
C(10)	1·839 (16)	0·114 (14)	−1·449 (17)
C(11)	2·872 (15)	−0·091 (16)	−2·474 (14)
C(12)	2·811 (18)	−1·187 (20)	−3·334 (17)
C(13)	3·904 (20)	−1·311 (25)	−4·288 (18)
C(14)	4·918 (19)	−0·413 (25)	−4·317 (18)
C(15)	4·934 (21)	0·679 (25)	−3·458 (18)
C(16)	3·946 (19)	0·824 (20)	−2·500 (17)
C(17)	3·020 (28)	−0·313 (19)	2·895 (21)
C(18)	4·963 (21)	0·503 (23)	1·007 (24)
C(19)	4·494 (20)	2·100 (23)	3·313 (19)
C(20)	1·010 (44)	5·460 (28)	0·734 (45)
C(21)	1·579 (57)	4·269 (34)	−1·703 (38)
C(22)	3·647 (29)	5·221 (35)	0·093 (47)
C(23)	0·897 (58)	5·051 (44)	−0·787 (78)
C(24)	3·274 (51)	4·123 (41)	−1·968 (38)
C(25)	3·664 (83)	5·163 (44)	0·692 (61)

Description

The compound occurs in the crystal as discrete tetramers which are centrosymmetric and nearly flat apart from the terminal phosphines. A diagram of the molecule, projected onto the mean plane through the copper and phenylethynyl carbon atoms, but with the methyl carbons omitted for reasons of clarity, is shown in Fig. 1. The bond lengths and angles are listed in Table 4. The four copper atoms are arranged in a zigzag chain with the crystallographic centre of symmetry between Cu(1) and Cu(1′). Two phosphorus atoms are bound to the terminal copper atom Cu(2), one above and the other below the mean molecular plane.

Cu(1) is end-on σ-bonded to the ethynyl carbon C(1) and side-on π-bonded to the ethynyl carbons C(9′) and C(10′). In addition it is close to C(9) so that the four atoms C(1), Cu(2), C(9) and Cu(1′) together with the point mid-way between C(9′) and C(10′), written as C(9′, 10′), lie at five vertices of a distorted hexagon. The four angles subtended at Cu(1) are respectively 59, 55, 50 and 67° and none of the atoms is more than 0·06 Å from their mean plane. The atoms C(1) and C(9) together with C(9′, 10′) are arranged approximately trigonally round Cu(1) with angles C(1)–Cu(1)–C(9), C(9)–Cu(1)–C(9′, 10′) and C(9′, 10′)–Cu(1)–C(1) of 114, 117 and 130° respectively and are coplanar within experimental error. Trigonal coordination is found in $KCu(CN)_2$ (Cromer, 1957).

Around Cu(2), the atoms P(1), P(2) and Cu(1) are arranged in an approximately trigonal manner, the angles P(1)–Cu(2)–P(2), P(2)–Cu(2)–Cu(1) and Cu(1)–Cu(2)–P(1) being 124, 127 and 109° respectively. Cu(2) lies at a distance of 0·04 Å from the plane through the other three atoms. More significantly, the four atoms P(1), P(2), C(1) and C(9) lie in a distorted tetrahedral arrangement about Cu(2) with the angles P(1)–Cu(2)–P(2) and C(1)–Cu(2)–C(9) equal to 124 and 103°. The plane of P(1), P(2) and Cu(2) is very nearly at right angles to the plane through the atoms C(1), C(9) and Cu(2).

Table 2. *Thermal vibration tensor components*, U_{ij} (Å²)

The standard deviations are 0·001 for the copper and 0·004–0·023 for the ordered carbon atoms.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu(1)	0·052	0·040	0·071	−0·002	−0·015	−0·004
Cu(2)	0·059	0·038	0·087	−0·006	−0·003	−0·007
P(1)	0·061	0·051	0·066	0·010	−0·001	0·005
P(2)	0·097	0·044	0·107	−0·014	0·010	−0·035
C(1)	0·075	0·052	0·087	0·016	−0·018	−0·016
C(2)	0·041	0·060	0·095	0·001	−0·014	−0·004
C(3)	0·089	0·033	0·062	0·005	−0·022	−0·012
C(4)	0·082	0·059	0·073	0·005	−0·021	0·014
C(5)	0·109	0·093	0·074	−0·022	−0·032	0·036
C(6)	0·110	0·053	0·087	−0·020	−0·007	−0·010
C(7)	0·087	0·075	0·061	−0·021	−0·013	−0·011
C(8)	0·050	0·072	0·082	−0·010	−0·025	−0·028
C(9)	0·056	0·041	0·066	−0·010	−0·006	−0·001
C(10)	0·061	0·048	0·078	−0·003	0·001	−0·013
C(11)	0·055	0·081	0·043	0·022	0·016	0·001
C(12)	0·079	0·100	0·080	0·018	−0·027	0·006
C(13)	0·075	0·164	0·072	0·005	0·006	−0·004
C(14)	0·065	0·191	0·064	−0·003	0·055	0·000
C(15)	0·101	0·155	0·060	−0·004	0·032	−0·010
C(16)	0·077	0·114	0·070	−0·018	0·023	0·010
C(17)	0·175	0·072	0·100	0·009	0·009	0·056
C(18)	0·096	0·128	0·127	0·057	−0·032	0·039
C(19)	0·085	0·131	0·093	0·009	−0·043	−0·008
C(20)	0·164	0·033	0·209	0·033	−0·006	0·028
C(21)	0·382	0·064	0·085	−0·056	0·021	−0·052
C(22)	0·040	0·107	0·242	−0·034	0·079	−0·065
C(23)	0·132	0·052	0·330	0·072	0·093	−0·100
C(24)	0·143	0·065	0·045	−0·021	0·010	0·027
C(25)	0·282	0·044	0·159	−0·101	0·028	−0·031

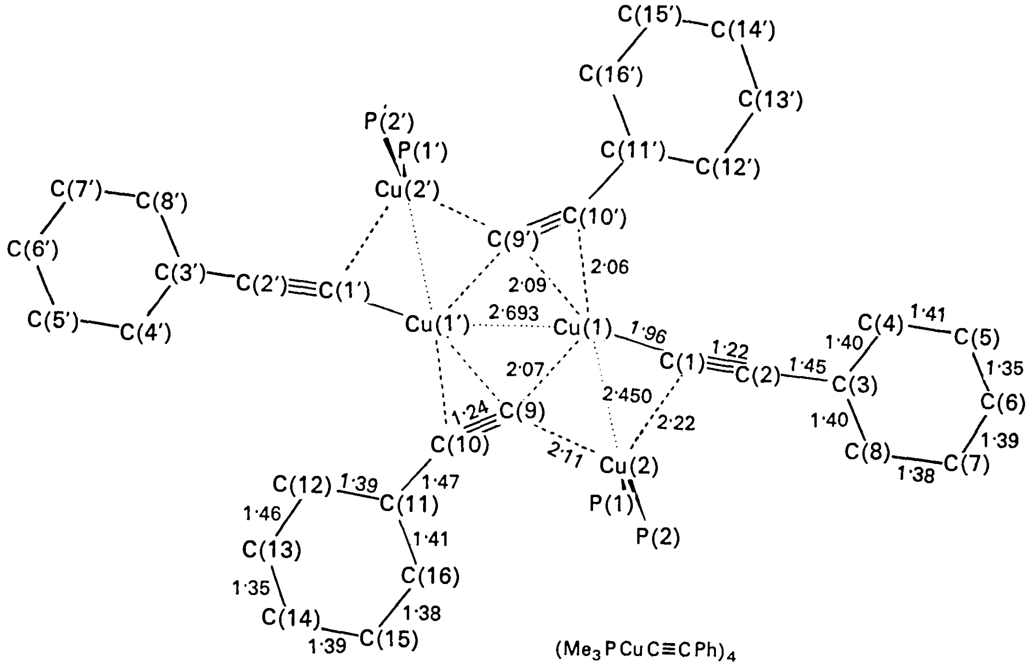

Fig. 1. The molecule in projection onto the mean plane of the copper and phenylethynyl carbon atoms. The carbon atoms attached to phosphorus are not shown.

Table 3. *Observed and calculated structire factors*

Successive columns give values of k, l, $|F_o|$ and F_c.

H= 0

0	0	----	1984
0	2	422	383
0	4	222	208
0	6	<18	-5
0	8	112	-101
0	10	117	-116
0	12	179	-174
0	14	84	-84
0	16	67	-65
0	18	24	22
0	20	75	71
0	22	29	26
0	24	27	27
2	0	193	179
2	1	149	-125
2	2	154	166
2	3	432	-413
2	4	277	-289
2	5	163	-182
2	6	75	-87
2	7	260	-233
2	8	149	-144
2	9	91	-83
2	10	152	-135
2	11	20	-21
2	12	102	-104
2	13	20	24
2	14	81	-79
2	15	64	61
2	16	<18	-12
2	17	93	90
2	18	22	21
2	19	80	74
2	20	26	22
4	0	143	144
4	1	226	-213
4	2	<11	6
4	3	78	-83
4	4	<12	4
4	5	328	-291
4	6	22	33
4	7	106	-91
4	8	40	36
4	9	29	25
4	10	127	119
4	11	15	-14
4	12	68	66
4	13	31	32
4	14	97	88
4	15	39	36
4	16	77	72
4	17	64	64
4	18	21	24
4	19	46	47
6	0	102	-104
6	1	32	27
6	2	94	-98
6	3	27	14
6	4	49	-46
6	5	33	-21
6	6	27	-24
6	7	38	34
6	8	23	23
6	9	100	95
6	10	74	-73
6	11	71	67
6	12	39	-36
6	13	48	49
6	14	<20	1
6	15	29	31
6	16	<20	27
6	17	<21	8
6	18	<21	1
6	19	21	18
6	20	27	-26
6	21	<21	-13
6	22	31	-26
6	23	21	-17
8	0	53	52
8	1	15	17
8	2	36	37
8	3	74	-70
8	4	90	72
8	5	97	-91
8	6	59	55
8	7	79	-76
8	8	37	35
8	9	<18	-10
8	10	27	29
8	11	<19	-9
8	12	<20	-8
8	13	44	43
8	14	<20	9
8	15	26	31
8	16	36	32
8	17	34	28
10	0	253	-242
10	1	<17	10
10	2	136	-128
10	3	34	-33
10	4	107	-98
10	5	114	-111
10	6	<18	18
10	7	96	-93
10	8	39	34
10	9	70	-66
10	10	41	37
10	11	<20	-7
10	12	35	30
10	13	41	38
10	14	45	37
10	15	62	60
10	16	<21	10
10	17	<21	17
10	18	<21	-14
10	19	<21	7
10	20	34	-33
12	0	119	-111
12	1	39	33
12	2	145	-137
12	3	112	112
12	4	49	-50
12	5	72	74
12	6	<19	-1
12	7	48	46
12	8	91	89
12	9	<20	14
12	10	132	120
12	11	<20	8
12	12	129	117
12	13	<21	3
12	14	57	57
12	15	<22	-23
12	16	27	27
12	17	34	-34
12	18	<22	-16
12	19	27	-30
14	0	<19	-4
14	1	71	65
14	2	<20	-12
14	3	130	119
14	4	44	-46
14	5	151	139
14	6	42	-44
14	7	106	95
14	8	<21	-10
14	9	79	77
14	10	21	18
14	11	<21	4
14	12	<21	-13
14	13	<21	-13
14	14	22	-22
14	15	41	-36
14	16	34	-31
14	17	44	-43
14	18	<22	-12
14	19	26	-26
16	0	165	147
16	1	<21	4
16	2	109	103
16	3	<21	10
16	4	37	31
16	5	<21	21
16	6	<21	2
16	7	46	38
16	8	25	-18
16	9	<22	-7
16	10	25	-22
16	11	31	-24
16	12	31	-27
16	13	49	-47
16	14	41	-34
16	15	25	-28
16	16	22	-21
18	0	<21	4
18	1	<22	-22
18	2	<22	9
18	3	<22	-22
18	4	<22	-7
18	5	<22	-8
18	6	22	-26
18	7	<22	-12
18	8	28	-26
18	9	<22	-8
18	10	35	-33

H= 1

0	2	51	-49
0	4	189	-190
0	6	106	-98
0	8	102	-80
0	10	25	-30
0	12	<14	-5
0	14	<16	2
0	16	41	36
0	18	70	65
0	20	53	53
1	1	---	287
1	2	126	-132
1	3	231	234
1	4	74	-74
1	5	<11	21
1	6	86	-90
1	7	84	-83
1	8	95	-94
1	9	117	-115
1	10	33	-35
1	11	164	-163
1	12	<21	2
1	13	91	-88
1	14	52	49
1	15	40	-34
1	16	42	43
1	17	<19	17
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2	2	34	55
2	3	102	-112
2	4	123	-113
2	5	67	66
2	6	49	49
2	7	23	23
2	8	28	32
2	9	39	43
2	10	<14	18
2	11	39	39
2	12	<17	-8
2	13	53	50
2	14	51	-54
2	15	76	74
2	16	<18	-10
2	17	19	24
3	1	<15	-7
3	2	79	-84
3	3	130	131
3	4	281	-283
3	5	44	-45
3	6	89	-102
3	7	<14	-8
3	8	175	-168
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3	12	28	27
3	13	<18	-5
3	14	57	57
3	15	<19	20
3	16	77	78
3	17	19	23
3	18	41	35
4	1	114	-106
4	2	165	174
4	3	51	-53
4	4	197	194
4	5	62	82
4	6	110	118
4	7	34	33
4	8	90	96
4	9	34	-38
4	10	54	51
4	11	46	-48
4	12	34	36
4	13	<18	0
4	14	<19	10
4	15	34	37
4	16	35	-33
5	1	57	-58
5	2	56	-54
5	3	72	-70
5	4	45	42
5	5	24	-34
5	6	118	-116
5	7	20	27
5	8	<16	-9
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5	10	<17	-2
5	11	33	37
5	12	75	78
5	13	61	61
5	14	56	55
5	15	20	26
5	16	52	52
6	1	110	103
6	2	<12	11
6	3	42	52
6	4	24	25
6	5	96	101
6	6	36	-38
6	7	21	-20
6	8	91	-87
6	9	82	-84
6	10	36	-41
6	11	114	-111
6	12	<18	22
6	13	68	-63
7	1	<13	6
7	2	42	-44
7	3	44	-43
7	4	82	-80
7	5	<15	-21
7	6	15	18
7	7	27	-33
7	8	81	-78
7	9	56	61
7	10	43	46
7	11	18	21
7	12	37	41
7	13	<19	10
7	14	37	29
7	15	<20	-11
7	16	29	24
8	1	<17	-12
8	2	<14	-12
8	3	<15	-4
8	4	<15	-6
8	5	26	-29
8	6	90	-95
8	7	<16	12
8	8	152	-148
8	9	17	22
8	10	49	-50
8	11	<18	25
8	12	27	31
8	13	<19	15
8	14	51	48
8	15	<20	5
8	16	25	30
9	1	60	-64
9	2	48	-50
9	3	25	-25
9	4	52	-58
9	5	34	-33
9	6	66	-60
9	7	44	50
9	8	<17	-9
9	9	59	62
9	10	<18	-9
9	11	74	75
9	12	<19	1
9	13	<40	19
9	14	<20	23
9	15	<20	14
9	16	47	44
10	1	109	-112
10	2	<16	3
10	3	108	-108
10	4	16	27
10	5	94	-94
10	6	<17	-14
10	7	<17	-20
10	8	25	-24
10	9	65	62
10	10	<19	-16
10	11	69	64
10	12	<19	8
10	13	43	33
10	14	<20	-10
10	15	29	18
11	1	163	-161
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4	3	54	-60
4	4	37	36
4	5	50	-53
4	6	<23	10
4	7	47	-39
4	8	29	-27
4	9	<24	-9
4	10	42	-46
4	11	<24	-1
4	12	39	-39
5	0	56	55
6	0	46	-44
7	0	<20	-4
8	0	107	-118
9	0	<19	1
10	0	39	-38
11	0	<21	-18
12	0	<21	-7
13	0	<21	-22
14	0	<21	-9
15	0	<21	-24
16	0	20	-16
K=11			
0	2	22	23
0	4	52	45
0	6	76	76
0	8	72	71
0	10	33	26
0	12	<19	-2
0	14	24	-21
1	1	39	35
1	2	<23	-3
1	3	23	34
2	1	42	46
2	2	<22	19
2	3	47	47
2	4	<22	-11
2	5	35	34
2	6	<22	24
2	7	<22	-14
2	8	<22	14
2	9	32	-38
2	10	<23	9
2	11	33	-39
3	1	29	31
3	2	41	-38
3	3	<24	30
3	4	34	-35
3	5	<24	9
3	6	24	-25
3	7	24	-19
3	8	<24	-1
3	9	<24	-22
3	10	<24	-5
3	11	30	-22
4	1	<24	6
4	2	<24	-16
4	3	<24	1
4	4	34	-26
4	5	<24	9
4	6	46	-43
K=12			
0	0	27	25
0	2	76	71
0	4	40	37
0	6	<19	11
0	8	23	-22
0	10	52	-47
0	12	33	-29
1	1	<24	-14
1	2	<24	23
1	3	<24	15
1	4	<24	13
1	5	50	50
1	6	<24	-5
1	7	41	45
1	8	<24	-20
1	9	<24	30
1	10	24	-20
2	0	<20	21
2	1	<23	-9
2	2	<23	6
2	3	<23	-16
2	4	<23	16
2	5	43	-48
2	6	<23	-5
2	7	40	-44
2	8	<23	-21
2	9	<25	-31
2	10	23	-28
3	0	34	29
3	1	<24	-7
3	2	34	32
3	3	<24	-11
3	4	30	26
3	5	<25	-13
3	6	<25	1
3	7	<25	-3
3	8	<25	-11
3	9	<25	1
3	10	25	-31
4	0	<21	-13
5	0	<21	-13
6	0	<21	-12
7	0	<21	1
8	0	<21	15
9	0	<21	21
10	0	<21	-29
11	0	<21	14
12	0	29	-33
13	0	23	-24
K=13			
0	2	19	16
0	4	31	22
0	6	19	17
1	1	51	50
1	2	<24	-9
1	3	24	24
1	4	24	-26
1	5	<24	10
1	6	24	-32
1	7	<24	-16
1	8	<24	-22
1	9	24	-27
1	10	<24	-13
1	11	34	-34
1	12	<25	-3
1	13	29	-28
3	1	<23	4
3	2	<23	-19
3	3	<24	-17
3	4	25	-26
3	5	<24	-6
3	6	51	-46
3	7	<25	-2
3	8	25	-28
K=14			
0	0	39	36
0	2	35	31
0	4	<19	1
0	6	27	-20
0	8	19	-19
0	10	22	-19
2	0	23	25
2	1	<23	-11
2	2	<23	19
2	3	24	-26
4	0	<20	-11
4	1	<27	-16
4	2	<27	-6
4	3	27	-27
5	0	29	32
6	0	<21	-9
7	0	25	25

Table 4. *Interatomic distances and angles and their standard deviations*

Cu(1)-Cu(2)	2·450	0·003 Å
Cu(1)-Cu(1′)	2·693	0·004
Cu(2)-P(1)	2·238	0·005
Cu(2)-P(2)	2·222	0·005
Cu(1)-C(1)	1·957	0·016
Cu(1)-C(9′)	2·085	0·014
Cu(1)-C(10′)	2·061	0·016
Cu(1)-C(9)	2·073	0·015
Cu(2)-C(9)	2·105	0·015
Cu(2)-C(10)	3·112	0·016
Cu(2)-C(1)	2·223	0·017
Cu(2)-C(2)	2·975	0·017
P(1)—C(17)	1·821	0·021
P(1)—C(18)	1·818	0·023
P(1)—C(19)	1·843	0·022
P(2)—C(20)	1·967	0·039
P(2)—C(21)	1·702	0·044
P(2)—C(22)	1·782	0·038
P(2)—C(23)	1·719	0·061
P(2)—C(24)	2·118	0·044
P(2)—C(25)	1·932	0·065
C(1)—C(2)	1·218	0·023
C(9)—C(10)	1·237	0·022
C(2)—C(3)	1·449	0·021
C(10)-C(11)	1·470	0·022

Cu(1)-Cu(2)-P(1)	109·4	0·2°
Cu(1)-Cu(2)-P(2)	126·7	0·2
C(1)—Cu(1)-C(9)	114·0	0·6
C(1)—Cu(1)-C(9′, 10′)	129·7	
C(9)—Cu(1)-C(9′, 10′)	116·5	
P(1)—Cu(2)-P(2)	123·8	0·2
P(1)—Cu(2)-C(1)	104·1	0·4
P(1)—Cu(2)-C(9)	101·9	0·4
P(2)—Cu(2)-C(1)	109·0	0·4
P(2)—Cu(2)-C(9)	113·0	0·4
C(1)—Cu(2)-C(9)	102·7	0·6
Cu(1)-C(9)—Cu(2)	71·8	0·5
Cu(1)-C(1)—Cu(2)	71·5	0·5
Cu(1)-C(1)—C(2)	172·0	1·4
Cu(2)-C(1)—C(2)	116·6	1·4
C(1)—C(2)—C(3)	178·9	1·7
C(9)—C(10)-C(11)	153·7	1·5
Cu(1)-C(9)—C(10)	152·3	1·3
Cu(2)-C(9)—C(10)	135·6	1·2
Cu(2)-P(1)—C(17)	113·4	0·7
Cu(2)-P(1)—C(18)	115·7	0·7
Cu(2)-P(1)—C(19)	119·0	0·7
C(17)-P(1)—C(18)	102·1	1·0
C(18)-P(1)—C(19)	101·0	1·0
C(19)-P(1)—C(17)	102·5	1·0

The Cu–Cu distances are 2·45 and 2·69 Å, the former being less than the separation in the metal (2·556 Å) and suggesting some bonding between Cu(1) and Cu(2). Apart from this metal–metal interaction, the coordination at Cu(1) appears trigonal and at Cu(2) tetrahedral. The environment at Cu(2) is closely similar to that found in CuCN.NH$_3$ (Cromer, Larson & Roof, 1965) where four ligands are situated round copper in a distorted tetrahedral manner with an additional copper atom at a distance of 2·42 Å, compared with 2·45 Å in the present work. In that compound, cyanide carbon atoms are bonded to two copper atoms with Cu–C distances of 2·09 and 2·13 Å similar to the lengths of 2·07 and 2·11 Å found for Cu(1)–C(9) and Cu(2)–C(9) and a Cu–C–Cu angle of 69·9° compared with 71·8° in the present case. The nature of this bonding is discussed later.

The bond length of 1·96 Å for Cu(1)–C(1) is similar to the distances found in the trigonally coordinated copper cyanide complexes, namely 1·92 Å in KCu(CN)$_2$

and 1·87, 1·89 and 1·90 Å in $KCu_2(CN)_3.H_2O$ (Cromer, 1957; Cromer & Larson, 1962). The π-bonding between Cu(1) and C(9′) and C(10′) results in the carbon atoms lying in the plane of hybridization of Cu(1). The Cu–C distances of 2·06 and 2·09 Å are equal within experimental error and are comparable with distances in π-bonded compounds of iron and nickel.

The triple bond distances are 1·22 Å for C(1)–C(2) and 1·24 Å for C(9)–C(10). The existence of two types of ethynyl environment, one being in stronger association with copper atoms, agrees with the finding of two ethynyl stretching frequencies. Neither of these distances is significantly longer than the standard ethynyl distance of 1·205 Å. The angle Cu(1)–C(1)–C(2) is 172° and the distortion from linearity decreases the separation Cu(2)–C(1), suggesting some interaction between them. The single bonds C(2)–C(3) and C(10)–C(11) have lengths of 1·45 and 1·47 Å, in good agreement with the value of 1·45 Å found for the corresponding bond in phenylethynyl(trimethylphosphine)silver(I). The angle C(1)–C(2)–C(3) is 179° so that these atoms are collinear within experimental error but the corresponding angle C(9)–C(10)–C(11) is 154°. A similar deformation was found in but-2-yne copper(I) chloride (Carter & Hughes, 1957) where the ethynyl group adopts the *cis* configuration. The bond lengths in the phenyl groups range from 1·35–1·46 Å with a mean value of 1·393 Å and the bond angles from 116 to 122° with a mean of 120·0°. Taking the individual values as estimates of the same quantity leads to a statistical standard deviation of 0·028 Å in bond lengths and 1·7° in bond angle, close to the average values of 0·026 Å and 1·6° derived from the least-squares estimates of the coordinate standard deviations.

The equation of the mean plane through the four copper atoms and all the phenylethynyl carbon atoms is

$$0{\cdot}4730x - 0{\cdot}6457y + 0{\cdot}5994z = 0$$

where x, y and z are in Å and are referred to the crystal axes. None of these atoms is displaced more than 0·3 Å from the plane and the mean displacement is 0·11 Å. The plane of the phenyl carbon atoms C(3)–C(8) is inclined at about 14° to this plane and that of the carbon atoms C(11)–C(16) at about 7°.

The ethynyl carbon atoms C(1) and C(2) are coplanar with the phenyl carbon atoms C(3)–C(8), the maximum displacement from the mean plane being 0·012 Å for C(7) and the mean displacement 0·006 Å. The atoms Cu(1) and Cu(2) lie at distances of 0·029 and −0·464 Å so that the bond Cu(1)–C(1) is very nearly in the plane of the phenylethynyl atoms. However C(9) and C(10) are at distances of 0·095 and 0·021 Å from the mean plane through the phenyl carbon atoms C(11)–C(16) and the bond C(10)–C(9) is tilted out of the plane by about 3°.

The Cu(2)–P(1) and Cu(2)–P(2) distances of 2·24 and 2·22 Å are less than the estimated value of 2·45 Å for a single covalent bond (Pauling, 1960). The contraction suggests some double bond character in these bonds, a view supported by the mean Cu–P–C angle of 116° and the mean C–P–C angle at P(1) of 102°. The lengths of the P–C bonds at P(1) do not differ significantly from one another and their mean value is 1·83 Å, very similar to that in trimethylphosphine (Lide & Mann, 1958). The P–C bond lengths and the Cu–P–C angles at P(2), which involve the positions of the disordered carbon atoms, vary considerably amongst themselves but their mean values of 1·87 Å and 116° agree reasonably well with those found at P(1). However the standard deviations of the disordered atoms, obtained from the block-diagonal least-squares calculations, appear to be seriously underestimated, possibly because of neglect of the interatomic interactions in the full matrix (Dunitz & Rollett, 1956). A discussion of the lengths involving these overlapping atoms does not appear justified.

The non-bonding contacts appear normal and the shortest of these are listed in Table 5. The approach distances between the molecules are all greater than 3·5 Å and within the tetramer the shortest contact is 3·40 Å.

Table 5. *Non-bonding contacts*

The superscripts refer to the asymmetric units as follows:

′	$-x$	$-y$	$-z$	iv	$\frac{1}{2}-x$	$y-\frac{1}{2}$	z
″	$1-x$	$-y$	$-z$	v	$x-\frac{1}{2}$	y	$\frac{1}{2}-z$
‴	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$-z$	vi	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$

Cu(1)–C(12′)	3·59 Å	C(18)–C(18″)	3·56 Å
C(1)–C(12′)	3·45	C(5)–C(15‴)	3·58
C(2)–C(12′)	3·74	C(12)–C(24^{iv})	3·59
C(1)–C(20)	3·59	C(18)–C(20^{iv})	3·70
C(2)–C(20)	3·40	C(4)–C(19^{v})	3·61
C(3)–C(20)	3·73	C(6)–C(21^{vi})	3·50
C(16)–C(18)	3·67		
C(16)–C(24)	3·41		

The temperature parameters tend to be greater for atoms further from the molecular centre. The major axes of the vibration ellipsoids of the copper and ethynyl carbon atoms point roughly in the same direction, at an angle of about 45° to the normal to the mean molecular plane. The phosphorus atoms vibrate mainly in directions perpendicular to the Cu–P bonds.

Discussion

By analogy with phenylethynyl(trimethylphosphine)silver(I), the molecule can be described formally as built up from $[(Me_3P)_2Cu]^+$ and $[(PhC{\equiv}C)_2Cu]^-$ units. Interaction between Cu(2) and the two ethynyl groups of the same $[(PhC{\equiv}C)_2Cu]^-$ unit leads to a tetrahedral arrangement of carbon and phosphorus atoms round Cu(2). The tetramer is produced by the formation of normal π-bonds between Cu(1) and C(9′) and C(10′) and between Cu(1′) and C(9) and C(10). In this description, the ethynyls adopt the *trans* configuration, as in the first excited state of acetylene (Ingold & King, 1953).

The ethynyl group C(1)–C(2) is associated with two copper atoms, Cu(1) and Cu(2). A σ-bond is formed with Cu(1), with slight distortion from linearity, the angle Cu(1)–C(1)–C(2) being 172°, and a weak unsymmetrical π-bond with Cu(2), the distances Cu(2)–C(1) and Cu(2)–C(2) being 2·22 and 2·98 Å. The environment resembles that found in phenylethynyl-(trimethylphosphine)silver(I), where the corresponding angle and distances are 173° and 2·55 and 3·04 Å. In both compounds, the metal atom forming the oblique bond with the ethynyl group is in tetrahedral coordination, with the molecular dimensions suggesting appreciable π-bonding between the copper or silver atom and two tertiary phosphine groups. In copper(I) compounds with tertiary phosphines, as in those of silver(I), the phosphorus atoms show a strong tendency towards π-bonding formation, so controlling the coordination round the metal atom (Cass, Coates & Hayter, 1954). Only two strong π-bonds can be formed by an atom in tetrahedral coordination so that other π-interactions will be weak, allowing an unsymmetrical type of bond to the ethynyl group.

The ethynyl group C(9)–C(10) is in close association with no fewer than three copper atoms, Cu(1′), Cu(1) and Cu(2). A normal π-bond is formed with Cu(1′), with Cu–C distances of 2·06 and 2·09 Å, and C(9) appears also to be bound to Cu(1) and Cu(2), with Cu–C distances of 2·07 and 2·11 Å. All four of these copper–carbon distances are equal within experimental error. The ethynyl group is not quite in the same plane as the copper atoms, C(9) and C(10) each being 0·12 Å from this plane.

An unsymmetrical π-bond, of the type described above, may be postulated between Cu(2) and the carbon atoms C(9) and C(10). If Cu(1) is regarded as part of an anionic unit and Cu(2) of a cationic one, this bonding scheme gives Cu(1) a share in 16 valence electrons (including the 10 electrons in its 3*d* orbitals) whereas Cu(2) shares in 18. Overlap of a filled 3*d* orbital of Cu(2) with the empty 4*pz* orbital of Cu(1) would account for the relatively short Cu(1)–Cu(2) distance and permit the 18-electron rule to become satisfied in both instances. The postulated scheme is shown in Fig. 2, where the Cu(2) → Cu(1) dative bond is indicated by a dashed line since the interaction may be relatively small. It is possible that the same Cu(1) *pz* orbital is conjugated with the entire phenylethynyl system, otherwise it is not easy to see why all four benzene rings should line so nearly in one plane.

An alternative description is to regard the ethynyl carbon atoms C(9) and C(10) as acting as a bridging group between Cu(1) and Cu(2). This would account for the lengths Cu(1)–C(9) and Cu(2)–C(9) being equal within experimental error, the small value of 72° for the angle Cu(1)–C(9)–Cu(2), and the Cu(1)–Cu(2) distance of 2·45 Å which would arise from the metal–metal bonding resulting from the three-centre electron pair bond. Further, the bridge bonds are 0·11 and 0·15 Å longer than Cu(1)–C(1). Some of this difference could arise from shortening of the bond Cu(1)–C(1) due to end-on π-bonding, but such shortening is not thought to be appreciable since Cu(1)–C(1) itself is longer than the Cu–C distances in the cyanide complexes, mentioned above. However, it is believed that the differences between these two descriptions of the bonding is only slight.

The environment of the ethynyl carbon atoms C(9) and C(10) with respect to Cu(1′), Cu(1) and Cu(2) resembles that found in phenylethynylcopper(I) (Corfield & Shearer, 1964). In this compound there are infinite

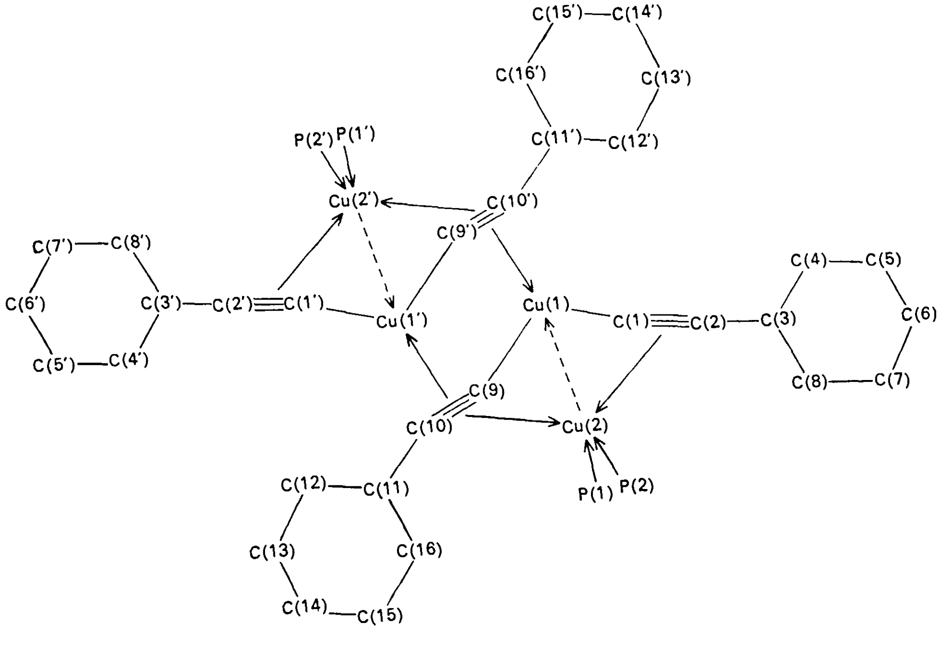

Fig. 2. Proposed bonding scheme.

zigzag chains of copper atoms. Each ethynyl group is bonded to three adjacent copper atoms and lies roughly in the plane of the zigzag chain. Each copper atom is bonded to three ethynyl groups in an approximately trigonal arrangement and also has two copper atoms as near neighbours at distances of 2·45 Å, the environment being similar to that of Cu(1) and Cu(1′) in the phosphine complex. Reaction of the tertiary phosphine with phenylethynylcopper(I) breaks down the infinite chain into units of four copper atoms, with the two outer atoms forming two bonds to phosphorus. The outer ethynyl groups C(1)–C(2) and C(1′)–C(2′), no longer able to form a normal π-bond with a copper atom, revert to the linear form with weak oblique bonding to Cu(2) and Cu(2′).

The authors would like to express their thanks to Dr C. Parkin for providing crystal specimens, to Professor D.W.J. Cruickshank for the use of his program, to Mr B.J. Nicholson for some helpful discussion and to Professor G.E. Coates for suggesting the problem and for his interest throughout the work.

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Structure Cristalline de l'Acide Undécanedioique $COOH[CH_2]_9COOH$ Localisation des Atomes d'Hydrogène

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(*Reçu le* 28 *avril* 1966, *revu le* 16 *juin* 1966)

The crystal structure of undecanedioic acid has been determined by three-dimensional X-ray crystallographic methods. The positions of the hydrogen atoms have been determined; bond lengths and angles of the CH_2 groups are consistent with the currently accepted values. The crystal is monoclinic with four molecules in the unit-cell: $a=5·61$, $b=9·55$, $c=32·54$ Å; $\beta=136°$.

Introduction

L'acide undécanedioïque $COOH[CH_2]_9COOH$ cristallise sous deux formes polymorphes: la forme β stable à température ordinaire et la forme α théoriquement stable à température plus élevée. Nous devons faire remarquer que l'on obtient très facilement des cristaux de la forme α vers 40°C et qu'ils restent stables très longtemps à température ambiante. Nous nous sommes ici tout particulièrement attachés à la détermination de la structure de la forme α. Ce travail est fait dans le cadre d'une étude plus générale entreprise au laboratoire sur les diacides aliphatiques saturés à chaine normale.

Données expérimentales

Nous avons obtenu de bons cristaux par évaporation très lente à température constante (40°C) d'une solution d'acide undécanedioïque dans un mélange d'acides acétique et formique. Ces cristaux se présentent sous forme de plaquettes (011) qu'il est facile de cliver pour obtenir un cristal allongé suivant la rangée [010].

Ce produit cristallise dans le système monoclinique avec les paramètres cristallins suivants:

$$a = 5{,}61 \pm 0{,}01 \text{ Å}$$
$$b = 9{,}55 \pm 0{,}01$$
$$c = 32{,}54 \pm 0{,}05$$
$$\beta = 136°$$