Structural Characterization of Sulfur Vulcanized Deproteinized Natural Rubber by Solid-State ^{13}C NMR Spectroscopy

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ABSTRACT: The structural changes in unfilled and filled vulcanized deproteinized natural rubber (DPNR), which is a highly purified natural rubber (NR), were investigated by solid-state ^{13}C NMR spectroscopy. The chemical shifts of new signal were assigned by calculation and compared with those observed by Koenig et al. for conventional vulcanized NR. The crosslink structure of sulfur vulcanized DPNR were similar to that of sulfur-vulcanized NR for CV system assigned by Koenig et al. The increase in the relative intensities of signals between 45 and 58 ppm, which was assigned to monosulfidic and polysulfidic bonds, was concerned with the increase in crosslink density. In this case, the crosslink density was increased after aging, which might be due to incomplete curing. Furthermore, the solid-state ^{13}C NMR spectrum of the aged sulfur vulcanizate DPNR showed new signals at around 73 ppm, which is assignable to carbon attached to hydroxyl group because of thermal oxidation. It can provide more complete understanding of the final vulcanizate crosslink structure of DPNR vulcanizates. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1875–1880, 2006

Key words: deproteinized natural rubber; solid-state ^{13}C NMR; swelling measurement; crosslink density; vulcanization; aging

INTRODUCTION

The majority of the studies on elastomeric vulcanization have been focused on the sulfur crosslinking of natural rubber (NR). The sulfur-vulcanized NR contributes to end-use performance and service life of the products, which is an important factor for industrial applications.

Swelling measurement has been used for a theoretical approach to determine the physical crosslink density. Physical crosslinks include chemical crosslink and chain entanglement in the sulfur vulcanizate. For structural studies, particularly on sulfur vulcanizate, the solid-state ^{13}C NMR spectroscopy has been proven as a powerful technique. The information on chemical crosslinking structures in cured elastomers occurring during the curing process can be observed directly by this technique.

Some of the structural features that are generally accepted as occurring in the elastomers were shown in Figure 1.[1,2] The structures include cyclic sulfides, pendant accelerator group, and *cis*-to-*trans* isomerization, in addition to the different crosslinking types.

A variety of techniques, including chemical, physical, and mechanical, have been used to characterize the rubber network. However, there is no evidence of the structural characterization of vulcanizate from highly purified NR, such as deproteinized NR (DPNR). Thus, the present work was an attempt to study the structure of vulcanized DPNR, by comparing with the conventional NR, using both solid-state ^{13}C NMR analysis and swelling measurement.

EXPERIMENTAL

Preparation of DPNR[3]

The fresh latex (RRIM 600) was diluted to 30% DRC and stabilized with 0.5% w/v sodium dodecyl sulfate (SDS). Then latex was added with 0.04% w/v proteolytic enzyme (KP-3939, Kao Co., Ltd., Bangkok, Thailand). The mixture was incubated at 37°C for 24 h, followed by centrifugation at a speed of 13,000 rpm, using ultracentrifuge machine (H 600 centrifuge) for 30 min. The cream fraction was separated
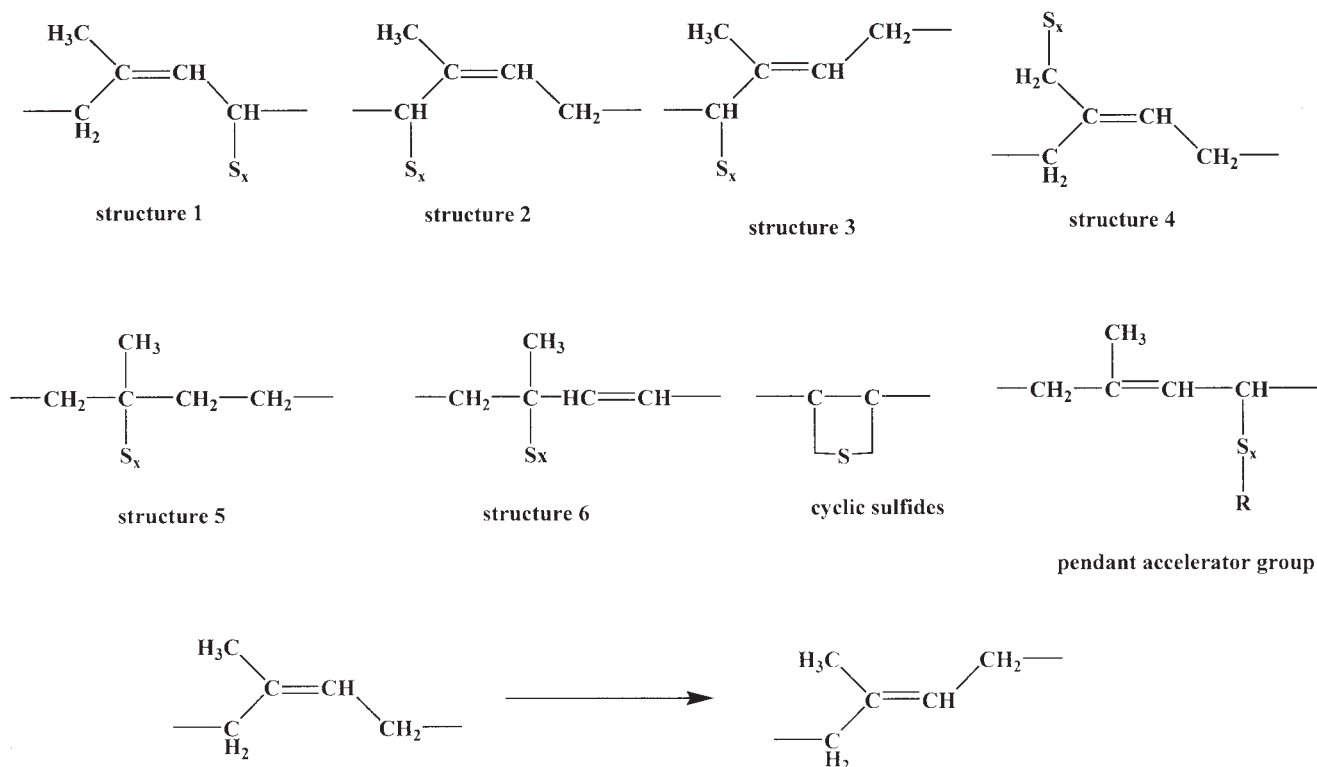
Figure 1 Structural features of sulfur-vulcanized NR.

from the liquid residue and redispersed in 0.5% w/v SDS aqueous solution and then subjected to centrifugation again with the same condition. The cream fraction from the second centrifugation was cast as before, and was recovered as a thin film by casting on a glass plate and was further dried *in vacuo* in an oven at 50°C. The dried film was stored in polyethylene bags in dark for further use.

Preparation of sulfur vulcanized DPNR

Three kinds of rubber formulations were compounded in two-roll mills, (Table I). The compounded rubbers were then left at room temperature overnight to get

TABLE I
Formulations for Vulcanization

Material	Formulation		
	1	2	3
DPNR	100	100	100
Carbon black (N330)	—	40	40
Sulfur	2.0	2.0	2.0
ZnO	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0
TMTD	0.5	0.5	—
TBBS	—	—	0.5
Antioxidant (Forte RD)	1.0	1.0	1.0

TMTD, tetramethyl thiuram disulfide; TBBS, *N-tert*-butyl-2-benzothiazole sulfenamide.

homogenous rubber sheets, and then subjected to curing by using a template in a temperature-controlled hydraulic press. The curing process was carried out at 155°C for various duration, which was defined as the time taken to accomplish a cure stage of 90% in the rheometer curves by oscillating disc rheometer (Monsanto 100s). Thin sheets of sulfur-vulcanized DPNR of about 1 mm thickness were produced.

Equilibrium swelling measurement

About 0.03 g of DPNR vulcanizate was swollen in 30 mL dried cyclohexane and left for one week in the dark without stirring. The swollen rubbers were picked out, blotted with a filter paper, then placed in clean stopper vial and weighed. The samples were dried under vacuum and then reweighed to get the weight of the dried crosslink gel and the amount of swelling solvent uptake.

Crosslink density determination

The modified Flory–Rehner equilibrium swelling equation[4] was used to determine the crosslink density, following the method of Shelton and Mc. Donald[5] and Adams and Johnson:[6]

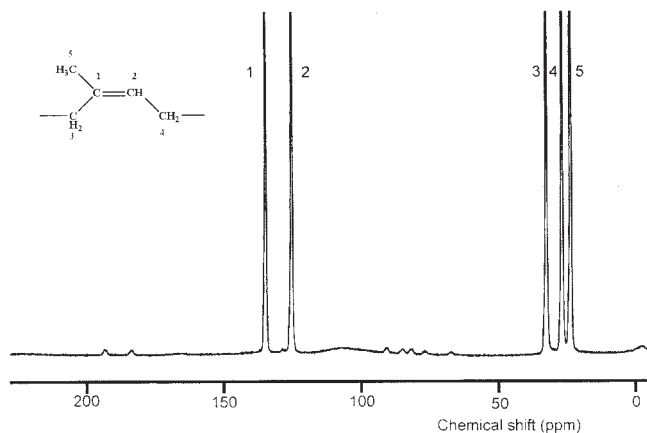$$v = 1/M_c = -[ln(1 - v_r) + v_r + \chi v_r^2]/[\rho_r v_0(v_r^{1/3} - v_r/2)]$$

Figure 2 Solid-state ^{13}C NMR spectrum of DPNR.

Figure 3 Solid-state ^{13}C NMR spectrum of unfilled sulfur-vulcanized DPNR using formulation 1.

ν = crosslink density per gram of rubber; M_c = molecular weight between crosslinks

v_r = volume fraction rubber χ = Huggins interaction constant

ρ = density of rubber v_0 = molar volume of the solvent

ρ_s = density of the solvent

The volume fraction, V_r, was calculated as follows:

$$V_r = [(\rho_r/\rho_s)((W_s - W_u)/W_u) + 1]^{-1}$$

W_s, W_u = weight of the swollen and unswollen rubbers at equilibrium

The values of the constant used in the above calculation were:

ρ_r = 0.915 g/cm^3; ρ_s = 0.779 g/cm^3; V_{48} = 108/cm^3/mol; χ = 0.399[7]

NMR measurement

The solid-state ^{13}C NMR measurement was performed on a JEOL GX-400 NMR spectrometer at 100 MHz with a pulse delay of 5 s and spin of 6000 Hz. The measurement mode was magic angle spinning (MAS) under gated high-power decoupling (GHPD) condition. All the rubber vulcanizates were purified by extraction with hexane and acetone for each 24 h before subjected to measurement of NMR spectroscopy, to remove excess additives.

RESULTS AND DISCUSSION

The solid-state ^{13}C NMR spectrum of uncured DPNR is shown in Figure 2. This spectrum is almost the same as observed for the NR before deproteinization[1]. There are two clear resolved spectral regions, i.e., the low-field (olefinic) appearing at 125.8 and 135.3 ppm and the high field (aliphatic) regions appearing at 24.1, 27.2, and 32.9 ppm.
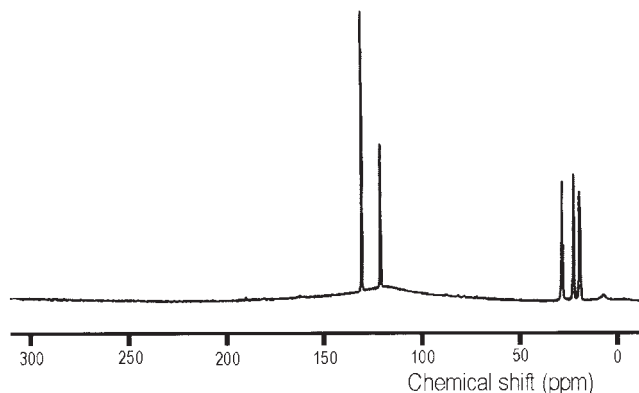
This spectrum was compared with that of sulfur vulcanized DPNR to elucidate the change of chemical structures during vulcanization process, which is shown in Figure 3. The expand aliphatic region of this spectrum is given in Figure 4. The new signals were observed at 16.5, 17.3, 25.6, 40.6, 45.7, 55.2, 58.1, and 64.6 ppm. The assignments of these new signals were summarized in Table II, in which the chemical shifts of the observed signals were compared with those calculated by the addition of the shift factors and those reported by Koenig et al.[8–10]

The signals at 16.5 and 40.6 ppm were assigned to *trans* C-5 methyl and C-1 methylene carbons, respectively. In addition, the signal at 25.6 ppm is assignable to methine carbon in cyclic sulfide structure.[11] This indicates that the modification of DPNR main-chain, such as *cis*-to-*trans* isomerization and cyclic sulfide structures could be induced by vulcanization process.
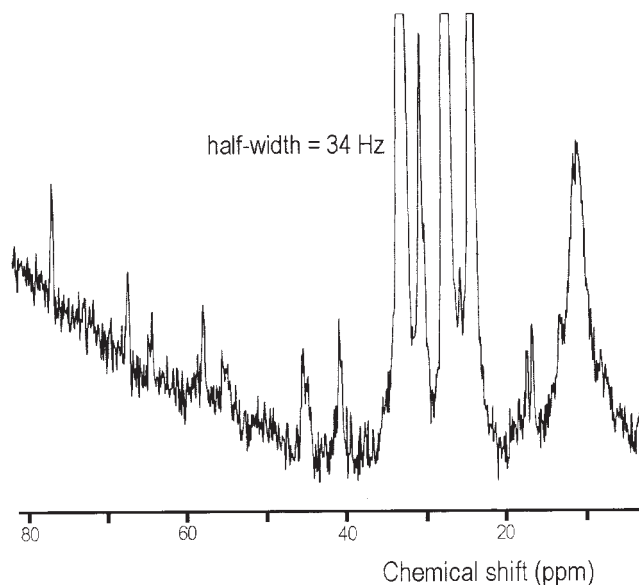

Figure 4 The aliphatic region of the spectrum of unfilled sulfur-vulcanized DPNR by using formulation 1.

TABLE II
Signal Assignment of Unfilled Sulfur-Vulcanized DPNR

| Structure	Carbon	Shift factor[a]	Chemical shift (ppm)		
			Calculated	Koenig[11]	Observed
1	4	−3.4	20.70	17	17.30
4	1	25.2	49.30	45	45.72
6 (mono)	1	17.9	44.30	—	—
1 (mono)	1	17.9	45.11	—	—
1	1	25.2	52.41	50.2	50.20
6	1	25.2	51.60	50.7	50.72
2	1	25.2	58.14	58	58.10
3	1	25.2	65.10	64	64.60

[a] See Tables AI and AII in Appendix.

The solid-state ^{13}C NMR spectrum of the carbon black filled DPNR by formulation 2 is shown in Figure 5. The new signals, which appeared by vulcanization, were the same as observed for the unfilled formulation. However, these signals became broader with a clear reduction of spectral resolution, as is evident from increase of the half-width of the typical signals. Because of shortening of T_2, which was caused by the carbon black filled DPNR, the system became more rigid, i.e., more densely packed than in the case of unfilled DPNR, which gives rise to an anisotropy of the segmental motion due to the chemical adsorption of the carbon black aggregates.[12,13] This polymer adsorption leads to a loss in the efficiency of the line narrowing applied by MAS in the high-resolution solid-state NMR.

The additional accelerators were used for different formulations in this study. A common accelerator used in the processing of vulcanizate is N-t-butyl-2-benzothiazole sulfenamide (TBBS). The resulting sol-
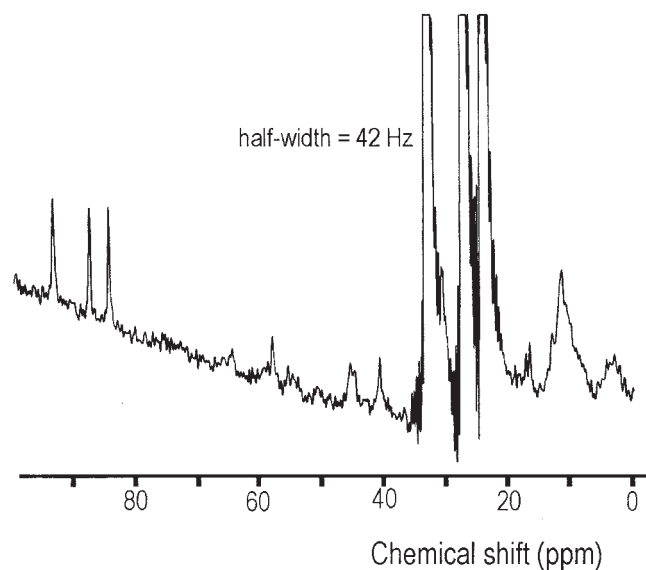
Figure 5 Solid-state ^{13}C NMR spectrum of carbon black filled DPNR (TMTD), as shown in formulation 2.
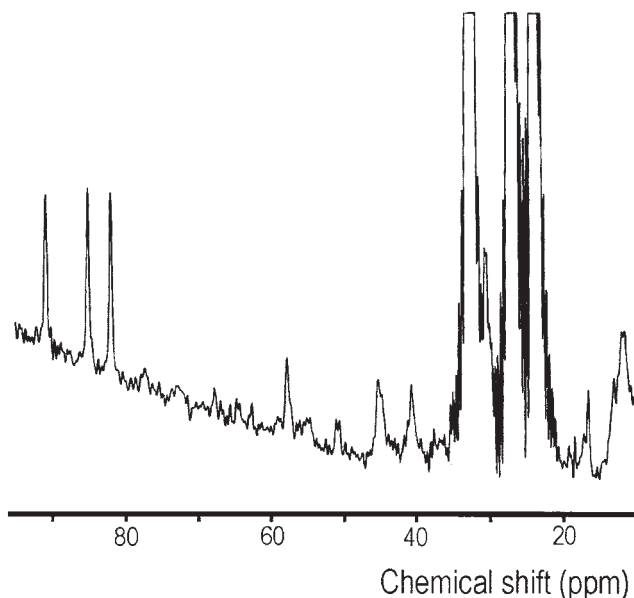
Figure 6 Solid-state ^{13}C NMR spectrum of TMTD-accelerated carbon black by TBBS, as in formulation 3.

id-state ^{13}C NMR spectrum of this system is shown in Figure 6. There were more signals observed in this spectrum than that of the TMTD accelerated carbon black filled vulcanizate DPNR. Two new doublet signals at 50.2 and 50.7 ppm assigned to a methine carbon of polysulfidic structure 1 and a quaternary carbon of polysulfidic structure 6, respectively, were clearly detected.[10] This might be due to the TMTD-accelerated carbon black filled vulcanizate DPNR exhibiting very shorter curing time when compared with that of the TBBS-accelerated vulcanized DPNR, as shown in Table III. Owing to the very fast curing system of TMTD, it might lead to a rapid change in the crosslink structures, which as a result of missing of some crosslink structures, detected at 50.2 and 50.7 ppm.

The relative intensities of the signals detected at 45 and 58 ppm are compared to the crosslink density as determined from swelling measurement in Table IV. It is remarkable that as the crosslink density increased the relative intensities also increased. This confirms that the signal at 45 and 58 ppm is associated with the crosslinking structure.

The aging test of DPNR vulcanizates at 100°C for 22 h was also studied in this work. The solid-state ^{13}C NMR spectrum of aged sample of TMTD accelerated carbon black filled vulcanizate DPNR is

TABLE III
**Cure Time of Filled Sulfur-Vulcanized DPNR**

Formulation	Cure time (t_{90}) (min)
2	3.4
3	17.0

TABLE IV
Comparison between Crosslink Density and Relative Intensity between Signals at δ 45 and 58

Formulation	Crosslink density $(1/2M_c) \times 10^{-4}$	Intensity ratio of signal at δ 45 against 24.1 and 27.21	Intensity ratio of signal at δ 58 against 32.94
2	2.94	1.76×10^{-2}	9.43×10^{-3}
3	1.50	1.53×10^{-2}	9.27×10^{-3}
2 (aging)	5.04	2.21×10^{-2}	1.54×10^{-2}

shown in Figure 7. It is clear that the relative intensities of the signals between 45 and 58 ppm increased after aging. These results correspond to the amount of crosslink density, as shown in Table IV.

Koenig et al. have established the mechanism of the curing process from the results obtained from solid-state ^{13}C NMR.[2,10,11] It has been reported that the dominant sulfurization products are presumed to be polysulfidic structure 1, and possibly, structures 5 or 6 for shorter curing time, as given in Figure 1. However, the polysulfidic structure 1 was presumed to be degraded and became as monosulfidic structure (δ 45 ppm) and other polysulfidic structures 2 (δ 58 ppm) and 3 (δ 64 ppm) for longer curing time. As long as the curing duration, the degradation would form until the elemental sulfur was consumed. This might be due to the curing process of the rubber vulcanizates was not completed, so the reaction can be continued to form more crosslink, if enough additional heating was applied.
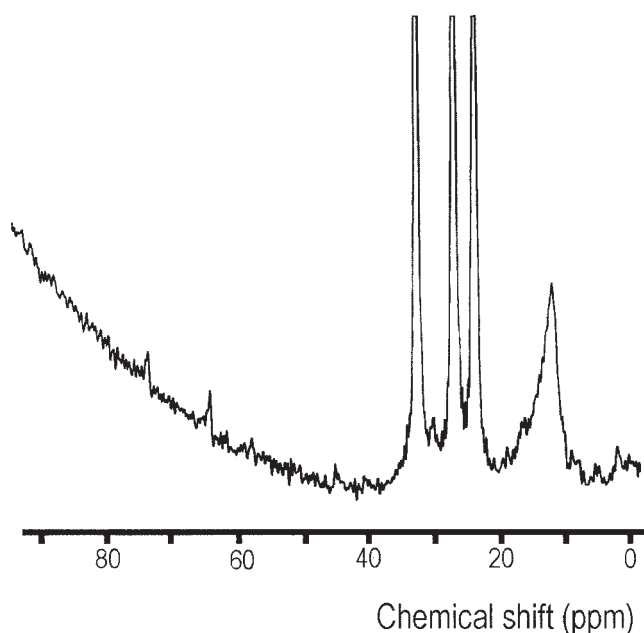

Figure 7 Solid-state ^{13}C NMR spectrum of filled vulcanizate DPNR at 100°C for 22 h.

CONCLUSIONS

The solid-state ^{13}C NMR spectroscopy has been proven to be a significant method to investigate the structural changes in unfilled and filled vulcanization systems of DPNR. Besides, it was found that the crosslink structure of sulfur-vulcanized DPNR were similar to that of sulfur-vulcanized NR for CV system assigned by Koenig et al. In the carbon black filled TMTD-accelerated DPNR system, similar signals were observed as in the case of unfilled TMTD accelerated system. Although the broader signal and the reduction of the spectral resolution were observed, the chemical shifts of new signal were assigned by calculation and compared with those by Koenig et al. It is apparent that the assignments correspond to the observed chemical shifts. The increase in the relative intensities of signals between 45 an 58 ppm, which was assigned to monosulfidic and polysulfidic bonds, was concerned with the increase in crosslink density. In this case, the crosslink density was increasing after aging, due to incomplete curing process. The sulfur can react with DPNR to form more crosslink structures. In the current study, the solid-state ^{13}C NMR technique had been extended to the basic study of the sulfur vulcanized DPNR. It can provide understanding of the final vulcanizate crosslink structure.

APPENDIX
Structure of DPNR
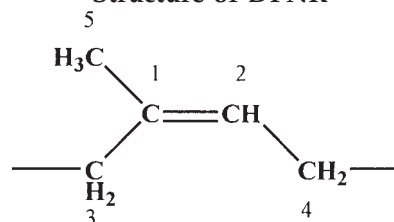
Calculated Chemical Shift of Sulfur Vulcanized DPNR

	Chemical shift (ppm)
C1	135.33
C2	125.81
C3	32.94
C4	27.21
C5	24.10

TABLE A.I
Shift Factor* of Sulfur Compounds**

Aliphatic	α	β	γ	ε
HS	+10.5	+11.5	−3.6	−2.0
$CH_2 - S$	+20.4	+6.2	−2.7	+0.3
R − S-S	+25.2	+6.6	−3.4	−0.1
R S	+17.9	+7.1	3.0	−0.1

From Sadtler ^{13}C-NMR Index [15].
**The shift factor of sulfur compounds was added to the initial chemical shifts of DPNR to determine the chemical shifts for the sulfurated species. The results were listed in Table A.II.

TABLE A.II
Calculated Chemical Shifts, ppm

Structure	Monosulfidic	Di (ply) sulfidic
	C1 32.94 + 17.90 = 50.84 C2 135.22 + 7.10 = 142.43 C3 27.21 + 7.10 = 34.31 C4 24.10 − 3.00 = 21.10	32.94 + 25.20 = 58.14 135.33 + 6.60 = 141.93 27.21 + 6.60 = 33.81 24.10 − 3.40 = 20.70
	C1 39.90 + 17.90 = 57.80 C2 134.80 + 7.10 = 141.90 C3 26.90 + 7.10 = 34.00 C4 16.50 − 3.00 = 13.50	39.90 + 25.20 = 65.10 134.80 + 6.60 = 141.40 26.90 + 6.60 = 33.50 16.50 − 3.40 = 13.10
	C1 27.21 + 17.90 = 45.11 C2 32.94 + 7.10 = 40.04 C3 125.81 + 7.10 = 132.91	27.21 + 25.20 = 52.41 32.94 + 6.60 = 39.54 125.81 + 6.60 = 132.41
	C1 26.90 + 17.90 = 44.80 C2 39.90 + 7.10 = 47.00 C3 124.40 + 7.10 = 131.50	26.90 + 25.20 = 52.10 39.90 + 6.60 = 46.50 124.40 + 6.60 = 131.00
	C1 24.10 + 17.90 = 42.00 C2 135.33 + 7.10 = 142.43	24.10 + 25.20 = 49.30 135.33 + 6.60 = 141.93
	C1 26.40 + 17.90 = 44.30 C2 22.90 + 7.10 = 30.00 C3 121.30 + 7.10 = 28.40 C4 22.90 − 7.10 = 30.00	26.40 + 25.20 = 51.60 22.90 + 6.60 = 29.50 121.30 + 6.60 = 127.90 22.90 − 6.60 = 29.50

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