Supplementary material to:

P. Singh, K. Bisetty and M.P. Mahajan, *S. Afr. J. Chem.,* 2009, **62**, 47–55.

Coordinates for optimized structure 1a/Å

HF/6–31+G(d) = –630.31962 H (gas phase), –630.33729 H (in dcm)
MP2/6–31+G(d) = –632.31974 H (gas phase), –632.33522 H (in dcm)
B3LYP/6–31+G(d) = –634.38558 H (gas phase), –634.40118 H (in dcm)

C	–1.01638500	–0.75561600	–0.19524100
C	0.31568700	–0.12933000	–0.05604300
C	1.45260900	–0.82716200	–0.19614100
C	2.80494800	–0.23347800	–0.05423200
C	–2.22669100	0.06613400	0.00435500
C	–3.46342000	–0.43696700	–0.11168500
N	–4.64395700	0.36145900	0.10349000
O	–1.11417000	–1.94086500	–0.47373800
C	–5.87395700	–0.28583400	0.56060800
C	–4.68388900	1.79862500	–0.18384000
C	3.88903300	–1.08589800	0.22065800
C	5.18269400	–0.57130500	0.35545100
C	5.41013100	0.79873100	0.20705800
C	4.34640800	1.65471900	–0.08272000
C	3.05040200	1.14579800	–0.21808500
H	0.34851300	0.92251400	0.19191900
H	1.39534800	–1.89335900	–0.38128700
H	–2.09288100	1.10427500	0.27947300
H	–3.58833300	–1.49369100	–0.31897600
H	–6.65918900	–0.19349400	–0.21898800
H	–6.22690600	0.20061800	1.49378100
H	–5.70885400	–1.36434900	0.77084500
H	–5.61127700	2.04790100	–0.74190400
H	–3.82716000	2.11173900	–0.81690300
H	–4.66859200	2.36848600	0.76818400
H	3.73222100	–2.15244300	0.33921300
H	6.00876000	–1.23583700	0.57382900
H	6.41187400	1.19548400	0.31026300
H	4.52582200	2.71501300	–0.21081800
H	2.25630000	1.83333600	–0.47401200

Coordinates for optimized structure 1b/Å

HF/6–31+G(d) = –744.19352 H (gas phase), –744.20912 H (in dcm)
MP2/6–31+G(d) = –746.50618 H (gas phase), –746.52017 H (in dcm)
B3LYP/6–31+G(d) = –748.90526 H (gas phase), –748.91922 H (in dcm)

C	–0.56064200	–2.39039800	0.32330700
C	0.75491200	–2.13666200	0.22231400
C	1.35058700	–0.86599200	–0.24611400
C	2.76031300	–0.56934100	0.08025100
C	3.37916200	0.53972900	–0.35444500
C	–1.63878100	–1.39121700	0.16534000
C	–2.76601900	–1.71296000	–0.60008900
C	–3.81945500	–0.80332400	–0.72434700
C	–3.77901400	0.43574700	–0.07143100
C	–2.65388500	0.74615000	0.72626200
C	–1.60177000	–0.16592900	0.84870600
O	0.70272900	–0.09423700	–0.93581400
O	–4.88283100	1.29731900	–0.24755100
N	4.75491100	0.84593800	–0.03881100
C	5.38106600	2.02689300	–0.63472300
C	5.55393800	0.01007000	0.86099100
C	–4.86329100	2.56351000	0.41108200
H	–0.86108800	–3.40624600	0.54980100
H	1.43603700	–2.94466000	0.45835200
H	3.29096100	–1.28625600	0.69211600
H	2.82499800	1.23725200	–0.97323600
H	–2.82653600	–2.66695300	–1.11007400

H	–4.67664100	–1.06329800	–1.33130300
H	–2.57815500	1.68087100	1.26381700
H	–0.76226900	0.08123100	1.48747400
H	4.68583000	2.55897100	–1.31939800
H	6.27657200	1.72163500	–1.21696300
H	5.68967000	2.73118300	0.16718200
H	6.56812900	0.44113200	1.01208800
H	5.67200500	–1.00450800	0.42770400
H	5.05894000	–0.05812400	1.85315000
H	–5.79710200	3.10936700	0.16470500
H	–4.00477600	3.17441400	0.05654000
H	–4.82285500	2.43010200	1.51403300

Coordinates for optimized structure 1c/Å.

HF/6–31+G(d) = –1089.20942 H (gas phase), –1089.22402 H (in dcm)
MP2/6–31+G(d) = –1091.34619 H (gas phase), –1091.35898 H (in dcm)
B3LYP/6–31+G(d) = –1093.97462 H (gas phase), –1093.98759 H (in dcm)

C	0.58332400	2.34154700	0.20018900
C	–0.73571600	2.11746700	0.08527000
C	–1.35857200	0.83169100	–0.30099700
C	–2.77778800	0.59396200	0.02815200
C	–3.42307700	–0.52170800	–0.34049300
C	1.63655800	1.30550400	0.14192700
C	2.80226000	1.55199700	–0.59858900
C	3.83221200	0.60602000	–0.63063900
C	3.71401600	–0.58456800	0.09339300
C	2.56738700	–0.82453000	0.85870100
C	1.53703400	0.11972500	0.89211800
Cl	5.00607500	–1.77000900	0.05222400
O	–0.72376400	–0.00241300	–0.92513300
N	–4.81136400	–0.74107200	–0.03251400
C	–5.57392200	–1.64771300	–0.88878600
C	–5.41285300	–0.29153700	1.22832200
H	0.90768700	3.36362400	0.35606000
H	–1.39853500	2.95986200	0.24512300
H	–3.30817700	1.36712300	0.57030200
H	–2.90874100	–1.25627900	–0.95060600
H	2.91093800	2.47351600	–1.15841200
H	4.72214400	0.80134000	–1.21598100
H	2.47794600	–1.73750700	1.43273500
H	0.66721900	–0.06996200	1.50946900
H	–5.38272300	–1.41311700	–1.95789100
H	–6.66432200	–1.54009200	–0.70154100
H	–5.27274600	–2.69642300	–0.68269600
H	–6.17357700	0.48871000	1.01792200
H	–4.65297300	0.11573800	1.92628900
H	–5.90291900	–1.14670400	1.73867900

Coordinates for optimized structure 2a/Å

HF/6-31+G(d) = –1216.49230 H (gas phase), –1216.51275 H (in dcm)
MP2/6-31+G(d) = –1219.15182 H (gas phase), –1219.16901 H (in dcm)
B3LYP/6-31+G(d) = –1222.26338 H (gas phase), –1222.25885 H (in dcm)

C	0.63884200	2.38670800	–0.42467500
C	–0.23187500	1.18720900	–0.43217100
C	–1.54080900	1.34854900	–0.12542300
C	–2.60697400	0.28709600	–0.32611400
C	–2.20873800	–1.06212500	0.30213700
O	0.31661400	–0.03438100	–0.87088400
S	–0.55858100	–1.45172200	–0.32643100
O	0.35598100	–2.13890700	0.71494300
O	–0.54478500	–2.44782200	–1.51041100
N	–3.92603600	0.79281600	0.13606600
C	–4.06826900	0.85909700	1.60177200
C	–5.04928100	0.05014400	–0.45914500
C	1.97547100	2.36658800	–0.31540600
C	2.78452500	1.17666400	0.01873400

C	3.94988400	0.90931200	–0.71490900
C	4.75403300	–0.18729900	–0.38630800
C	4.41105400	–1.01012400	0.69036800
C	3.26790200	–0.73257200	1.44476500
C	2.46062600	0.36080900	1.11705000
H	0.16906600	3.35191200	–0.57487000
H	–1.88345700	2.33613100	0.16526800
H	–2.65735700	0.13208100	–1.42743700
H	–2.91068300	–1.86439600	–0.00322000
H	–2.15238100	–1.00912900	1.40924300
H	–4.94437600	1.49124200	1.86156000
H	–3.17577900	1.32618900	2.06745500
H	–4.22361100	–0.15017300	2.04278500
H	–4.97617000	0.05848900	–1.56735500
H	–6.01078500	0.53706400	–0.19165300
H	–5.07431900	–1.00282100	–0.10235500
H	2.50790900	3.29773900	–0.46663200
H	4.23087700	1.54280300	–1.54730700
H	5.64430500	–0.39740200	–0.96350300
H	5.03576200	–1.85652900	0.94576400
H	3.01086900	–1.36124500	2.28674000
H	1.58885200	0.57444300	1.72273000

Coordinates for optimized structure 2b/Å

HF/6–31+G(d) = –1330.37928 H (gas phase), –1330.40219 H (in dcm)
MP2/6–31+G(d) = –1333.34402 H (gas phase), –1333.36349 H (in dcm)
B3LYP/6–31+G(d) = –1336.77452 H (gas phase), –1336.79335 H (in dcm)

C	–0.35589400	–0.47284100	–0.11166600
C	1.06574100	–0.07621400	–0.21538900
C	2.01273100	–1.04415800	–0.17971500
C	3.48324400	–0.80601800	–0.47084100
C	4.07179200	0.33287900	0.38601400
O	1.36786100	1.29073900	–0.38293500
S	2.94985300	1.74362700	0.21624100
O	2.68813200	2.48308300	1.54944100
O	3.46205000	2.87220400	–0.71133200
C	–1.34743600	0.42968200	–0.13656200
C	–2.78755800	0.08008900	–0.05061800
N	4.23998700	–2.08178600	–0.36671000
C	5.52300500	–2.03018500	–1.08657100
C	4.44314400	–2.55223800	1.01602300
H	4.73613100	–3.62320700	1.00410700
H	3.50633200	–2.47215000	1.60648500
H	5.24554000	–1.97844600	1.52812400
C	–3.73261900	1.01921700	–0.49065000
C	–5.10175700	0.74364600	–0.42325400
C	–5.55805800	–0.48663000	0.09913900
C	–4.61353100	–1.41474200	0.55289500
C	–3.24453600	–1.13845100	0.48761100
O	–6.91883500	–0.84507400	0.19964500
C	–7.89978000	0.09694500	–0.23339200
H	–0.58671400	–1.52726800	–0.03788100
H	1.69701800	–2.07466900	–0.05782400
H	3.51605600	–0.46601500	–1.53166200
H	5.07601400	0.62461600	0.01559000
H	4.12895500	0.06587700	1.46023000
H	–1.10171400	1.47754000	–0.26628300
H	5.36373800	–1.73212000	–2.14517200
H	5.99029300	–3.03819800	–1.09867000
H	6.22928800	–1.31778300	–0.60888100
H	–3.41114100	1.97058300	–0.89765800
H	–5.78764700	1.49800600	–0.78074600
H	–4.94419400	–2.35755100	0.96914400
H	–2.55760400	–1.87398600	0.88184000
H	–8.90695800	–0.34103200	–0.08174300
H	–7.77945000	0.31638300	–1.31578800
H	–7.83609000	1.03039500	0.36721100

Coordinates for optimized structure 2c/Å

HF/6–31+G(d) = –1675.39513 H (gas phase), –1675.41765 H (in dcm)
MP2/6–31+G(d) = –1678.18410 H (gas phase), –1678.20283 H (in dcm)
B3LYP/6–31+G(d) = –1681.84330 H (gas phase), –1681.86169 H (in dcm)

C	–0.38947800	–0.40022400	–0.17416200
C	1.04522700	–0.04456300	–0.25292600
C	1.96213700	–1.04039300	–0.21269800
C	3.44607400	–0.84327600	–0.46556000
C	4.04722000	0.26893500	0.41629000
O	1.38915000	1.31441300	–0.39693800
S	2.97086400	1.71325600	0.24105000
O	2.70119300	2.44302500	1.57923000
O	3.53470000	2.83816300	–0.65959900
C	–1.35451200	0.53065200	–0.20202400
C	–2.80322600	0.21765200	–0.12545500
C	–3.72334400	1.16759200	–0.60326100
C	–5.09807400	0.92177500	–0.53960500
C	–5.57164600	–0.27139600	0.01184800
C	–4.66862400	–1.21679400	0.50618000
C	–3.29249500	–0.97556200	0.44426300
Cl	–7.29756400	–0.57405600	0.10227900
N	4.16251100	–2.14229500	–0.35555500
C	5.47352400	–2.11735100	–1.02449500
C	4.29767000	–2.64357800	1.02559400
H	–0.65317800	–1.44730900	–0.11137900
H	1.61253500	–2.06231400	–0.11396300
H	3.51537300	–0.49524500	–1.52155400
H	5.06546500	0.53552200	0.06843700
H	4.07544400	–0.01236000	1.48814000
H	–1.07982600	1.57174200	–0.32567900
H	–3.37572700	2.09933700	–1.03361400
H	–5.79334100	1.66020600	–0.91631200
H	–5.03173700	–2.13668600	0.94689300
H	–2.62502500	–1.71406200	0.86672200
H	5.36577900	–1.78851000	–2.08070000
H	5.90833200	–3.14013700	–1.04310200
H	6.18468600	–1.44094200	–0.50144300
H	5.08336800	–2.09060800	1.58591900
H	4.57670000	–3.71756900	1.00417300
H	3.33528100	–2.56376200	1.57532800

Co–ordinates for optimized structure 3a/Å

HF/6–31+G(d) = –1082.23802 H (gas phase), –1082.26134 H (in dcm)
MP2/6–31+G(d) = –1084.44719 H (gas phase), –1084.46629 H (in dcm)
B3LYP/6–31+G(d) = –1087.07614 H (gas phase), –1087.07614 H (in dcm)

C	–0.93030100	0.72426200	–0.09830600
C	–1.65430500	1.86563900	–0.25734800
C	–3.13478800	1.99231800	–0.28322500
C	–3.95943900	0.96450500	–0.14295200
C	0.54689500	0.83839300	–0.10421200
C	1.34430700	–0.23238600	0.02447900
C	2.82564100	–0.16119300	0.01743400
O	–1.48428100	–0.56307800	0.07443600
S	–3.22914900	–0.63049200	0.08636200
O	–3.63608500	–1.31486500	1.41236900
O	–3.64256800	–1.66723300	–0.98436100
C	3.55488300	–1.31963900	–0.30372900
C	4.95252400	–1.30032700	–0.31217100
C	5.63916000	–0.12890900	0.01169200
C	4.92846500	1.02501200	0.35044800
C	3.53005000	1.01309900	0.35808500
H	–1.12121800	2.80126500	–0.38083200
H	–3.55775900	2.97780100	–0.42304300
H	–5.03454100	1.09277000	–0.16634900
H	0.98504800	1.81784200	–0.24292300
H	0.89798800	–1.21763900	0.09777900

H	3.04065500	–2.23855900	–0.55681700
H	5.50504100	–2.19535600	–0.56876800
H	6.72154300	–0.11588500	0.00754700
H	5.46233000	1.92910400	0.61482900
H	3.01221700	1.91328200	0.65606400

Co–ordinates for optimized structure 3b/Å

HF/6–31+G(d) = –1196.12137 H (gas phase), –1196.14571 H (in dcm)
MP2/6–31+G(d) = –1198.64102 H (gas phase), –1198.66111 H (in dcm)
B3LYP/6–31+G(d) = –1201.59329 H (gas phase), –1201.61282 H (in dcm)

C	–0.36902700	0.92016500	–0.08963500
C	–1.84028400	0.74359300	–0.07979600
C	–2.61378800	1.85411600	–0.22306400
C	–4.09849000	1.91794800	–0.24000700
C	–4.87807700	0.85226500	–0.12408600
C	0.47278600	–0.11143900	0.07319700
C	1.95154000	0.01535500	0.05949000
O	–2.33848900	–0.56883500	0.07900900
S	–4.07821200	–0.71504900	0.05918500
O	–4.47798200	–1.47469700	1.34674500
O	–4.42387100	–1.72222800	–1.06343100
C	2.72118500	–1.13613100	–0.16590600
C	4.11825500	–1.07409400	–0.17623100
C	4.78047200	0.15291300	0.04831400
C	4.00973800	1.29702900	0.28577400
C	2.61368300	1.23509600	0.29749700
O	6.18352700	0.30251900	0.05140500
C	6.98793900	–0.85678100	–0.16219500
H	0.02389400	1.91470200	–0.25833200
H	–2.12174700	2.81344500	–0.33600600
H	–4.56494500	2.88803700	–0.35552900
H	–5.95722000	0.93477300	–0.14164900
H	0.06606500	–1.10938200	0.18426600
H	2.23955000	–2.09096100	–0.34174900
H	4.66307200	–1.98854300	–0.36119000
H	4.50001800	2.24452100	0.47018300
H	2.06710600	2.14110300	0.51867300
H	8.05559400	–0.56021100	–0.13244700
H	6.78394900	–1.29498800	–1.16284400
H	6.81496900	–1.60599400	0.63973800

Coordinates for optimized structure 3c

HF/6–31+G(d) = –1541.12662 H (gas phase), –1541.14904 H (in dcm)
MP2/6–31+G(d) = –1543.47744 H (gas phase), –1543.49577 H (in dcm)
B3LYP/6–31+G(d) = –1546.65077 H (gas phase), –1546.66865 H (in dcm)

C	1.16338300	2.62047200	0.08411300
C	1.84266900	1.30982900	–0.02879500
C	3.03498900	1.27148400	–0.67912500
C	3.89247000	0.07901800	–0.90697500
C	3.56665300	–1.14267100	–0.50699700
C	–0.16201100	2.78795700	0.21170100
C	–1.17375900	1.71618000	0.07765400
O	1.23623500	0.20535700	0.60893200
S	2.03523800	–1.32646700	0.36139000
O	1.01778400	–2.23801200	–0.36592200
O	2.17344800	–1.99021800	1.75261000
C	–2.24230400	1.66447200	0.98469600
C	–3.22539200	0.67770200	0.86153200
C	–3.15974000	–0.25228200	–0.18155800
C	–2.11522200	–0.18757100	–1.10879000
C	–1.13206300	0.79896300	–0.98893400
Cl	–4.39279100	–1.49071700	–0.33328400
H	1.78158000	3.51098200	0.10680300
H	3.41841600	2.19358800	–1.10275700
H	4.82597400	0.21685000	–1.43818300
H	4.21232200	–1.99097500	–0.69502100

H	–0.52579900	3.78699100	0.42014800
H	–2.30752500	2.37946300	1.79580600
H	–4.03841800	0.63797800	1.57579500
H	–2.06761900	–0.89658200	–1.92554400
H	–0.34307000	0.84903300	–1.72954800

Coordinates for optimized structure dimethylamine/Å

HF/6–31+G(d) = –134.24264 H (gas phase), –134.24711 H (in dcm)
MP2/6–31+G(d) = –134.67395 H (gas phase), –134.67902 H (in dcm)
B3LYP/6–31+G(d) = –135.16935 H (gas phase), –135.17364 H (in dcm)

N	0.00000000	0.00000000	0.00000000
C	1.45628054	0.00000000	0.00000000
C	–0.58801308	1.33231401	0.00000000
H	–0.35474003	–0.54505752	–0.77295395
H	1.91042930	0.50210641	–0.87229986
H	1.83933997	–1.03248636	0.04240737
H	1.81732636	0.51399119	0.90517013
H	–1.68708085	1.26561485	0.03893920
H	–0.30990526	1.95004904	–0.87151906
H	–0.26638823	1.86878485	0.90645546

Coordinates for optimized structure sulphene/Å

HF/6–31+G(d) = –586.13165 H (gas phase), –586.14322 H (in dcm)
MP2/6–31+G(d) = –586.77078 H (gas phase), –586.78054 H (in dcm)
B3LYP/6–31+G(d) = –587.83197 H (gas phase), –587.84705 H (in dcm)

S	0.00000000	0.00000000	0.00000000
O	1.43060092	0.00000000	0.00000000
C	–0.69636681	1.38704660	0.00000000
H	–1.75479895	1.48624657	0.22293220
H	–0.14031796	2.29644644	–0.21200376
O	–0.73083764	–1.08295718	0.58286456

Table 1a Total energies of reactants and products in gas phase.

Compound	R^1	Gas phase total energies/H		
		HF/6-31+G(d)//HF/6-31+G(d)	B3LYP/6-31+G(d)//B3LYP/6-31+G(d)	MP2/6-31+G(d)//B3LYP/6-31+G(d)
1a	Ph	–630.31962	–634.38558	–632.31974
1b	p-CH_3O-Ph	–744.19352	–748.90526	–746.50618
1c	p-Cl-Ph	–1089.20942	–1093.97462	–1091.34619
2a	Ph	–1216.49230	–1222.26338	–1219.15182
2b	p-CH_3O-Ph	–1330.37928	–1336.77452	–1333.34402
2c	p-Cl-Ph	–1675.39513	–1681.84330	–1678.18410
3a	Ph	–1082.23802	–1087.07614	–1084.44719
3b	p-CH_3O-Ph	–1196.12137	–1201.59329	–1198.64102
3c	p-Cl-Ph	–1541.12662	–1546.65077	–1543.47744
Sulfene	–	–586.13165	–587.83197	–586.77078
DMA	–	–134.24264	–135.16935	–134.67395

Table 2a Total energies of reactants and products in DCM.

Compound	R^1	SCRF total energies/H		
		HF/6-31+G(d)//HF/6-31+G(d)	B3LYP/6-31+G(d)//B3LYP/6-31+G(d)	MP2/6-31+G(d)//B3LYP/6-31+G(d)
1a	Ph	–630.33729	–634.40118	–632.33522
1b	p-CH_3O-Ph	–744.20912	–748.91922	–746.52017
1c	p-Cl-Ph	–1089.22402	–1093.98759	–1091.35898
2a	Ph	–1216.51275	–1222.25885	–1219.16901
2b	p-CH_3O-Ph	–1330.40219	–1336.79335	–1333.36349
2c	p-Cl-Ph	–1675.41765	–1681.86169	–1678.20283
3a	Ph	–1082.26134	–1087.07614	–1084.46629
3b	p-CH_3O-Ph	–1196.14571	–1201.61282	–1198.66111
3c	p-Cl-Ph	–1541.14904	–1546.66865	–1543.49577
Sulfene	–	–586.14322	–587.84705	–586.78054
DMA	–	–134.24711	–135.17364	–134.67902