7504 *Macromolecules* **1999,** *32,* 7504−7508

Vulcanization of Butadiene Rubber by Means of Cyclic Disulfides. 1. A 2D NMR Study on the Cross-Link Structure of a BR Model Compound Vulcanizate

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Received April 16, 1999; Revised Manuscript Received July 30, 1999

ABSTRACT: The vulcanization of *cis,cis,cis*-1,5,9-cyclododecatriene (*ccc*-1,5,9-CDT) by means of 1-oxa-4,5-dithiacycloheptane, zinc dimethyl dithiocarbamate (ZDMC), and 1,12-diaminododecane was studied as a model compound for true vulcanizates using several 1D and 2D NMR techniques in order to determine cross-linking sequence and overall molecular structure. Because of the relatively high solubility of the products, typical *solution* 2D NMR pulse sequences could be applied offering a framework of reference for the *solid state* NMR studies on true vulcanizates to follow. ^{13}C DEPT spectra yielded the multiplicity of the ^{13}C resonances, followed by HETCOR techniques to identify the corresponding ^{1}H resonances. COSY, DQF−COSY (*d*ouble *q*uantum *f*iltered COSY) and TOCSY (*to*tal *c*orrelation *s*pectroscop*y*) experiments provided the homonuclear (long-range) through-bond connectivities leading to the complete elucidation of the molecular framework. The experimentally found ^{13}C chemical shifts were compared with the calculated shifts and appeared to be in good agreement. Using this “model compound” the applicability of several NMR techniques to determine structural characteristics proved to be possible. Moreover, the study allowed the comparison of the solution NMR techniques mentioned with the solid state NMR techniques used in the elucidation of the cross-link sequence and overall structure of true vulcanizates.

Introduction

Several sulfur-free vulcanization systems have been developed in order to covalently cross-link native rubbers.[1] These systems do not use molecular sulfur as the cross-linking agent and are believed to prevent reversion accompanying sulfur vulcanization.[2] Recently, Nordsiek and Wolpers used a cyclic disulfide (1,2-dithiacyclooctane) as an alternative for sulfur vulcanization of natural rubber (NR).[3,4] The resulting networks showed no reversion, and from XANES measurements (*X*-ray *a*bsorption *n*ear *e*dge *s*tructure), it was concluded that bis(alkenyl)−dithiaalkane cross-links were formed during the vulcanization process.[3] The resistance toward reversion was explained by assuming that these dithiaalkane cross-links behaved similarly to monosulfidic cross-links upon overcure or aging at elevated temperatures.

We were especially interested in the relationship between the type of cross-link and mechanical properties in vulcanizates of high *cis*-1,4-polybutadiene (BR). It was assumed that the kind of cross-links could be varied in a controlled way by using cyclic disulfides, resulting in well-defined networks. To gain insight into the cross-linking sequence, visualized by *addition* at or *substitution* α to the olefinic double bonds and underlying reaction mechanism of formation, a low molecular weight model compound vulcanization study was carried out to establish the applicability of several solution NMR techniques for this purpose.

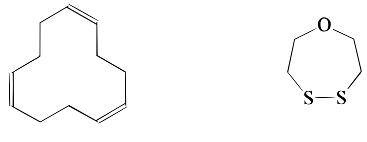

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Figure 1. *ccc*-1,5,9-CDT (**1**) and 1-oxa-4,5-dithiacycloheptane (**2**).

Table 1. ^{13}C Chemical Shift Values of *ccc*-1,5,9-CDT and *cis*-1,4-BR

compound	^{13}C chemical shift (ppm) −CH=	^{13}C chemical shift (ppm) −CH$_2$−
ccc-1,5,9-CDT	130.2	27.9
cis-1,4-BR	129.6	27.5

According to Gregg and Lattimer,[5] a suitable model olefin with comparable reactivity as BR should be ring-shaped, containing at least three homoallylic bonds such as, e.g., *cis,cis,cis*-1,5,9-cyclododecatriene (*ccc*-1,5,9-CDT) shown in Figure 1.

In Table 1 the ^{13}C chemical shifts are given together with those of *cis*-1,4-monomeric units present in high *cis*-BR;[6,7] the resemblances in chemical shifts between *ccc*-1,5,9-CDT and *cis*-1,4-BR are obvious.

Vulcanization of *ccc*-1,5,9-CDT with 1-oxa-4,5-dithiacycloheptane as a cyclic disulfide, which was chosen for both its reactivity and presence of NMR distinguishable methylene groups, under the influence of ZDMC and 1,12-diaminododecane can lead to the formation of several products, of which several are shown in Figure 2. Exclusive α *substitution* would result in the formation of bis(alkenyl) cross-linked product **3**, analogous to the formation of the sulfidic bis(alkenyl) cross-linked prod-

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10.1021/ma990594u CCC: $18.00

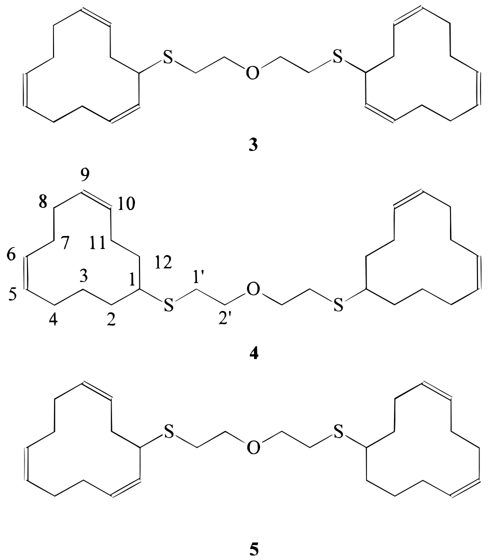


Figure 2. Possible products of the reaction of 1-oxa-4,5-dithiacycloheptane and *ccc*-1,5,9-CDT.

Table 2. Composition Used in the Model Vulcanization Reaction

component	contents (g)	contents (mmol)
ccc-1,5,9-CDT	2.0	12.3
1-oxa-4,5-dithiacycloheptane	0.14	1.1
ZDMC	0.67	2.2
1,12-diaminododecane	0.44	2.2

uct during the TMTD (*t*etra*m*ethyl*t*hiuram *d*isulfide) accelerated sulfur vulcanization of TME (*t*etra*m*ethyl*e*thene = 2,3-dimethyl-2-butene) observed by Versloot.[8] *Addition* at the double bonds, however, leads to the formation of the bis(alkyl) cross-linked compound **4**. The combination of both addition and α substitution could, alternatively, yield alkenyl−alkyl cross-links (product **5**).

In the present paper, the application of several solution NMR techniques in the elucidation of the molecular structure of 1-oxa-4,5-dithiacycloheptane vulcanized *ccc*-1,5,9-CDT is described. The results obtained on this "model compound" serve as reference for the introduction of solid state NMR techniques in the structural elucidation of true vulcanizates of BR itself.[9,10]

Experimental Section

Materials. 1,12-Diaminododecane (Aldrich) and ZDMC (Perkacit-ZDMC, Flexsys) were used without further purification.

1-Oxa-4,5-dithiacycloheptan*e* was prepared by means of oxidative cyclization of dimercaptodiethyl ether using iodine.[11] Yield: 80%. n_D^{20} = 1.5820 (lit.[12] n_D^{20} = 1.5823). ^1H NMR ($CDCl_3$, 250 MHz): δ 2.95 (t, 4H, CH_2S), 4.10 (t, 4H, CH_2O). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 41.1 (CH_2S), 72.4 (CH_2O).

cis,cis,cis-1,5,9-Cyclododecatriene was prepared as described by Trauer and Haufe.[13] Yield: 6%. n_D^{20} = 1.5115 (lit.[14] n_D^{20} = 1.5116). ^1H NMR ($CDCl_3$, 250 MHz): δ 2.08 (m, 12H, CH_2), 5.59 (m, 6H, CH). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 28.0 (CH), 130.4 (CH_2).

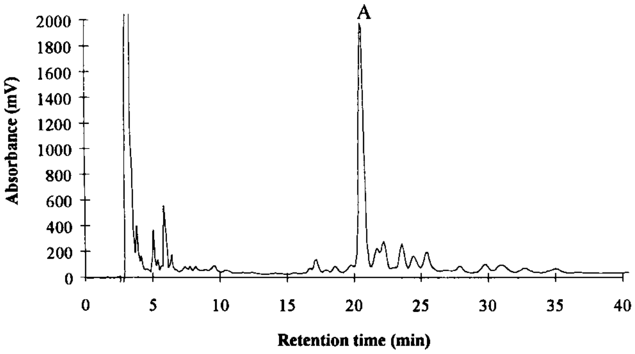


Figure 3. HPLC chromatogram of the first fraction collected (fraction A).

Vulcanization of *cis,cis,cis*-1,5,9-Cyclododecatriene. The model compound vulcanization was carried out in a small glass vessel equipped with a Teflon-coated screw cap under continuous stirring. The compound composition used is given in Table 2. The vessel was heated at 140 °C in an oil-bath for 3 h. After vulcanization the vessel was cooled to room temperature and excess *ccc*-1,5,9-CDT was removed by Kugelrohr distillation. The product was *pre*separated by means of column chromatography (Merck Kieselgel 60, toluene/ethyl acetate/acetone 100:20:8 v/v/v). The first eluted fraction was further purified by means of HPLC (Figure 3).

High Performance Liquid Chromatography. HPLC was carried out using a Waters 610 Fluid unit coupled to a Waters 600E HPLC controller unit and a Waters 712 WISP autosampler. The products were separated by means of reversed phase HPLC over a 25 × 0.4 cm stainless steel column filled with Nucleosil 100−5 C18 (Marchery and Nagel). As mobile phase, a 10:1:1 (v/v/v) eluent mixture of acetonitrile/water/tetrahydrofuran was used. The injection volume was 10 μL and the flow rate 1 mL min^{-1}. For detection, a Waters 410 differential refractometer was used. The fractions of 50 injections were accumulated, concentrated, and used as such for further manipulations and studies.

NMR and Mass Spectroscopy. ^1H and ^{13}C NMR spectra were recorded using a Bruker AC 250 NMR spectrometer operating at 250 and 62.5 MHz, respectively. COSY,[15] DQF−COSY,[16] clean-TOCSY (MLEV-17),[17] HMQC,[18] and HMBC[19] spectra were recorded using a Varian Unity 400 WB spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Pulse widths are 6.4 μs (^1H) and 28.0 μs (^{13}C) with relaxation delays of 3−5 s, typically. The number of data points averaged 2048 in both dimensions; the number of increments was 256, and the number of transients was 32. The mixing times in the TOCSY experiments were arrayed between 30 and 100 ms. All 2D spectra were collected using 2D hypercomplex data.[20] After being weighted with shifted sine−bell functions, the data were Fourier transformed in the phase-sensitive mode. For processing of the data, standard Varian VnmrS/VnmrX software packages were used.

The ^{13}C chemical shifts were calculated using the commercially available software program ACD/CNMR version 2.51.

A Finnigan MAT 90 double focus mass spectrometer was used to record the mass spectra, using chemical ionization with ammonia.

Results and Discussion

We focused on the isolation and subsequent structural elucidation of fraction A, eluting after 21 min under the conditions described (Figure 3).

The ^1H 1D NMR spectrum showed the presence of both ether and unsaturated bonds. Mass spectrometry suggested that structure **4** (Figure 2), formed due to addition at the double bonds, was formed exclusively (*m/e* 480, M^{+18}, NH_4^+). However, *conclusive detailed* information on the cross-linking sequence and exact molecular structure was obtained from 1D and 2D NMR analysis.

Starting from the ^{13}C DEPT spectra, various ^{13}C resonances and the corresponding multiplicities were identified. The *key resonance*, belonging to methine carbon 1 in structure **4**, was found at δ 41.5 ppm, whereas the corresponding proton 1 was situated at a

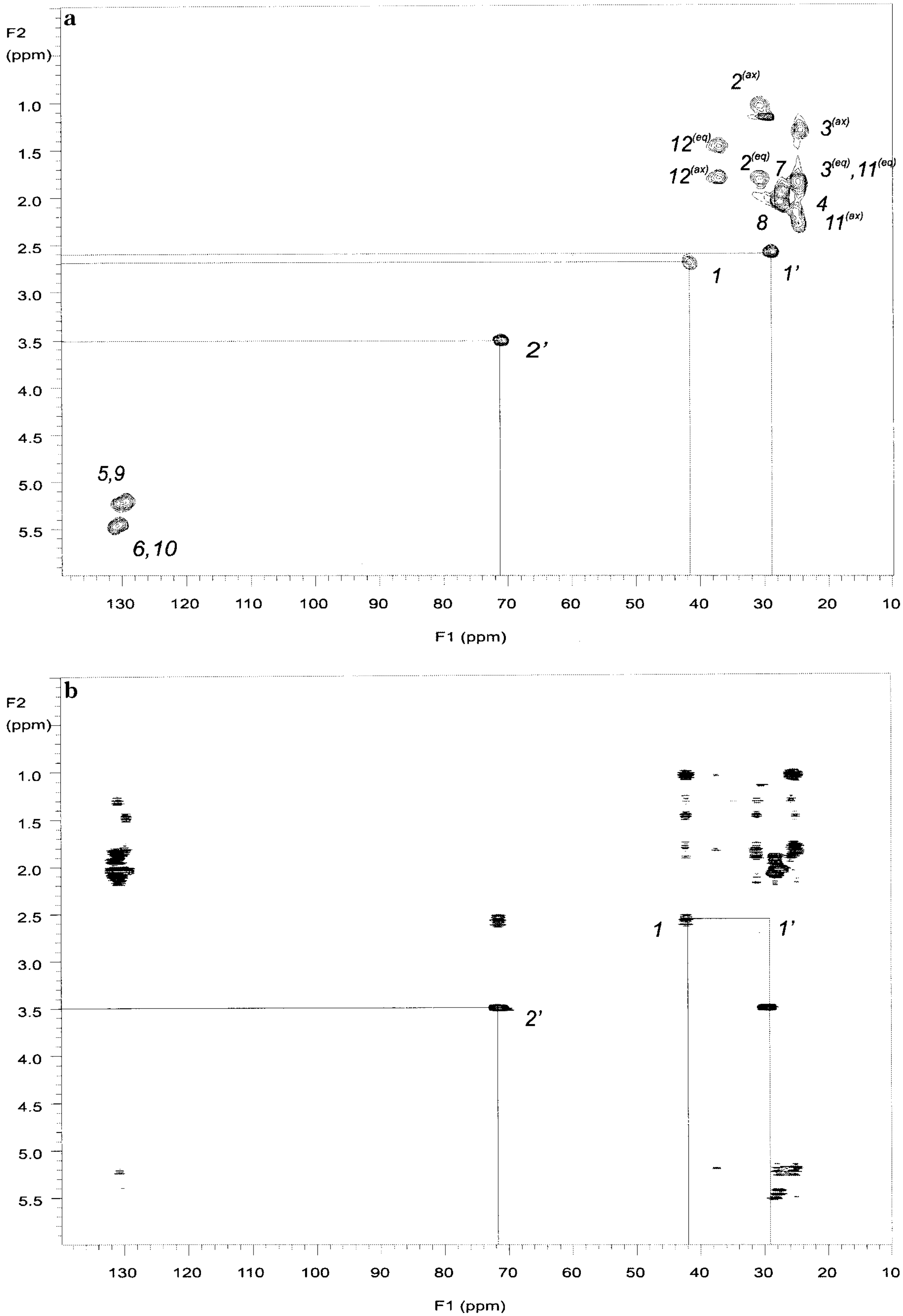


Figure 4. HMQC (a) and HMBC (b) spectra of fraction A, recorded at 30 °C, in $CDCl_3$.

chemical shift of δ 2.75 ppm using HMQC spectroscopy (Figure 4a).

The observation of *only one* aliphatic ^{13}C-methine resonance (Figure 4) provided also the first indication that a symmetric cross-link had been formed, thus excluding structure **5**. Furthermore, the absence of $^3J_{HH}$ couplings in the COSY spectra between methine proton 1 (δ 2.75 ppm) and the olefinic region of the spectrum

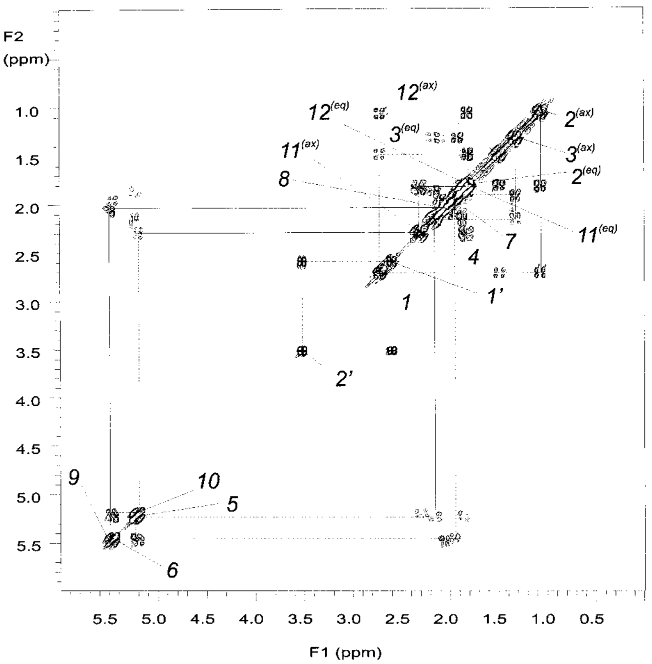


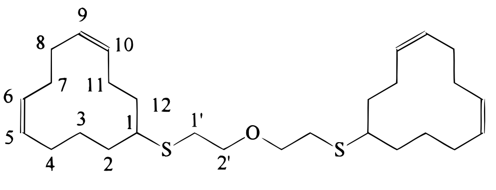
Figure 5. DQF−COSY spectrum of fraction A recorded at 30 °C, in $CDCl_3$.

(Figure 5), unambiguously excluded the presence of cross-linked structures **3** and **5**. Instead, two $^3J_{HH}$ correlations were found with resonances at δ 1.10 and δ 1.55 ppm due to protons 2 and 12, respectively. These results also indicated that bis(alkyl) cross-links were formed upon reaction of *ccc*-1,5,9-CDT and 1-oxa-4,5-dithiacycloheptane under the employed conditions, suggesting **4** as the only product.

Addition of the cross-linking unit will introduce a stereogenic center in the cyclic part of the system. As a consequence, the neighboring methylene protons of 1 (2 and 12) are rendered diastereotopic and can possibly be anisochronous. When it is assumed that the large *S*−*R*−*S* cross-linking group occupies the "pseudoequatorial" position, methine proton 1 is forced into the "pseudoaxial" orientation. In general, the strongest *J* coupled contacts will be established between two axial or two equatorial neighboring protons, while contacts between an axial and equatorial neighbor are far less intense. From the HMQC spectrum (Figure 4a), two $^1J_{CH}$ correlations between the carbon resonating at δ 35.2 ppm (12) and the protons residing at δ 1.55 and δ 1.81 ppm, were observed. The protons also showed a mutual $^2J_{AB}$ coupling from the COSY spectrum, whereas only the proton located at δ 1.55 ppm (12^{ax}) showed a $^3J_{HH}$ contact with proton 1 at δ 2.75 ppm (1^{ax}). Evidently, these two protons were axially oriented, whereas the proton at δ 1.81 ppm occupies the equatorial position (12^{eq}). Using the same methodology, the resonances of neighboring methylene group 2 were assigned: the carbon resonance was found at δ 29.3 ppm, whereas the protons resided at δ 1.10 (2^{ax}) and δ 1.80 ppm (2^{eq}), respectively. From a combination of COSY and HMQC walks, the carbon and proton resonances of methylene moieties 3 (diastereotopic), 4 (shows no diastereotopicity), and 11 (diastereotopic) could be assigned as well (Table 3).

Unfortunately, the COSY spectra showed insufficient resolution to assign the olefinic protons. However, TOCSY and DQF−COSY spectra (Figure 5) showed a much higher resolution and provided the desired information. From the TOCSY spectra (not shown), long-range contacts were traced between protons $2^{ax}/2^{eq}$ and the protons 5 and 6 situated at δ 5.22 and δ 5.40 ppm, respectively. From protons 12, long-range contacts toward the olefinic protons located at δ 5.45 (9) and δ 5.20 ppm (10) were identified unambiguously. Direct correlations between protons 6 and 9 and the aliphatic protons 7 and 8, respectively, were extracted from DQF−COSY experiments, as shown in Figure 5.

Table 3. Experimental and Calculated Chemical Shift Assignment of Structure 4



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atom	^1H shift (ppm)[a]	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.75	41.5	44.6
2	1.10 (ax) 1.80 (eq)	29.3	33.1
3	1.30 1.90	23.8	28.0
4	2.1	28.0	28.7
5	5.22	129.8	128.9
6	5.40	130.1	128.1
7	1.95	27.7	26.6
8	2.05	28.0	26.6
9	5.45	129.8	128.1
10	5.20	130.1	129.0
11	2.30 1.80	24.1	25.1
12	1.55 (ax) 1.81 (eq)	35.2	34.1
1′	2.65 2.66	27.8	32.7
2′	3.50	70.7	70.1

[a] Key: ax, axial; eq, equatorial.

These spectra provided additional proof for the exact chemical shifts of protons 4 and 11, thus completing the ^1H and ^{13}C assignment of the cyclic part of structure **4** (Table 3).

Now that the resonances of the ring system had been assigned, the bridging unit had to be identified, as well as the mono- or disulfidic character of the cross-link unit. The methylene resonance located at δ 70.7 ppm, was shown to have a $^1J_{CH}$ correlation with the proton resonating at δ 3.50 ppm (HMQC, Figure 4a). These ^{13}C and ^1H chemical shifts are characteristic for a methylene moiety attached to oxygen and are accordingly assigned to 2′ in structure **4**. The COSY spectrum (not shown) identified neighboring protons 1′ resonating at δ 2.65 ppm from the $^3J_{HH}$ coupling with methylene group 2′. The corresponding ^{13}C chemical shift (δ 27.8 ppm) was extracted from the HMQC spectrum. The sequence of methylene groups 1′ and 2′ is also shown by the presence of the expected $^2J_{CH}$ couplings in the HMBC spectrum (Figure 4b). The absence of other ^1H and ^{13}C resonances of this kind demonstrated the symmetry of cross-linking, visualized by the presence of one 1-oxa-4,5-dithiacycloheptane unit identically connected with two *ccc*-1,5,9-CDT systems. Also COSY, HMQC, and HMBC spectra showed symmetrical cross-linking.

The $^3J_{CH}$ correlation observed between the ^{13}C of methine group 1 and the protons of the bridging methylene moiety 1′ indicated that a monosulfidic bond was formed, since $^{13}C-^{1}H$ correlations over more than one sulfur atom were not observed in HMBC spectra of symmetrical di- and polysulfidic model compounds.[1] Moreover, also a $^{4}J_{CH}$ correlation between the ^{13}C of methine group 1 and the 2′ protons of the bridging methylene moiety was observed, yielding additional evidence for monosulfidic connectivity (since $^{5}J_{CH}$ couplings are very unlikely to be observed for these systems). The results are collected in Table 3.

The experimentally found ^{13}C chemical shifts were in good agreement with the calculated values. It should, however, be mentioned that the ACD/CNMR program used does not account for conformational effects. Moreover, due to the relatively limited number of compounds, we were unable to add enough experimental values for the training set. Therefore, pronounced differences between experimental and calculated values were expected for those ^{13}C atoms that experience the largest through space interactions caused by surrounding effects. Consequently, the largest deviations were found for the ^{13}C atoms near the point of attachment of the sulfur atoms, as became apparent for, e.g., carbons 2 and 3 whereas comparable carbons 11 and 12 showed much better resemblance between experimental and calculated data.

Conclusions

The model vulcanization of *ccc*-1,5,9-CDT with 1-oxa-4,5-dithiacycloheptane under the influence of ZDMC and 1,12-diaminododecane indicated that symmetrical cross-linking took place by means of *addition* at the double bonds of the ring system. The presence of the bis(alkyl) cross-links was proven by using several solution NMR techniques such as COSY, TOCSY, DQF−COSY, HMQC, and HMBC NMR spectroscopy provided proof for the presence of monosulfidic coupling, as found from COSY and HMBC experiments. The assignment of the relative stereochemistry and the elucidation of the complete structure on a molecular level proved possible by combining all the applied NMR techniques. The experimentally determined chemical shifts appeared to be in good agreement with calculated values.

NMR proved to be a valuable tool for the study of this type of systems. Moreover, the study described can serve as a reference for further studies on BR vulcanizates using less definitive *solid state* NMR techniques. These results will be presented separately.

Acknowledgment. Mrs. J. M. Visser, Mr. M. Ankoné, Mr. E. C. van der Linden, and Mr. J. F. van Duijl (UT) are gratefully acknowledged for their technical assistance. The Dutch Foundation for Chemical Research (SON) and the Foundation for Technical Sciences (STW) are acknowledged for financial aid.

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