

SUPPORTING INFORMATION FOR

**The conformational changes of 2,11-dithia[3.3]metacyclophane - A new look
using VT NMR and calculation**

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Table S1. Energies of the rotational transition states between conformers for 1 (X=H) (kcal/mole) by various calculation methods, relative to Scc = 0.

Method	PCM ^a	RHF ^b	MM94 ^c	MM3 ^d	AM1 ^e	PM3 ^f	DFT
Process							
Scc to Sbc	12.61	12.13	18.79	10.33	7.10	7.32	12.95 ^g
Sbc to Sbb	13.34	10.67	19.33	10.60	7.87	8.23	i
Scc to Acc	10.39	10.34	16.27	11.45	6.81	7.19	8.92 ^g (8.35 ^h)
Sbc to Abc	7.56	6.78	11.93	11.97	4.81	5.21	6.98 ^{g,i} (4.06 ^h)
Sbb to Abb	7.66	6.10	11.96	8.73	5.48	5.74	5.43 ^g (5.13 ^h)
Acc to Atbc	5.04	4.31	5.88	5.99	2.31	2.66	i
Atbc to Abc	6.16	5.30	6.60	6.40	2.75	3.96	6.15 ^g (2.44 ^h)

^a PCMODEL⁹ MMX = MM2 + π -SCF; ^b SPARTAN¹⁰ Hartree Fock 6-31G*; ^c SPARTAN¹⁰ MMFF94 (an MM2 type); ^d PCMODEL⁹ MM3; ^e SPARTAN¹⁰ AM1; ^f SPARTAN¹⁰ PM3;

^g SPARTAN¹⁰ pBP/DN* (perturbative Becke-Perdew with numerical polarization); ^h pBP/DN** (with full polarization); ⁱ calculation would not complete.

Table S1A. Corresponding Absolute Energies (Hartrees) of the rotational transition states between conformers for 1 (X=H).

Process	Method:	RHF	DFT(*)	DFT(**)
Scc to Sbc		-1410.2162544	-1415.99788	-
Sbc to Sbb		-1410.2185870	-	-
Scc to Acc		-1410.2191089	-1416.00430	-1416.04308
Sbc to Abc		-1410.2247785	-1416.00750	-1416.04992

Sbb to Abb	-1410.2258677	-1416.00986	-1416.04822
Acc to Atbc	-1410.2287204	-	-
Atbc to Abc	-1410.2271330	-1416.00871	-1416.05250

See notes under Table S1

Table S2. Absolute Conformer Energies (Hartrees)

Method	RHF	DFT(*)	DFT(**)	DFT(B3LYP)^a
Scc	-1410.2355837	-1416.01851	-1416.05639	-1415.74608400550
Sbc	-1410.2343135	-1416.01565	-1416.05393	-1415.74485438718
Sbb	-1410.2316128	-1416.01426	-1416.05283	
Actb	-1410.2341300	-1416.01640	-1416.05449	-1415.74467258172
Acc	-1410.2302846	-1416.01334	-1416.05257	
Acb	-1410.2289325	-1416.01250	-1416.05082	

See notes under Table S1; ^a Performed using Jaguar¹³ (see text in paper).

^a Co-ordinates for these geometries are below

Scc

H1	1.2784324090	0.0000000000	1.8999487981
C2	1.5760181600	0.0000000000	.8534250933
C3	2.3539854737	0.0000000000	-1.8069419520
C4	1.7409305354	1.2222996192	.1939027385
C5	1.7409305354	-1.2222996192	.1939027385
C6	2.1429065036	-1.2113522906	-1.1472769982

C7	2.1429065036	1.2113522906	-1.1472769982
C8	1.4613419741	2.5160203576	.9220323095
C9	1.4613419741	-2.5160203576	.9220323095
H10	2.2704232979	-2.1507897529	-1.6787476564
H11	2.2704232979	2.1507897529	-1.6787476564
H12	2.6709321978	0.0000000000	-2.8461485347
H13	2.2854859810	3.2252170824	.7904070675
H14	-1.3545697928	2.3411032787	1.9972554957
H15	1.3545697928	2.3411032787	1.9972554957
H16	2.2854859810	-3.2252170824	.7904070675
H17	1.3545697928	-2.3411032787	1.9972554957
H18	-1.3545697928	-2.3411032787	1.9972554957
C19	-1.4613419741	2.5160203576	.9220323095
S20	0.0000000000	-3.4965393417	.3413237945
H21	-2.2854859810	3.2252170824	.7904070675
C22	-1.7409305354	1.2222996192	.1939027385
S23	0.0000000000	3.4965393417	.3413237945
C24	-2.1429065036	-1.2113522906	-1.1472769982
C25	-2.1429065036	1.2113522906	-1.1472769982
C26	-1.5760181600	0.0000000000	.8534250933
C27	-1.7409305354	-1.2222996192	.1939027385
C28	-2.3539854737	0.0000000000	-1.8069419520

H29	-2.2704232979	2.1507897529	-1.6787476564
C30	-1.4613419741	-2.5160203576	.9220323095
H31	-2.6709321978	0.0000000000	-2.8461485347
H32	-2.2704232979	-2.1507897529	-1.6787476564
H33	-2.2854859810	-3.2252170824	.7904070675
H34	-1.2784324090	0.0000000000	1.8999487981

Sbc

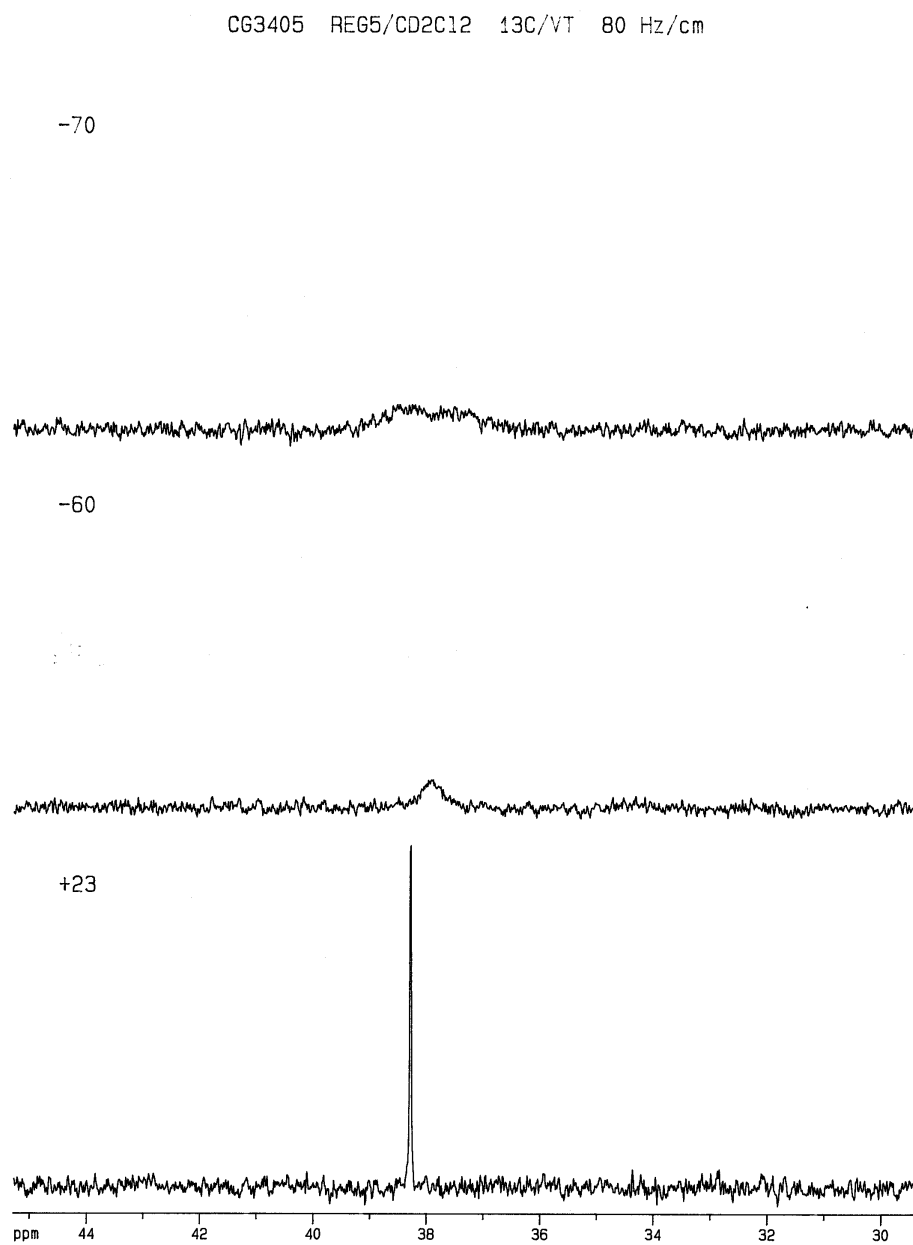
H1	-.3393380913	-1.3000164292	-1.7043819948
C2	-.1813913323	-1.5857846586	-.6679689566
C3	.2140598565	-2.2779549536	1.9915078681
C4	-1.2924465158	-1.7134343707	.1751623196
C5	1.1205121643	-1.7391423786	-.1890045999
C6	1.3108649875	-2.1014157534	1.1532508809
C7	-1.0823052487	-2.0671866438	1.5108617990
C8	-2.7004121408	-1.4661459815	-.3287937237
C9	2.2946368807	-1.4734512669	-1.1021413619
H10	2.3192007411	-2.2157677160	1.5419608657
H11	-1.9319253784	-2.1691220335	2.1819398939
H12	.3649226682	-2.5560408264	3.0308123070
H13	-3.0356026663	-2.2908040746	-.9696261460
S14	-2.9674776301	.0023433870	-1.4167299949

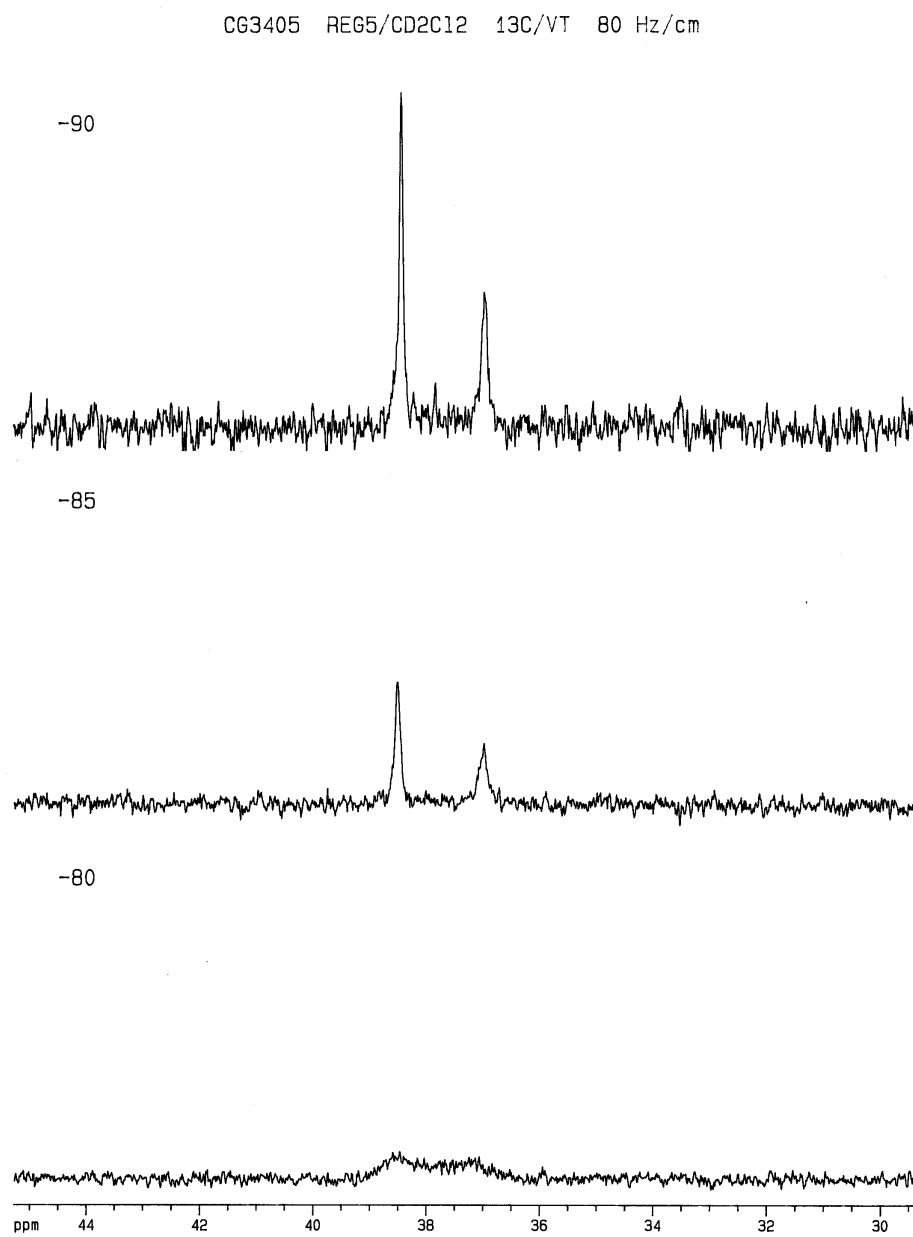
H15	-3.3997793181	-1.4144998297	.5114203380
H16	3.0169547641	-2.2959924883	-1.0640433577
H17	1.9648972423	-1.3788555088	-2.1411498821
H18	1.9590410678	1.3514937716	-2.1479043508
C19	-2.6980463995	1.4512108431	-.3049297429
S20	3.3488393939	-.0070499369	-.6838372286
H21	-3.0509089238	2.2854096290	-.9236876925
C22	-1.2855023921	1.7058895701	.1847176204
H23	-3.3847180370	1.3767168162	.5440810215
C24	1.3228498376	2.1207790290	1.1387172318
C25	-1.0678962188	2.0848254940	1.5125349343
C26	-.1796276221	1.5666058966	-.6627825059
C27	1.1250281115	1.7333974034	-.1951901299
C28	.2306203394	2.3087257762	1.9807932033
H29	-1.9134825499	2.1963372706	2.1872257925
C30	2.2939620677	1.4565200807	-1.1115736240
H31	.3871135265	2.6064704937	3.0138119324
H32	2.3331908328	2.2466412141	1.5186550622
H33	3.0174851950	2.2784035925	-1.0854899326
H34	-.3434934780	1.2625209734	-1.6928789036

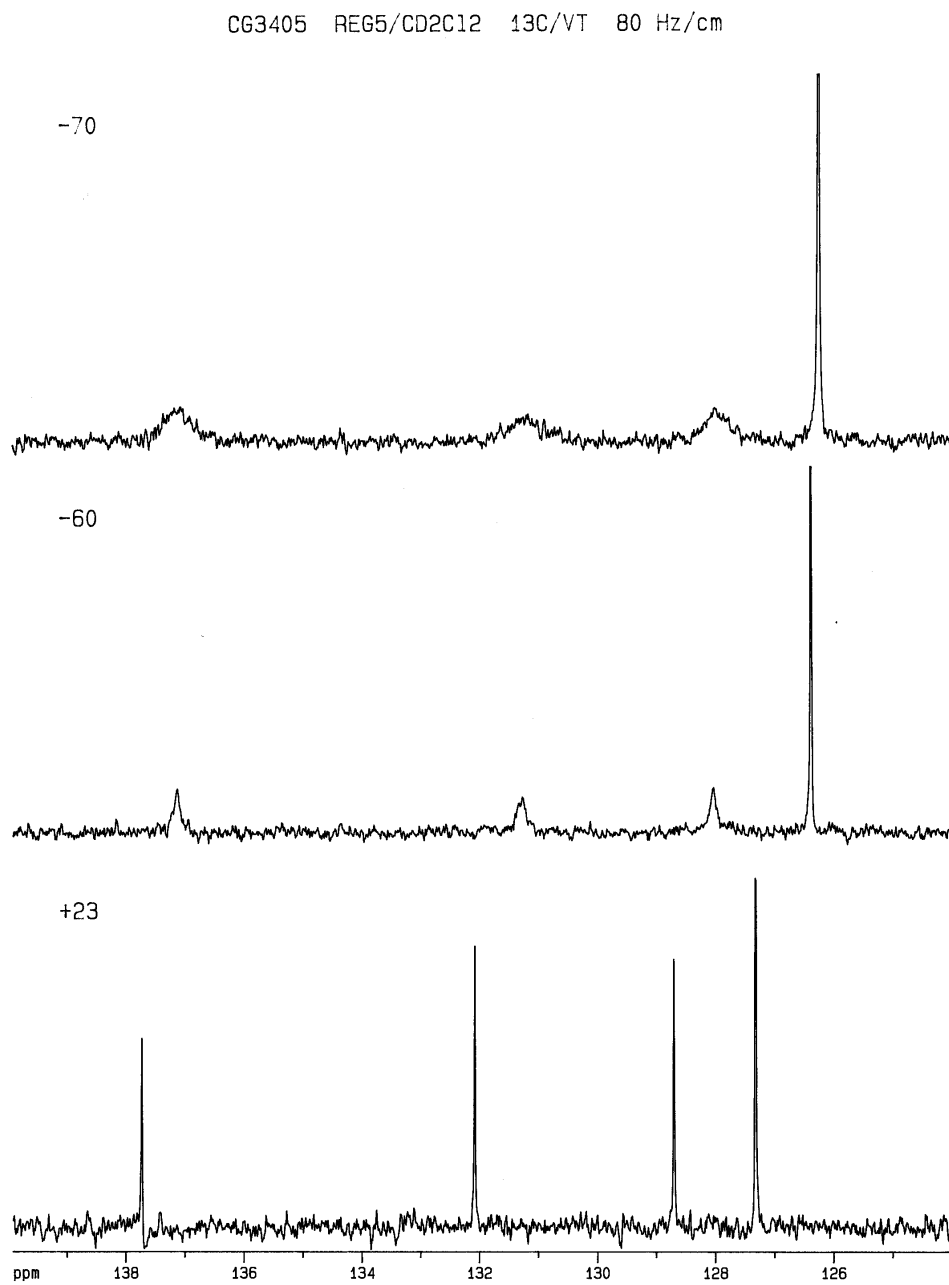
Actb

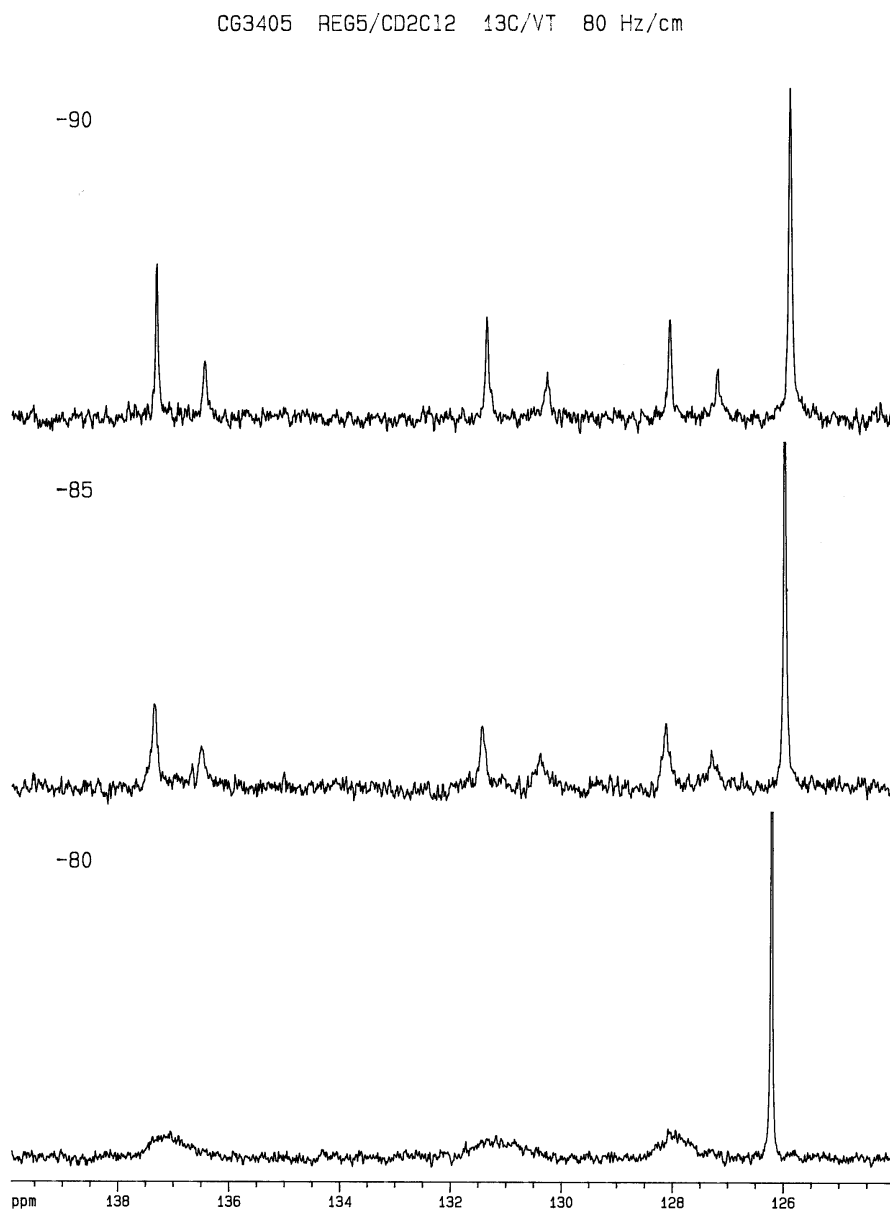
H1	.1319384587	-.1920355316	1.5685214252
C2	-.0014722730	-1.1200050634	1.0200408226
C3	-.3505675194	-3.4842833512	-.3854613676
C4	1.1273683692	-1.8286069797	.5955908711
C5	-1.2976142593	-1.5378476710	.7019129905
C6	-1.4654409483	-2.7371493704	-.0035336759
C7	.9392551392	-3.0291325288	-.1008006140
C8	2.5091583883	-1.2636921184	.8187243739
C9	-2.4610996934	-.6589501616	1.0885466486
H10	-2.4655673132	-3.0738821398	-.2635485158
H11	1.8016120458	-3.6008472249	-.4353775860
H12	-.4858048603	-4.4191553794	-.9222518513
H13	2.5362037875	-.5904653776	1.6800285877
H14	3.4078222187	1.7279353546	.6060748069
H15	3.2340115953	-2.0625319406	.9983255067
H16	-3.2485011786	-1.2276550429	1.5944048983
H17	-2.1252863322	.1265503255	1.7699608822
S18	-3.3794086995	.1383675564	-.3136076998
C19	2.8520572240	1.4323223659	-.2896507258
C20	-2.0466265429	.8430863787	-1.3907457027
H21	3.3355579363	1.9364235090	-1.1361038507
S22	3.2055445031	-.3420446606	-.6464625674

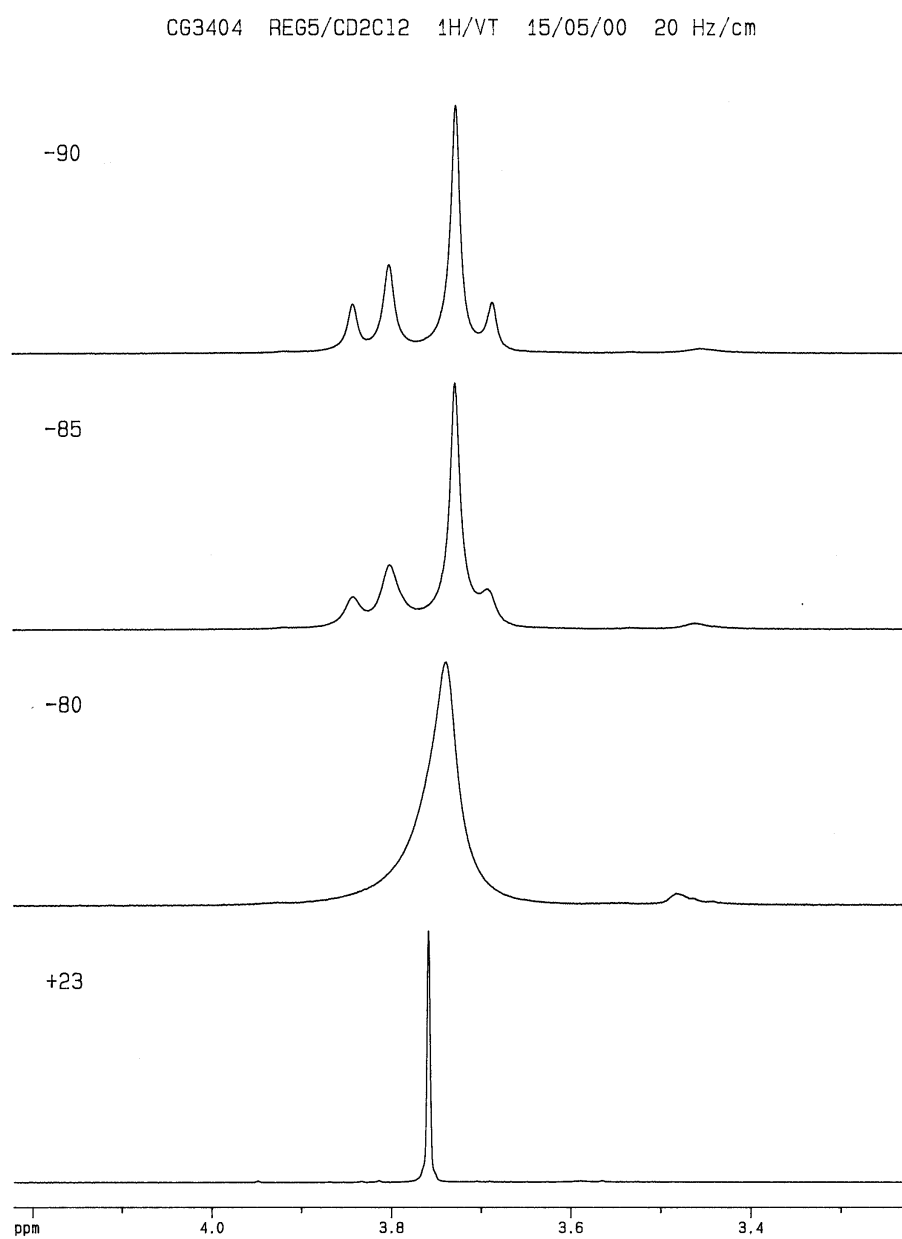
C23	1.4052425261	1.8764468516	-.1619574548
C24	-1.2629944468	2.6999705876	.1729789300
C25	.3695036772	1.2633136933	-.8734776649
C26	1.0882129845	2.9254147459	.7104018446
C27	-.2361836243	3.3461231570	.8601274541
C28	-.9665547123	1.6380786729	-.6926394572
H29	.6061891941	.4280808699	-1.5258195730
H30	1.8771244734	3.4100321235	1.2812771970
H31	-.4683825591	4.1644634345	1.5361387311
H32	-2.6153146810	1.4644510156	-2.0919478553
H33	-2.2976725001	2.9925039814	.3301873264
H34	-1.5949783720	.0287651352	-1.9622069894

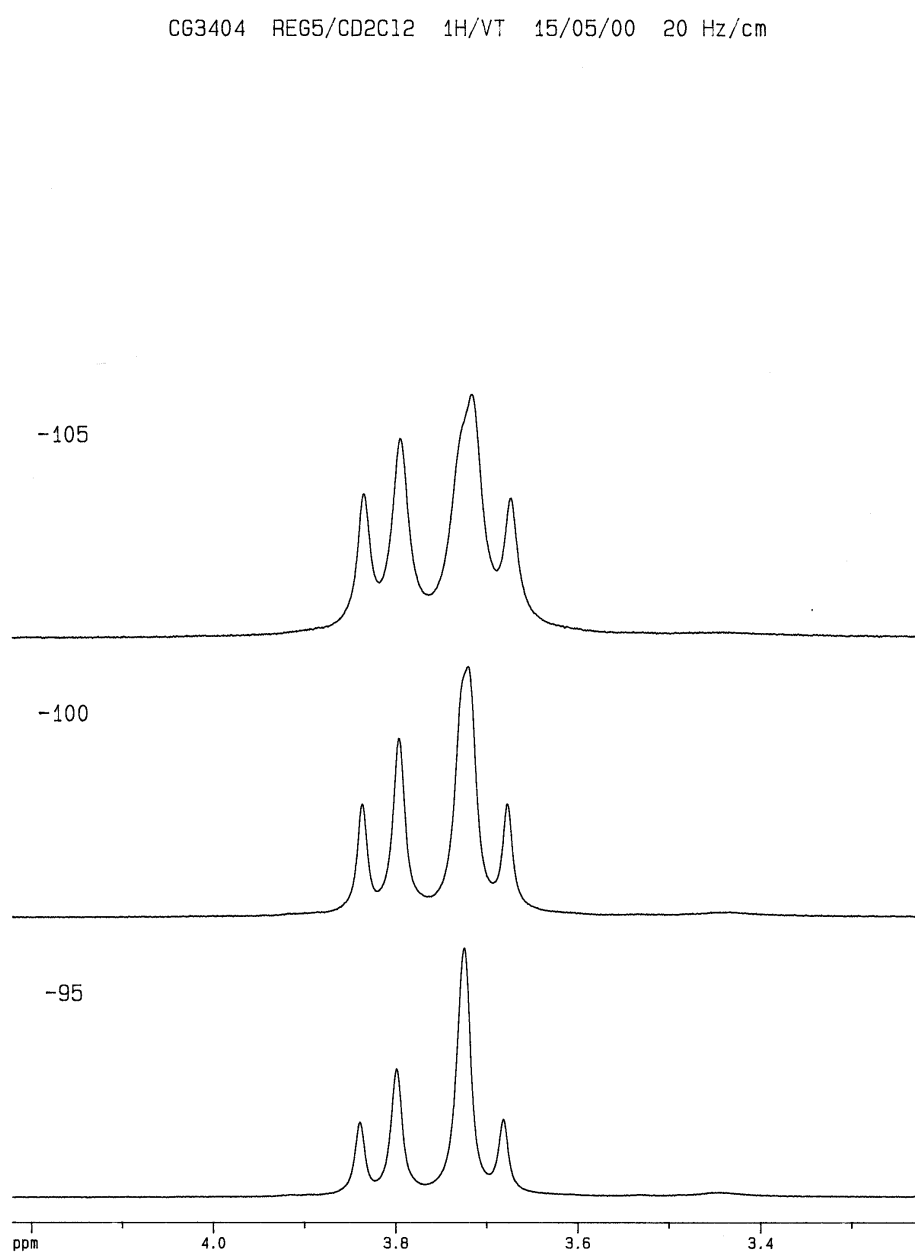
VT ^{13}C NMR spectra [Bruker AMX 360 , run at 90.6 MHz in CD_2Cl_2]Bridge region-1

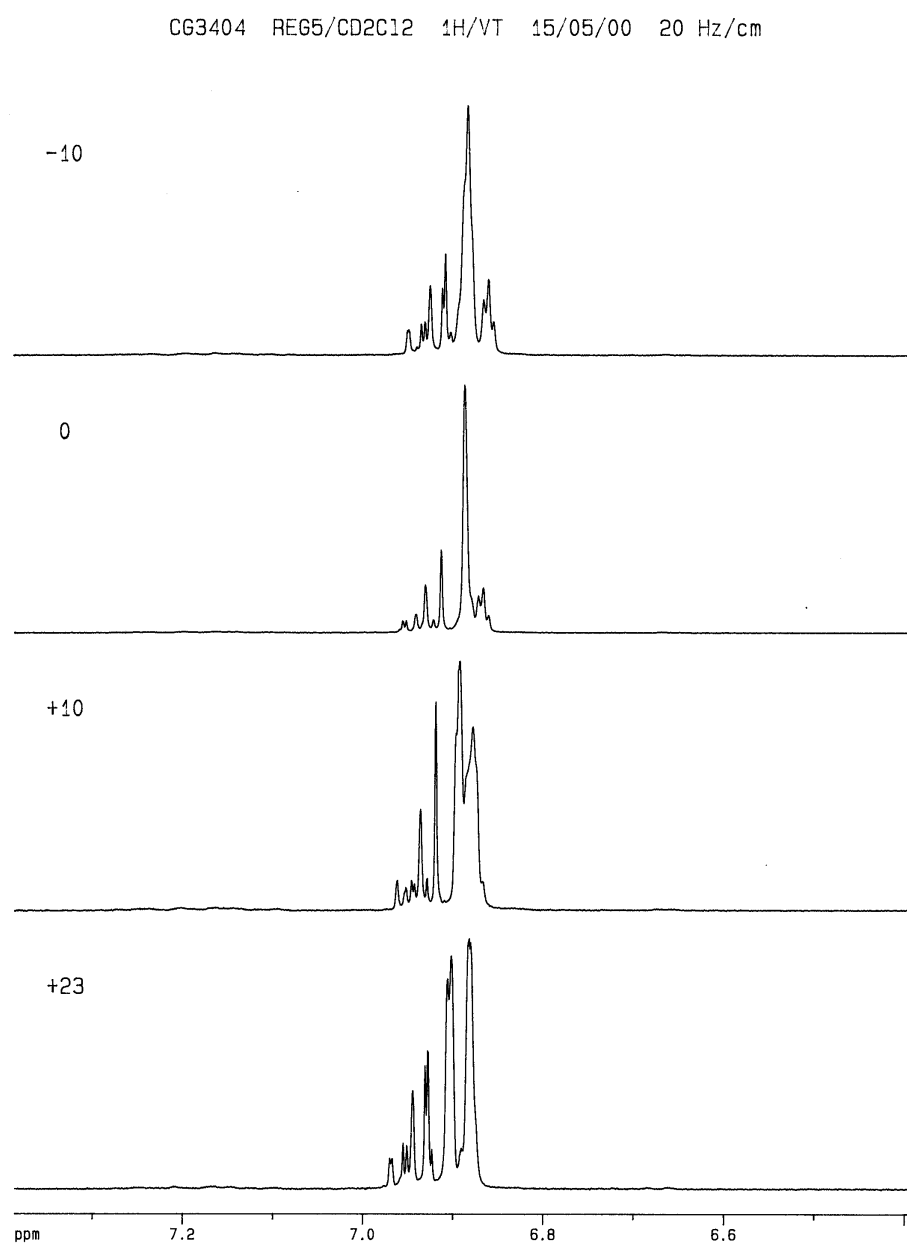
VT ^{13}C NMR spectra [Bruker AMX 360 , run at 90.6 MHz in CD_2Cl_2]Bridge region-2

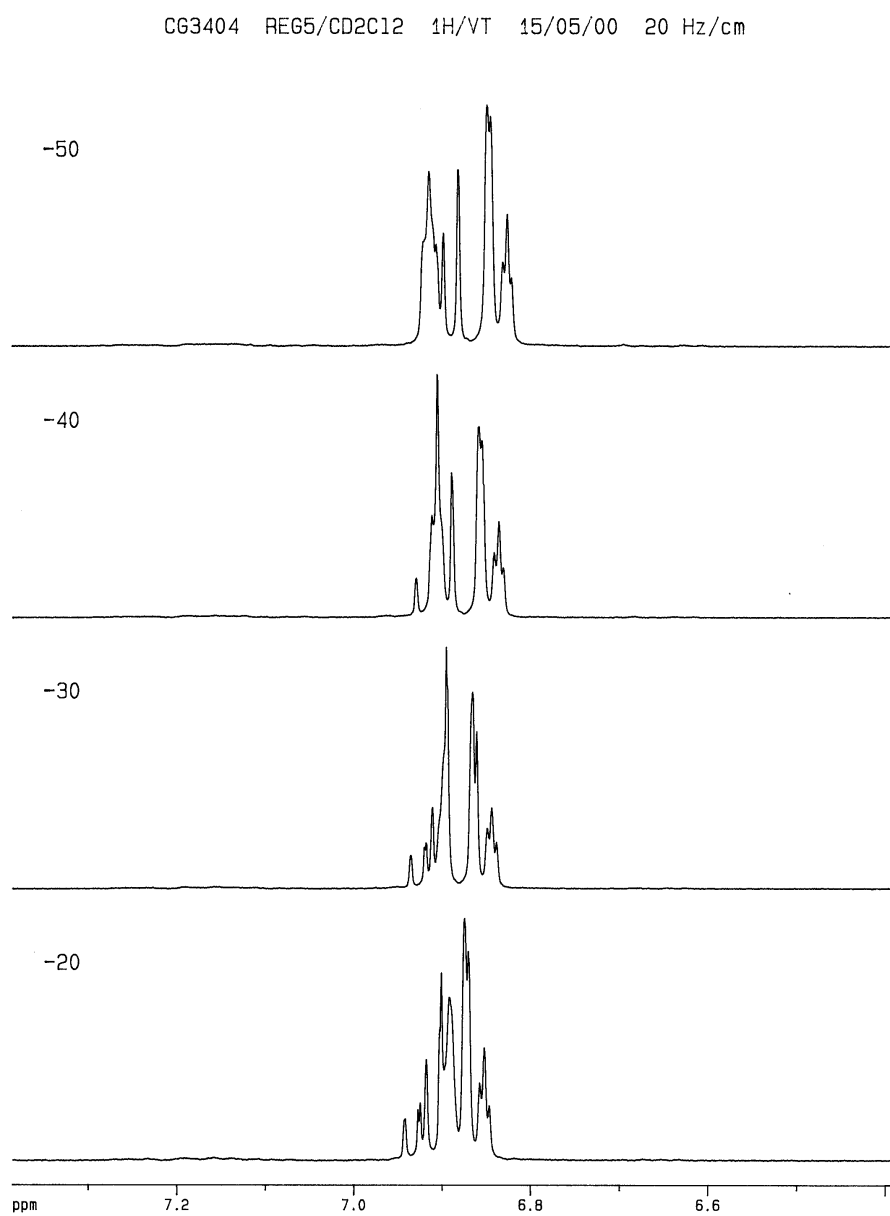
VT ^{13}C NMR spectra [Bruker AMX 360 , run at 90.6 MHz in CD_2Cl_2]Aromatic region-3

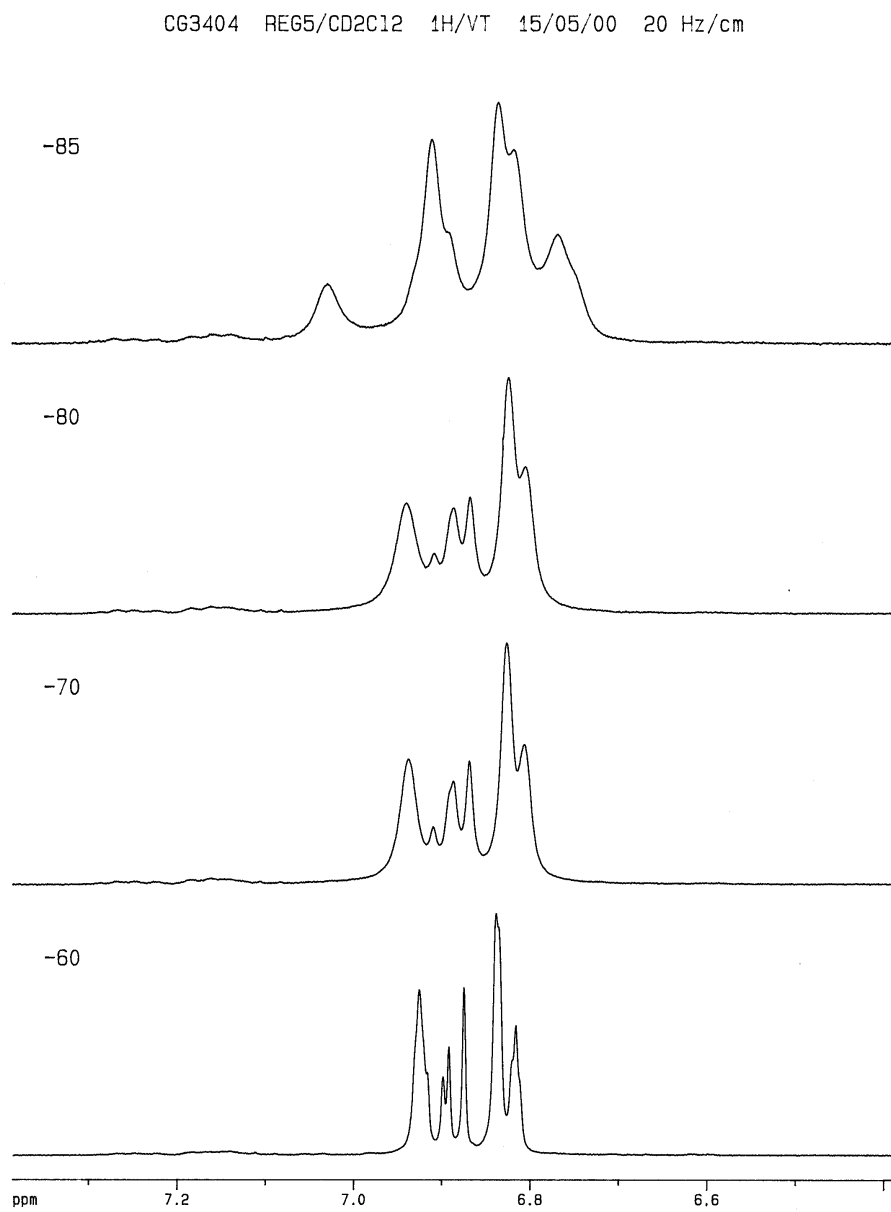
VT ^{13}C NMR spectra [Bruker AMX 360 , run at 90.6 MHz in CD_2Cl_2]Aromatic region-4

VT ^1H NMR spectra [Bruker AMX 360 MHz in CD_2Cl_2] Bridge region-5

VT ^1H NMR spectra [Bruker AMX 360 MHz in CD_2Cl_2] Bridge region-6

VT ^1H NMR spectra [Bruker AMX 360 MHz in CD_2Cl_2] Aromatic region-7

VT ^1H NMR spectra [Bruker AMX 360 MHz in CD_2Cl_2] Aromatic region-8

VT ^1H NMR spectra [Bruker AMX 360 MHz in CD_2Cl_2] Aromatic region-9

VT ^1H NMR spectra [Bruker AMX 360 MHz in CD_2Cl_2] Aromatic region-10