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SYNTHESIS AND NMR SPECTRA OF 3-ARYL-1,1,2,2-TETRACYANOCYCLOPROPANES

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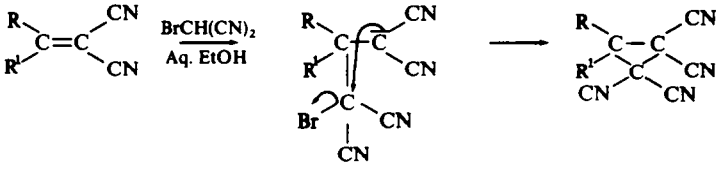
Abstract—The synthesis of seventeen 3-aryl-1,1,2,2-tetracyanocyclopropanes is described, by a general route. The cyclopropane hydrogen, which appears in the range τ 4·5–5·3 in these compounds, couples with the *ortho* aromatic protons ($J \cong 0{\cdot}9$ Hz). This is appreciably larger than comparable coupling of the vinyl proton in the corresponding arylidenemalononitriles.

IN A general synthesis of tetracyanocyclopropanes which has recently been described,[1] alkylidenemalononitriles prepared from various ketones and malononitrile were converted to tetracyanocyclopropanes by treatment with bromomalononitrile in aqueous ethanol at room temperature. The reaction, which presumably proceeds via a carbanion path as shown, was successful with a variety of dialkyl, arylalkyl and



cyclic ketones. In this paper we describe the extension of this synthesis to aromatic aldehydes, and discuss some interesting features of the NMR spectra of the resulting 3-aryl-1,1,2,2-tetracyanocyclopropanes.

RESULTS

The arylidene malononitriles listed in Table 1 were prepared from aromatic aldehydes and malononitrile by standard literature procedures.[2–7] Treatment of the arylidenemalononitrile with an equimolar amount, or sometimes an excess, of bromomalononitrile in ethanol usually resulted in the appearance of the crystalline tetracyanocyclopropane within a few minutes. The reaction mixtures were generally allowed to stand for several hours at room temperature prior to work-up, which consisted of filtration and recrystallization from ethanol or ethanol-acetone. Table 2 describes the results of seventeen such syntheses. In some cases (**29**, **31**) special procedures were required, and these are given in the Experimental section. The NMR spectra of the tetracyanocyclopropanes are given in Table 3.

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TABLE 1. ARYLIDENEMALONONITRILES ($ArCH=C(CN)_2$)

Compd. No.	Ar	Yield (%)	m.p.°, recryst. solv.[a] (lit. value and ref.)	IR (Nujol)[b] cm^{-1}	NMR[c] τ (protons, multiplicity, assignment)
1	C_6H_5	84	78–80, P (83·5–84[2])	2240, 1588, 1567	1·86–2·60 (5, m, arom) 1·83 (1, s, vinyl)
2	*o*-ClC_6H_4	76	92–95, EA (95–96[2])	2230, 1580	1·70–1·94 (1, m, arom) 2·23–2·51 (3, m, arom) 1·47 (1, s, vinyl)[d]
3	*m*-ClC_6H_4	38	109–111, E (116–117[6])	2240, 1569, 1560	[e]
4	*p*-ClC_6H_4	74	158–161, E (162–163[6])	2248, 1581, 1554	1·87, 2·29 (4, A_2B_2d, J = 9 arom) 1·62 (1, s, vinyl)
5[f]	*o*-$NO_2C_6H_4$	82	137–139, EA (137·5–138[4])	2275, 1592, 1560	1·49–2·27 (4, m, arom) 1·17 (1, s, vinyl)[d]
6[f]	*m*-$NO_2C_6H_4$	79	100·5–103, EA (104·5–105[2])	2260, 1592, 1569	1·03–2·18 (4, m, arom) 1·43 (1, s, vinyl)
7	*p*-$NO_2C_6H_4$	65	158–161, E (159–160[6])	2250, 1597, 1575	1·20, 1·43 (4, A_2B_2d, J = 9·4 arom) 1·13 (1, s, vinyl)
8	*o*-BrC_6H_4	51	80–83, E (90–90·5[6])[h]	2260, 1589	1·77–2·55 (4, m, arom) 1·55 (1, s, vinyl)[d]
9	*p*-CNC_6H_4	78	152–153, EA (154[5])	2235, 1582, 1550	1·50, 1·64 (4, A_2B_2d, J = 9·0 arom) 1·21 (1, s, vinyl)
10	*p*-$CH_3C_6H_4$	30	133–135, EA (134[5])	2225, 1663, 1643	7·54 (3, s, CH_3) 2·02, 2·56 (4, A_2B_2d, J = 8·5, arom) 1·73 (1, s, vinyl)
11	*p*-$CH_3OC_6H_4$	99	111–113, HOAc (114·5–115[2])	2255, 1607, 1576, 1523	6·15 (3, s, CH_3O) 1·94, 2·82 (4, A_2B_2d, J = 8·8, arom) 1·90 (1, s, vinyl)

12	2,4-$Cl_2C_6H_3$	82	148–149, EA (150[5])	2230, 1576	[g]1·80 (1, d, J = 8·3, t, J = 0·55, arom) 2·17 (1, d, J = 2·0, d, J = 0·55, arom) 2·34 (1, d, J = 8·3, d, J = 2·0, d, J = 0·55, arom) 1·45 (1, t, J = 0·55, vinyl)
13	2,6-$Cl_2C_6H_3$	90	78–80, E (89–90[6])[h]	2270, 1605, 1580, 1560	2·29–2·51 (3, br s, arom) 1·53 (1, s, vinyl)[g]
14	3,4-OCH_2O—C_6H_3	97	197–200, N (199–200[2])	2240, 1609, 1570	[i]3·87 (2, s, methylene) 0·99–1·23 (1, m, arom) 2·50–3·07 (2, m, arom) 1·72 (1, s, vinyl)
15	1-$C_{10}H_7$	68	164–166, E (170–171·5[6])	2260, 1693, 1591	[i]1·57–2·43 (7, m, arom) 0·60 (1, s, vinyl)
16	2-$C_{10}H_7$	91	141–143, E (141[7])	2260, 1626, 1591, 1571	[i]1·50 (1, br s, arom) 1·72–2·44 (6, m, arom) 1·32 (1, d, J = 0·6, vinyl)
17	2-Furyl	79	67–72, EA (72·5–73[2])	2225, 1600, 1529	1·94 (1, d, J = 1·65, d, J = 0·4, arom) 2·47 (1, d, J = 3·6, d, J = 0·4, arom) 3·13 (1, d, J = 3·6, d, J = 1·65, arom) 2·13 (1, s, vinyl)[j]

[a] Abbreviations: P = n-propyl alcohol, E = 95% ethanol, A = acetone, N = acetonitrile, HOAc = acetic acid.

[b] Only C≡N, aromatic and olefinic frequencies are recorded.

[c] Acetone or acetone-d_6 solvent unless otherwise noted, with TMS internal reference. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The τ_{vinyl} values are in reasonable agreement with those previously reported,[7] especially when one considers that these values are subject to rather large solvent effects.

[d] Slightly split, but <0·2 Hz.

[e] Not determined.

[f] This compound is a skin irritant and causes sneezing.

[g] Solvent was tetrahydrofuran.

[h] Attempts to raise the m.p. by recrystallization were unsuccessful.

[i] Solvent was DMSO.

[j] If the vinyl substituent is at C-2 of the furan ring, then the aromatic protons are respectively those at C-5, C-3 and C-4 (cf. **34**).

TABLE 2. 3-ARYL-1,1,2,2-TETRACYANOCYCLOPROPANES

Compd. No.	Ar	Reaction Time (min)[a]	Yield (%)	m.p.[o]	Analysis					
					Calc.			Found		
					C	H	N	C	H	N
18	C_6H_5	<5	92	227–230[b]						
19	o-ClC_6H_4[c]	<5	98	246–248	61·80	2·00	22·18	61·87	2·21	22·20
20	m-ClC_6H_4[d]	30	82	183–185	61·80	2·00	22·18	61·85	2·16	22·16
21	p-ClC_6H_4	<5	86	248–250[e]						
22	o-$NO_2C_6H_4$	30	96	211–213	59·32	1·92	26·61	59·40	1·71	26·59
23	m-$NO_2C_6H_4$	<5	74	246–248[f]						
24	p-$NO_2C_6H_4$	<5	94	232–235	59·32	1·92	26·61	59·38	2·12	26·50
25	o-BrC_6H_4[g]	<5	88	249–252	52·55	1·70	18·86	52·74	1·85	18·85
26	p-CNC_6H_4	<5	97	263–264	69·13	2·07	28·80	68·89	2·27	28·24
27	p-$CH_3C_6H_4$	20	91	227–230	72·40	3·47	24·13	72·46	3·46	24·22
28	p-$CH_3OC_6H_4$	120	75	209–210	67·74	3·25	22·57	67·62	3·26	22·40
29	2,4-$Cl_2C_6H_3$[h,i]	—	93	225–228	54·38	1·40	19·52	54·46	1·50	19·45
30	2,6-$Cl_2C_6H_3$[j]	60	92	227–230	54·38	1·40	19·52	54·49	1·46	19·54
31	3,4-$OCH_2OC_6H_3$[i]	—	68	222–223	64·12	2·31	21·37	64·18	2·50	21·20
32	1-$C_{10}H_7$	<1	99	249–252	76·11	3·01	20·89	76·21	3·06	20·82
33	2-$C_{10}H_7$	<5	99	236–240	76·11	3·01	20·89	75·99	3·01	20·80
34	2-Furyl	10	49	203–208[k]						

[a] Time elapsed between mixing of reactants and appearance of the first crystals of product.
[b] lit. value[8] 221°.
[c] Chlorine: Calc. 14·03, Found 14·21.
[d] Chlorine: Calc. 14·03, Found 14·20.
[e] lit. value[9] 240–241°.
[f] lit. value[9] 245–246°.
[g] Bromine: Calc. 26·90, Found 26·92.
[h] Chlorine: Calc. 24·70, Found 24·60.
[i] See Experimental for special reaction conditions.
[j] Chlorine: Calc. 24·70, Found 24·65.
[k] lit. value[8] 190–200°.
[l] All compounds except 20 and 29 decompose at the m.p.

TABLE 3. NMR SPECTRA[a] OF 3-ARYL-1,1,2,2-TETRACYANOCYCLOPROPANES

Compd. No.	Ar	Cyclopropyl H τ[b]	Aromatic H's τ[b]
18	C_6H_5	5·13 (t, 0·8)[c]	2·11–2·65 (m)
19	*o*-ClC_6H_4	5·03 (d, 1·0)	1·78–2·55 (m)
20	*m*-ClC_6H_4	5·07 (t, 0·9)[d]	2·02–2·59 (m)
21	*p*-ClC_6H_4	5·06 (t, 0·9)[e]	2·14, 2·46 (A_2B_2, 8·5)
22	*o*-$NO_2C_6H_4$	4·51[f]	1·32–2·08 (m)
23	*m*-$NO_2C_6H_4$	4·85[g]	0·96–1·09 (m), 1·41–1·68 (m), 1·94 (s), 2·07 (s), 2·22 (s)
24	*p*-$NO_2C_6H_4$	4·94 (t, 0·8)	1·67, 1·87 (A_2B_2, 9·0)[h]
25	*o*-BrC_6H_4	5·14 (d, 0·9)	1·93–2·74 (m)
26	*p*-CNC_6H_4	4·77 (t, 0·6)[i]	1·74, 1·88 (A_2B_2, 9·0)
27	*p*-$CH_3C_6H_4$	5·16 (br)	2·27, 2·64 (A_2B_2, 8·0)
28	*p*-$CH_3OC_6H_4$	5·27 (br)	2·27, 2·95 (A_2B_2, 8·7)[j]
29	2,4-$Cl_2C_6H_3$	5·02 (d, 1·0)	1·87 (d, 8·3, d, 1·0, d, 0·4), 2·16 (d, 2·0, d, 0·4), 2·40 (d, 8·3, d, 2·0)[k]
30	2,6-$Cl_2C_6H_3$	4·94 (s)[l]	2·26 (s)[l]
31	3,4-$OCH_2OC_6H_3$	5·23 (t, 0·95)	2·55–3·20 (m)[m]
32	1-$C_{10}H_7$	4·56 (s, br)	1·66–2·43 (m)
33	2-$C_{10}H_7$	4·84 (d, 1·1)	1·50 (s, br, 1H), 1·87–2·19 (m, 4H), 2·19–2·47 (m, 2H)
34	2-Furyl	4·60 (s)	2·22 (d, 1·9, d, 0·7), 3·10 (d, 3·4, d, 0·7), 3·41 (d, 3·4, d, 1·9)[n]

[a] In acetone solution unless otherwise stated.

[b] TMS was the internal reference. Multiplicities and *J*'s are given in parentheses. Abbreviations are the same as in Table 1. Relative areas of aromatic: cyclopropyl hydrogens agreed with expectation.

[c] In DMSO, this peak appeared at τ 4·85.

[d] The central peak was further split into a triplet, J = 0·4 Hz.

[e] Slight further splitting was detectable.

[f] Appeared as two doublets, each J = 0·9 Hz, about τ 0·01 units apart.

[g] Appeared as a poorly resolved quartet, J = 0·9 Hz.

[h] The high field doublet was broadened by coupling with the cyclopropyl hydrogen.

[i] In DMSO, this peak appeared at τ 4·52.

[j] Methoxyl singlet at τ 6·16.

[k] See text for assignment.

[l] In DMSO, these appeared at τ 4·38 (cyclopropyl) and τ 2·35 (arom).

[m] The methylene group appeared as a sharp singlet at τ 3·95.

[n] If the cyclopropyl is substituted at C-2 of the furan ring, these are respectively the protons at C-5, C-3 and C-4.

DISCUSSION

Syntheses. From the yields shown in Table 1 and 2 it is clear that the two-step synthesis of aryl tetracyanocyclopropanes (Eq. 1 and 2) proceeds efficiently. If the aryl group contains electron-donating substituents (as in the synthesis of **27**, **28** or

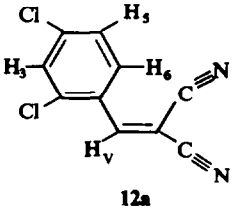
$$ArCHO + CH_2(CN)_2 \xrightarrow{\text{piperidine}} ArCH{=}C(CN)_2 + H_2O \quad (1)$$

$$ArCH{=}C(CN)_2 + BrCH(CN)_2 \xrightarrow{EtOH} \text{Ar, H, CN, CN, CN, CN} + HBr \quad (2)$$

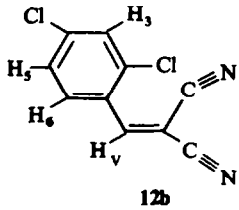
31) the second step may be a little slow, but with electron-withdrawing substituents the reaction is over in a few minutes. Exceptions may occur with ortho substituents

(Table 2, compounds **22**, **29** and **30**). The high yields, generally short reaction times and ease of work-up and purification of the product are advantages of the synthesis.

NMR spectra. The NMR spectra of the arylidenemalononitriles (Table 1) were consistent with their structures, and a few of them showed special features worthy of comment. The vinyl proton appeared at low field, between τ 0·6–2·13, depending on the substituents. Except for cases to be noted it was a sharp singlet, indicating slight if any coupling between it and the aryl protons. When an ortho substituent was present, which might restrict the available geometries and hinder aryl rotation, some slight broadening or splitting of the vinyl proton signal was noted (compounds **2**, **5**, **8**, **12**, **13**, **16**). The spectrum of **12** was particularly interesting. Of the two planar conformations, **12a**, which minimizes the repulsions, would appear from models to be favored. If the reasonable assumption is made that the largest observed coupling



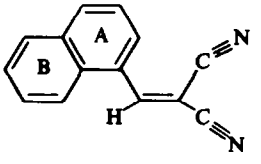
12a



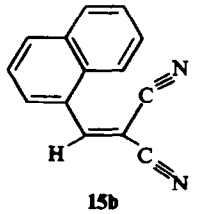
12b

constant (J = 8·3 Hz) is $J_{5,6}$ then only four assignments are possible. Of these, by far the most reasonable assigns chemical shifts of H_v, H_6, H_3 and H_5 as τ 1·45, 1·80, 2·17 and 2·34 respectively, with $J_{v,5}$ = 0·55, $J_{v,6}$ = 0·55, $J_{3,5}$ = 2·0 and $J_{3,6}$ = 0·55 Hz. This assignment gives the most reasonable chemical shift to Hv (the other alternative is τ 2·17, higher than for any of the other compounds in Table 1) and also the most reasonable relative values of $J_{3,5}$ and $J_{3,6}$. Regardless of which assignment is chosen, however, the vinyl proton will be coupled to H_5 and H_6. It is significant that *H_v is coupled with only one of the two* meta *protons.* This becomes reasonable if conformation **12a** predominates, and the *trans* zig-zag path is traced.[10] The 4- and 5-bond coupling constants ($J_{v,5}$ and $J_{v,6}$) have the same magnitude.

The only other items worthy of special attention in Table 1 are the complete assignments for **17** and certain features of the spectra of the two naphthyl compounds (**15** and **16**). The unusually low field position for the vinyl proton in **15** is probably due to the strong steric preference for conformation **15a** over **15b**, which would bring the vinyl proton in the deshielding region of ring B. In **16**, neither of the most probable conformations (**16a** or **16b**) would have this effect on the vinyl proton. It is interesting that in **16** some small coupling (J = 0·6 Hz) between the vinyl and one of the aromatic protons is observed.

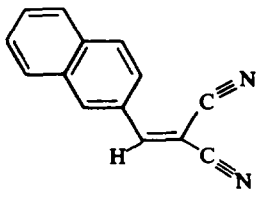


15a

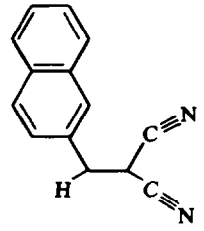


15b

The cyclopropyl protons (H_c) in **18–34** appear between τ 4·51–5·27, which is consistent with the few previously reported values.[9] This low-field position for a cyclopropyl hydrogen is due to the four cyano groups (which bring the value to



16a

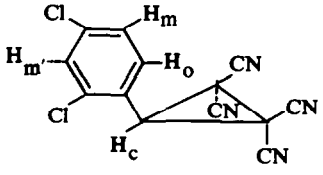


16b

about τ 6·5[9]) and the aryl group. Although there are inconsistencies, electron-withdrawing groups on the aryl ring tend to deshield the cyclopropyl proton.

The most interesting feature of the spectra in Table 3 is the coupling between the cyclopropyl proton (H_c) and the *ortho* protons of the aromatic ring. Although clean-cut splitting of H_c was not observable in every case, the splitting pattern strongly supports this contention. Thus in **18**, **20**, **21**, **24**, **26** and **31**, H_c appears as a distinct triplet, $J \simeq 0{\cdot}9$ Hz. Each of these compounds has two *ortho* protons. In **19**, **25** and **29**, which have only one *ortho* proton, H_c is a doublet, $J \cong 1{\cdot}0$ Hz. And in **30**, with no ortho protons, H_c is a sharp singlet. In some cases the H_c signal is broadened with a shape indicative of the expected splitting for coupling with the *ortho* protons (triplets in **27** and **28**, doublet in **32**). When the aryl substituent was in the *ortho* or *meta* position, the aryl protons were generally a complex multiplet, but when the substituent was *para* (**21**, **24**, **26**, **27** and **28**) the signal for one of the two protons in the A_2B_2 pattern was either broadened or split, and the other was not. With *p*-NO_2, the high-field signal was broadened, and with *p*-OCH_3 it was the low-field signal, suggesting that in both cases coupling occurred with the *ortho* protons.

The NMR spectrum of **29** shows most clearly that it is the *ortho* proton which couples with H_c. As with **12**, an essentially complete first order analysis of the spectrum is possible. The preferred conformation would seem to be



H_c appears at τ 5·02 as a doublet (J = 1·0 Hz). Only one reasonable assignment of the aryl protons is possible, with H_o, $H_{m'}$ and H_m at τ 1·87, 2·16 and 2·40 respectively, and $J_{o,m} = 8{\cdot}3$, $J_{o,m'} = 0{\cdot}4$, $J_{m,m'} = 2{\cdot}0$ and $J_{o,c} = 1{\cdot}0$ Hz. The *ortho* chlorine forces H_o in the vicinity of the cyano groups, which is probably why H_o appears at even lower field than the proton which is between the chlorines.

Several of the spectra are somewhat exceptional. Although a complete discussion of these will require further study, attention is called to these discrepencies here. For

example H_c in **33** appears as a doublet (J = 1·1 Hz), rather than as the expected triplet. Coupling occurs with only one of the two *ortho* protons of the naphthalene ring. It is probably H_1, but this remains to be proved. The cyclopropyl protons in **20** and **21** showed some slight further splitting of the triplets, indicating small additional coupling. The cyclopropyl protons in **22** and **23** also show additional splitting beyond that expected from the other results. For example in **22**, H_c seems to consist of two doublets (rather than one), slightly displaced but with about the same coupling constant (J = 0·9 Hz). Finally, with the heterocyclic 2-furyl group (**34**), H_c is a sharp singlet.

To summarize, coupling between the cyclopropyl hydrogen and *ortho* aryl protons in 3-aryl-1,1,2,2-tetracyanocyclopropanes (Table 3) seems reasonably general with $J \cong$ 0·8–1·0 Hz, whereas similar coupling of the vinyl proton with *ortho* aryl protons in arylidene malononitriles (Table 1) was either absent or much smaller, the best case being **12** where $J \cong$ 0·5 Hz. Yet the bonding in the alkenes presumably has greater *s* character than in the cyclopropanes.

EXPERIMENTAL

All m.ps are uncorrected. Analyses were performed by Spang Microanalytical Laboratories, P.O. Box 1111, Ann Arbor, Michigan. The NMR spectra were run on a Varian A-60 spectrometer using TMS as an internal reference, and the IR spectra were determined on a Unicam SP 200 instrument, and calibrated with polystyrene.

Preparation of arylidene malononitriles

All of the compounds described in Table 1 were prepared from the corresponding aldehydes, obtained commercially, and malononitrile, using the procedure of Corson and Stoughton,[2] with the exception of **10**, where the procedure of Cope and Hancock[3] for ethyl 3-pentylidenecyanoacetate was employed.

Preparation of 3-aryl-1,1,2,2-tetracyanocyclopropanes

General procedure. An ethanolic soln (about 0·5–1M) of arylidene malononitrile was mixed with an equimolar amount or an excess of an ethanolic soln of bromomalononitrile.[11] Usually a ppt of the desired product formed within a few min (see Table 2). The mixture was allowed to stand for several hr, then filtered and the product was recrystallized from 95% EtOH–Me_2CO mixtures (with **28–31**, the recrystallization solvent was 95% EtOH, and with **27**, a mixture of Me_2CO and water was used).

Typical procedure—preparation of **18**. To 1 g (6·5 mmole) of **1** in 10 ml EtOH was added, at room temp, a soln containing 1·16 g (8 mmole) bromomalononitrile in 10 ml EtOH. Crystals formed within a few min. After 5 hr the ppt was collected and recrystallized from an EtOH–Me_2CO, to yield 1·35 g (91·7%) of **18**, m.p. (dec) 227–230°.

3-(2',4'-Dichlorophenyl)-1,1,2,2-tetracyanocyclopropane (**29**). Because of solubility problems, a modified procedure was used. A soln of 1·0 g (4·48 mmole) of **12** and 0·95 g (6 mmole) bromomalononitrile in 80 ml EtOH–THF mixture was kept at room temp for 9 days. The solvent was removed and the residue was recrystallized from EtOH (Table 2).

3-Piperonyl-1,1,2,2-tetracyanocyclopropahe (**31**). Because of solubility problems, a modified procedure was used. A soln of 1 g (5 mmole) of **14** and 1·09 g (7·5 mmole) bromomalononitrile in 300 ml EtOH was kept at room temp for 24 hr. The ppt which formed when 100 ml water was added was collected and recrystallized from EtOH (Table 2).

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