Supplementary Material (ESI) for PCCP

Supporting Information

Title

Chemically Reactive Species Remain Alive inside Carbon Nanotubes: A Density Functional Theory Study

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Contents

1. General Remarks:

We obtained from PW91 DFT calculations optimized geometries for an alkyl radical (methyl, ethyl, isopropyl, and *tert*-butyl radicals) inside tubes with different diameters. The optimized geometries inside the (8,8) and (12,12) tubes are shown in Figures S1 and S2 (Supporting Information). All calculations for the encapsulation of an alkyl radical into a tube were spin polarized. Kinetic energy cutoff of the plane-wave basis is 349.5 eV with ultrasoft Vanderbilt-type pseudopotentials. In this study, a hexagonal supercell is used, containing 160 (240) C atoms of the (8,8) ((12,12)) nanotube and one alkyl radical guest to avoid interactions between the guests located on the neighboring unit cells. We allow full geometry relaxation in the axial direction, but we fixed the inter-tube distances at 6 Å, which is large enough to avoid significant inter-tube interactions. Partially we used Gaussian 03 program to obtain potential energy surfaces of pyramidalization of an isolated alky radical using the same functional with the 6-31G* basis set.

2. Optimized structures for an alkyl radical inside the (8,8) nanotube

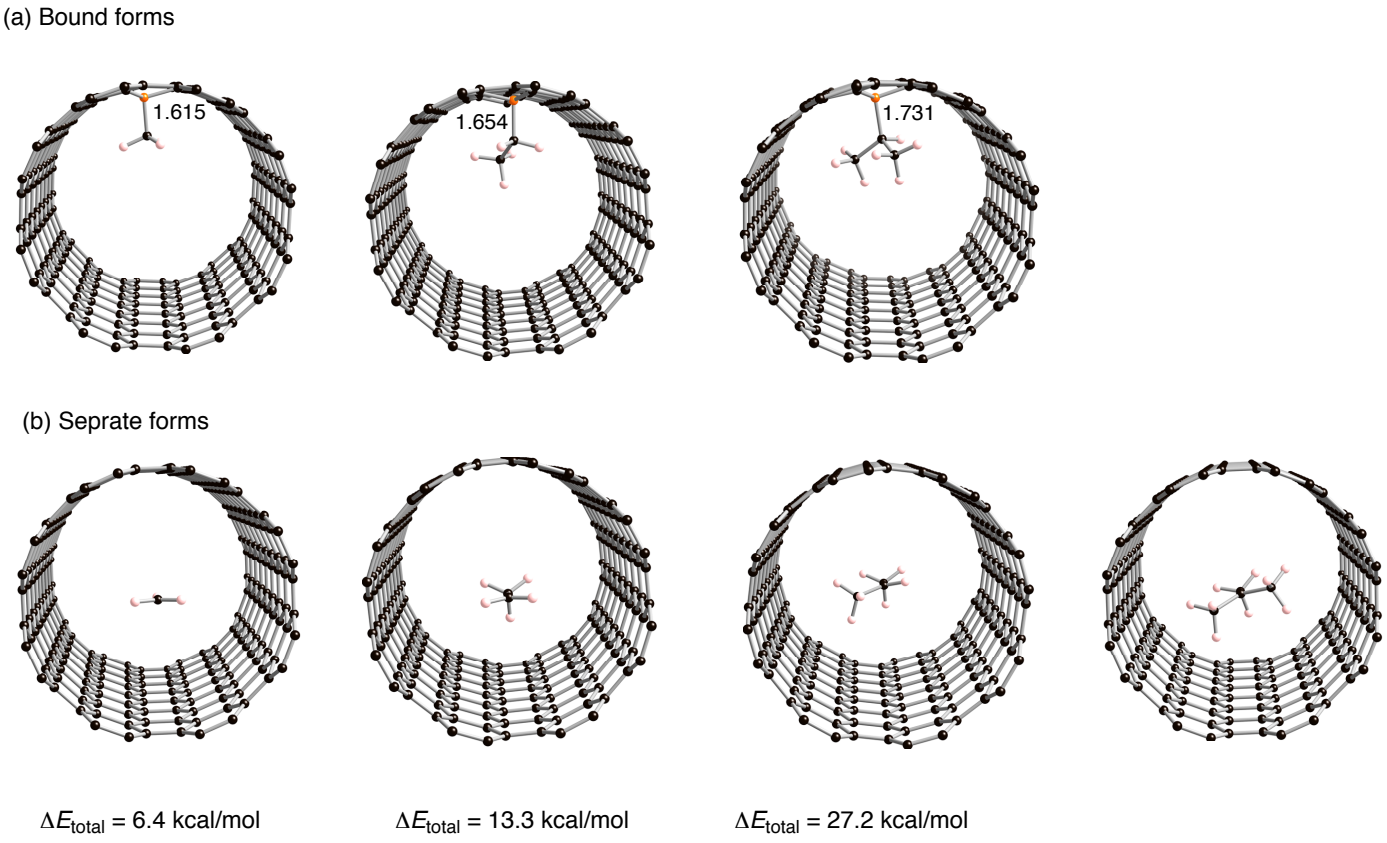

Fig. S1 Optimized structures for an alkyl radical inside the (8,8) nanotube. Methyl, ethyl, isopropyl, *tert*-butyl radicals are considered as a guest from left to right. At the upper structures, an alkyl radical binds into an orange C atom of a tube to make a covalent bond with the inner wall (bound form), whereas at the bottom structures, an alkyl radical exists separately from the tube wall (separate form). Energy differences between the bound and separate forms in an alkyl radical inside a tube, ΔE_{total}, defined as E_{total}(bound form) – E_{total}(separate form). A positive ΔE_{total} value indicates that a separate form is energetically stable relative to a bound form. Bond lengths of the CC bonds formed inside a tube are given in Å.

3. Optimized structures for an alkyl radical inside the (12,12) nanotube

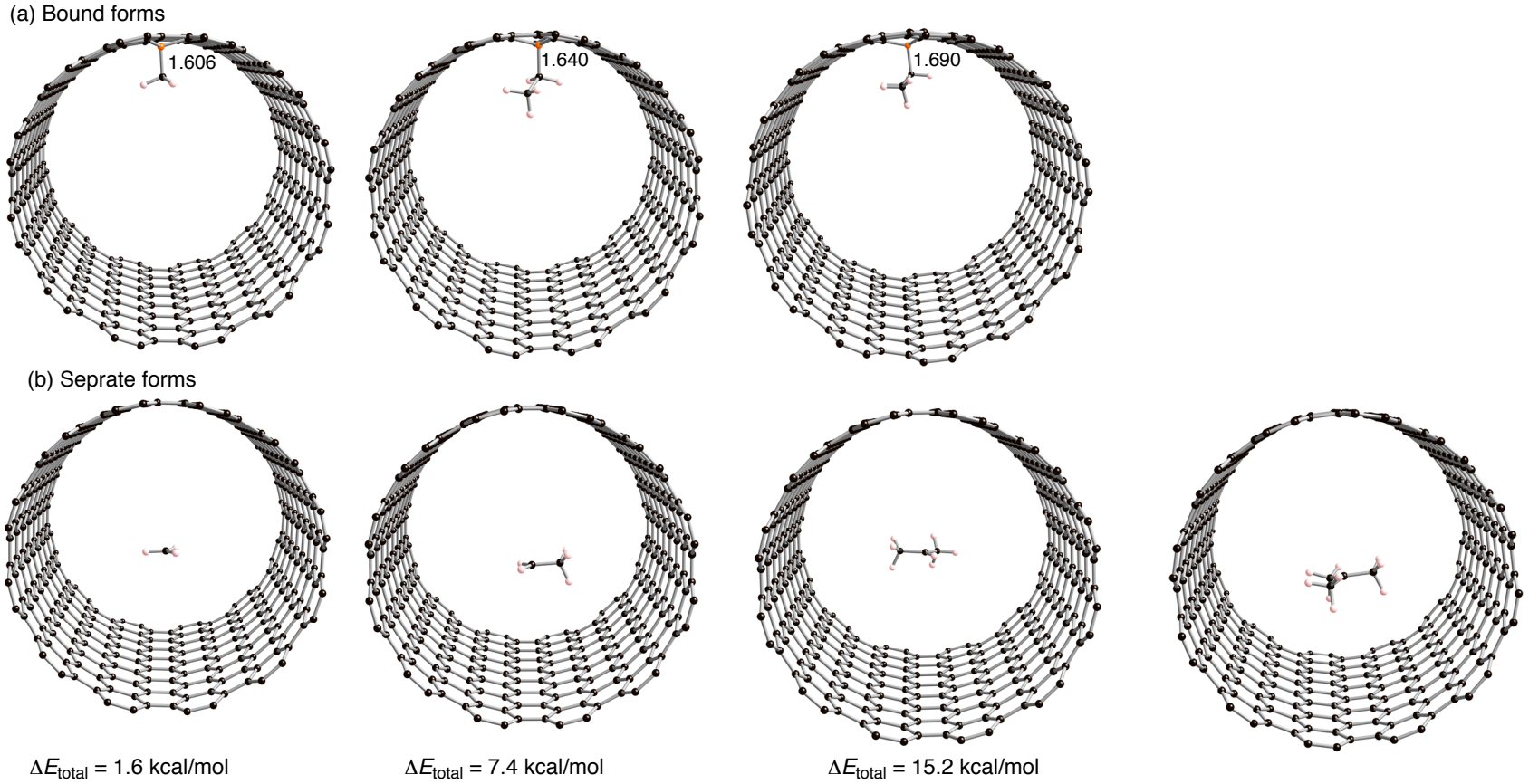

Fig. S2 Optimized structures for an alkyl radical inside the (12,12) nanotube. Methyl, ethyl, isopropyl, *tert*-butyl radicals are considered as a guest from left to right. At the upper structures, an alkyl radical binds into an orange C atom of a tube to make a covalent bond with the inner wall (bound form), whereas at the bottom structures, an alkyl radical exists separately from the tube wall (separate form). Energy differences between the bound and separate forms in an alkyl radical inside a tube, ΔE_{total}, defined as E_{total}(bound form) – E_{total}(separate form). A positive ΔE_{total} value indicates that a separate form is energetically stable relative to a bound form. Bond lengths of the CC bonds formed inside a tube are given in Å.

4. Optimized structures for an alkyl radical binding to graphene.

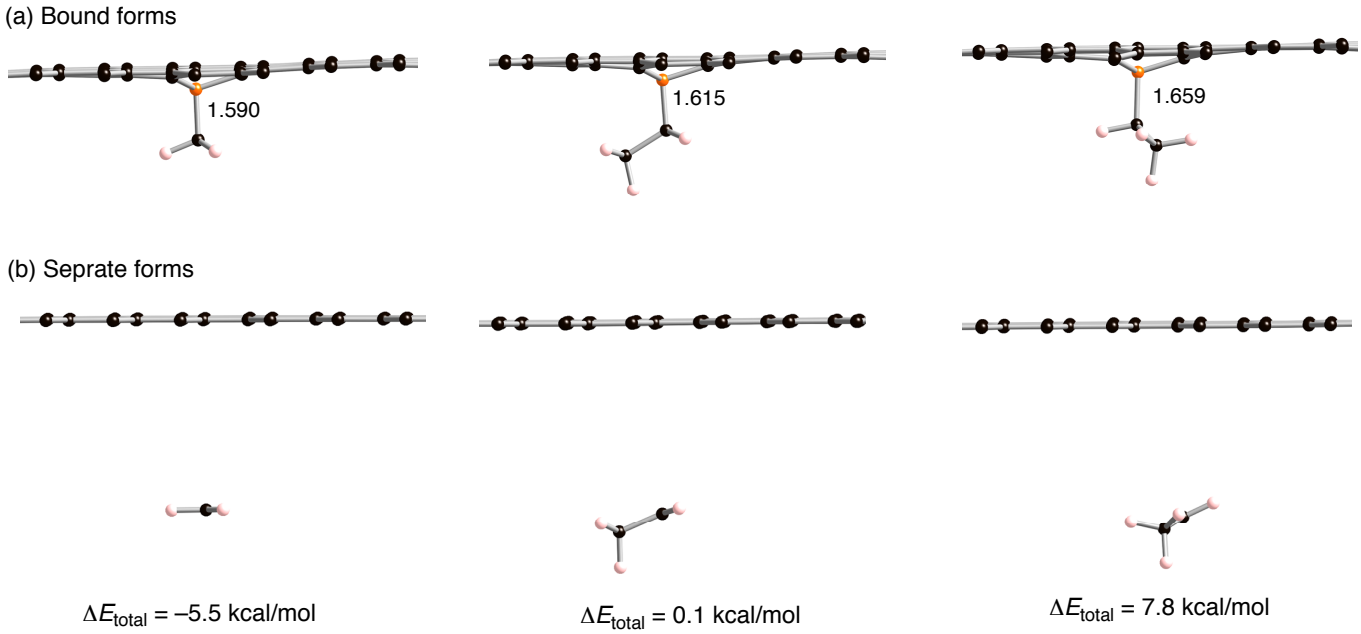

Fig. S3 Optimized structures for an alkyl radical near graphene. Methyl, ethyl, and isopropyl radicals are considered as a guest from left to right. At the upper structures, an alkyl radical binds into an orange C atom of graphene to make a covalent bond with the wall (bound form), whereas at the bottom structures, an alkyl radical exists separately from the graphene wall (separate form). Energy differences between the bound and separate forms in an alkyl radical near graphene, ΔE_{total}, defined as E_{total}(bound form) – E_{total}(separate form). A positive ΔE_{total} value indicates that a separate form is energetically more stable relative to a bound form. Bond lengths of the CC bonds formed inside a tube are given in Å.

5. Pyramidalization of an islocated methyl radical.

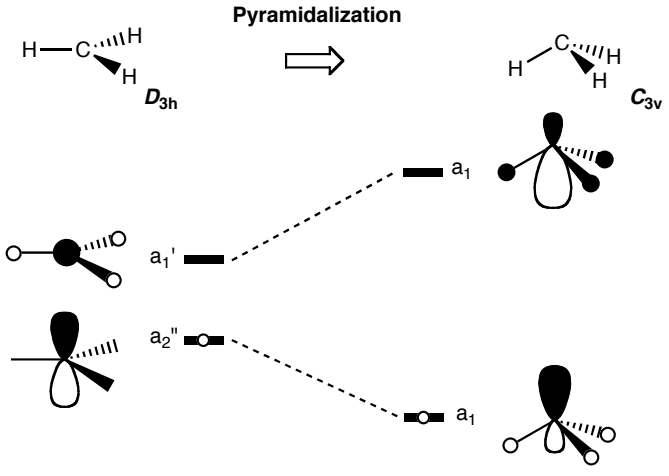

Fig. S4 Pyramidalization of an islocated methyl radical.

6. Detailed information of methyl radicals inside the (10,10) tube and methyl radical bound to graphene.

[A] Optimized geometry for methyl radical existing separately from the (10,10) tube wall

(a) Total energy

-1862.883197 eV

(b-1) Direct lattice vectors

a= (16.9699999999999989 9.8000000000000007 0.0000000000000000)

b= (-16.9699999999999989 9.8000000000000007 0.0000000000000000)

c= (0.0000000000000000 0.0000000000000000 12.3043990035802810)

(b-2) position of ions in fractional coordinates (direct lattice)

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H	0.8622154000932180	0.0967587588655412	0.9237483293025821

H 0.8621826005685885 0.0967460924093186 0.0763931853963103

[B] Optimized geometry for methyl radical bound to the (10,10) tube

(a) Total energy

-1862.761276 eV

(b-1) Direct lattice vectors

a= (16.9699999999999989 9.8000000000000007 0.0000000000000000)

b= (-16.9699999999999989 9.8000000000000007 0.0000000000000000)

c= (0.0000000000000000 0.0000000000000000 12.3079753769969713)

(b-2) position of ions in fractional coordinates (direct lattice)

C 0.1865286753582910 0.3668215000778559 0.0002547190294235

C 0.1207955878210890 0.3843149031914220 0.0002286049698250

C 0.3278717370887701 0.3645016865695438 0.0002320885477938

C 0.9590884295015861 0.3281032495525407 0.0002301602790488

C 0.3973488289798789 0.1256872701618878 0.0002726864403309

C 0.4075322833029990 0.2026323645925587 0.0002634142660682

C 0.3244116730855107 0.9593613129922112 0.0003033505138685

C 0.3724124911968149 0.3261251577390454 0.0002198752784523

C 0.0390127449274156 0.6774660301791200 0.0003164024637735

C 0.1207400503132876 0.7341030994245891 0.0003228057859563

C 0.8728347622172258 0.6068957056907534 0.0003184357346810

C 0.2661805939284113 0.8781220389697030 0.0003250802174542

C 0.7335999801909712 0.1272588408296610 0.0002537673161958

C 0.6781706272758770 0.0451739847995324 0.0002651556506664

C 0.8769722907367269 0.2723353478296532 0.0002452880535157

C 0.6097740473930324 0.8791401748247816 0.0002723669222186

C 0.6321331373580200 0.6766436804020057 0.0002793553151146

C 0.6729504323270378 0.6335922818645578 0.0002804767476575

C 0.5998611550397031 0.8020774800069805 0.0002688939962491

C 0.7960039148689053 0.5976283199350956 0.0003360196696233

C 0.9135751671561910 0.6184767708425465 0.1003691200829057

C 0.7608248287820428 0.6000295011273621 0.1004153149297170

C 0.9970939734275592	0.6539259400405016	0.1003295584531284
C 0.6989537185199638	0.6181105657990210	0.1003532036380963
C 0.3484416446016117	0.0011592433895077	0.1004314674254234
C 0.2329447292117379	0.8390791396584028	0.1003872418017082
C 0.3852056903463204	0.0847397174626187	0.1004519470815027
C 0.1599979136293981	0.7668109803557502	0.1003842346841547
C 0.3004738936745215	0.3785984047051305	0.1011327498538700
C 0.3884634663946109	0.3004464372178108	0.1006864209828211
C 0.2344467671185600	0.3886889878177347	0.1022164467629322
C 0.4058132874109734	0.2382441737552147	0.1004998906797082
C 0.6012464516119718	0.7665246103458769	0.1003443414330360
C 0.6207865741496090	0.9197369784779054	0.1002990839749286
C 0.6174721211041857	0.7034223969955790	0.1002841103127297
C 0.6551895599772568	0.0031483214480481	0.1002145717376578
C 0.8380733677801632	0.2395419481890879	0.1004100905047060
C 0.0009476947337952	0.3498837713102805	0.1002978652709333
C 0.7658772120400456	0.1665152713465377	0.1003724986383866
C 0.0836440636586214	0.3789919635772954	0.0998821860765556
C 0.7608114548505851	0.5999403123490588	0.9002411775255604
C 0.9135513157322720	0.6183603332936507	0.9002989511651925
C 0.6989334821485930	0.6180254685211396	0.9002643436871316
C 0.9970793191475870	0.6538898658438422	0.9003279418008088
C 0.6208967830409793	0.9197558135446461	0.9002478149458414
C 0.6013438369253894	0.7665519341337739	0.9002204065920474
C 0.6552648134337559	0.0031622618761194	0.9003023625633786
C 0.6175233290381642	0.7034271262231155	0.9002656965712020
C 0.0009505555296008	0.3498849322161932	0.9001698615126100
C 0.8380558025964910	0.2395592083186925	0.9000960446455832
C 0.0836444220764110	0.3789762109827390	0.9005731491203943
C 0.7658604209724355	0.1665276198849860	0.9001560468244202
C 0.2329684944861475	0.8390922272669571	0.9002784113757194
C 0.3485584522897552	0.0011670912694554	0.9001860363733409
C 0.1600029369874580	0.7668323249775681	0.9003184672104825
C 0.3852901683482066	0.0847425633386726	0.9001215879409262
C 0.3885033599138927	0.3004461080221242	0.8997951437464767
C 0.3004840736482244	0.3785888943851375	0.8993291898611894

C	0.4058310271104889	0.2382235301258790	0.9000136616853307
C	0.2344735841997568	0.3887170637840835	0.8982573112690020
C	0.6729168351355160	0.6337397622349544	0.2002352400482403
C	0.6318469152367094	0.6765394355679816	0.2003068589422363
C	0.7960754918555851	0.5979843532018982	0.2004388262339882
C	0.5994063789111141	0.8019768171258573	0.2002908517344252
C	0.1208284723225960	0.7340043487046682	0.2002785515372165
C	0.0390210821310050	0.6773427221410884	0.2002714165698209
C	0.2661142274696591	0.8778769896242711	0.2003379049032325
C	0.8729137626939816	0.6072839575360073	0.2003131813035535
C	0.4075796951020559	0.2028221903586280	0.2004969353632580
C	0.3971480665582970	0.1255591985142914	0.2003986693247909
C	0.3732074828232915	0.3268332841586805	0.2005034049675698
C	0.3241258969033687	0.9592781134228175	0.2003435011292511
C	0.6777760139542945	0.0449963695697576	0.2002264649484883
C	0.7335391075941865	0.1270648594874424	0.2002427740049400
C	0.6092283945660900	0.8790189304209960	0.2002995840253192
C	0.8774423873621913	0.2717881528670007	0.2004806411566352
C	0.1245687342646980	0.3878031338452571	0.2000987508386807
C	0.2014464595929842	0.3956861744945510	0.1997197555822468
C	0.9596275990482775	0.3271348572205565	0.2005158824949021
C	0.3298139854035826	0.3673570825450950	0.2009756137377259
C	0.2014150076412704	0.3955952724693052	0.8007305329671983
C	0.1245567156347510	0.3877416588119276	0.8003509531140142
C	0.3298201102008471	0.3673293113050204	0.7994843249826052
C	0.9596347205115600	0.3271183737973244	0.7999593720699921
C	0.3972704280412058	0.1255643432418410	0.8001460245853138
C	0.4076150062233431	0.2027917548844582	0.8000228056245065
C	0.3242821977674307	0.9592982473570306	0.8002554596238479
C	0.3732400523305880	0.3268221734343645	0.7999671885663796
C	0.0390084009736496	0.6773568626505805	0.8003986245860524
C	0.1208083158931492	0.7340210045232357	0.8004300716342790
C	0.8728809404898881	0.6071025525161591	0.8003372018857599
C	0.2661690809916438	0.8779166559437194	0.8002954113415330
C	0.7335601194972280	0.1270777893774144	0.8002665618888070
C	0.6778645402312471	0.0450146125921640	0.8002796300130848

C	0.8774451324833941	0.2717936504064962	0.8000058570694767
C	0.6093769846203093	0.8790481580634516	0.8002367413314951
C	0.6319113852917450	0.6765335008885341	0.8002585889466931
C	0.6729202494001407	0.6336583771027257	0.8003558314929271
C	0.5995437046739026	0.8019996248605946	0.8002444459128142
C	0.7960413852918624	0.5978336746898131	0.8001942143891347
C	0.3016560490807312	0.3810075390566309	0.3004000315765379
C	0.3878730482922222	0.3002867709493396	0.3005356722646964
C	0.2384104817259657	0.3969634722564240	0.3001638861777489
C	0.4055040493628398	0.2382184297059110	0.3004548647885644
C	0.8386400295770393	0.2388456844312318	0.3005262207963315
C	0.0020829232777978	0.3480210325080438	0.3002237835257409
C	0.7660572649164736	0.1661942617360634	0.3004333646253056
C	0.0854884610537500	0.3794866908927577	0.2997635853737153
C	0.6006880259171903	0.7663585243575688	0.3003614249370695
C	0.6201261406511694	0.9195863798001842	0.3003500156004609
C	0.6171153876478217	0.7033455141025950	0.3002816261112802
C	0.6546285492749137	0.0029902987794250	0.3002287113360188
C	0.3479165211254130	0.0010181775964831	0.3004206527226970
C	0.2329055286611042	0.8389307897404557	0.3003838162301585
C	0.3847919513633513	0.0846209702724794	0.3003953072124576
C	0.1600309205188658	0.7666516359349445	0.3004227917771925
C	0.9136797758513763	0.6190394999527223	0.3003932467567926
C	0.7608997347146039	0.6004579274686656	0.3004541251929473
C	0.9971397874648774	0.6540132888766419	0.3003203199811618
C	0.6990867037282774	0.6185556725173647	0.3003920924200954
C	0.7608861009846044	0.6003415738897341	0.7001493591242698
C	0.9136463220862441	0.6188499768755470	0.7002579948447237
C	0.6990505846821784	0.6184245779232542	0.7002011974090473
C	0.9971179663582072	0.6539573092397976	0.7003522033636856
C	0.6202294756330281	0.9195983362543423	0.7001782755886986
C	0.6007973853818560	0.7663771894829350	0.7001660697008908
C	0.6547110302020143	0.0030042582286889	0.7002882647196236
C	0.6171917547305489	0.7033480226271720	0.7002801399128151
C	0.0020935707945950	0.3480200667640015	0.7002431325134237
C	0.8386313559622378	0.2388473281027317	0.6999445264869413

C	0.0854783886433992	0.3794478775719820	0.7006811232331039
C	0.7660554172495297	0.1662002347578403	0.7000554382006144
C	0.2329286800663938	0.8389406256557210	0.7002672908132521
C	0.3480687927468109	0.0010408844737218	0.7001437244197382
C	0.1600320040587086	0.7666732897673948	0.7003115971442891
C	0.3849025888824532	0.0846296655027781	0.7001308454309314
C	0.3879267631154354	0.3002822074349381	0.6999330871475301
C	0.3016651936180813	0.3809789950579769	0.7000529129952066
C	0.4055126229950976	0.2381752540565856	0.7000417760269682
C	0.2383651168455279	0.3968562144942081	0.7002809947951142
C	0.6729277608613040	0.6340102320106602	0.4002853678667150
C	0.6316401374144888	0.6765457818005400	0.4002965767837160
C	0.7961958019962310	0.5984135911866765	0.4003733757676866
C	0.5989386481197531	0.8018549790632377	0.4002859289959345
C	0.1208949304976927	0.7338338998643613	0.4003849949333712
C	0.0390693259236111	0.6772332051438387	0.4003383737551845
C	0.2660045927927809	0.8777449074652738	0.4003570511051603
C	0.8730251664079269	0.6078334385648915	0.4003410300743193
C	0.4071258569980440	0.2026400222038390	0.4004151065420868
C	0.3967107597124063	0.1254689615022896	0.4003693465155037
C	0.3717508393209895	0.3260441075806491	0.4004224902644512
C	0.3237200369982829	0.9591468591535991	0.4003492491838300
C	0.6773349995717105	0.0448477197654895	0.4002543905667727
C	0.7334571386351824	0.1268626309434388	0.4002636628843990
C	0.6087274916263689	0.8788664337955879	0.4002830222063385
C	0.8781371016379741	0.2709116181304856	0.4003488089231257
C	0.1262898623573449	0.3901551717490991	0.4001950812405257
C	0.2030165297337947	0.3992704560520226	0.4001641051944186
C	0.9605545608661017	0.3257345786300818	0.4003187236133795
C	0.3285717068594756	0.3665655703101474	0.4005400582013715
C	0.2029926745084674	0.3992070880689820	0.6002712750480640
C	0.1262777850503872	0.3901232185167383	0.6002354974185308
C	0.3285836176211798	0.3665576795639970	0.5999142905235791
C	0.9605563206072020	0.3257495381924189	0.6001658204877045
C	0.3967620247516668	0.1254674457028465	0.6001399595839517
C	0.4071399952125850	0.2026233849314290	0.6000686730276077

C	0.3237975467041285	0.9591605554927591	0.6002245204421793
C	0.3717890265945396	0.3260530285501161	0.6000584617944436
C	0.0390526077844546	0.6772264134514449	0.6003672131485370
C	0.1208698876248449	0.7338351147305030	0.6004103038830224
C	0.8729935585616571	0.6076947455772654	0.6003010890917440
C	0.2660405757750527	0.8777657283744733	0.6002804706622344
C	0.7334643790912009	0.1268623398506439	0.6002566482088244
C	0.6773721966247034	0.0448487960712789	0.6002616283783965
C	0.8781387319153440	0.2709213464024941	0.6001236456005055
C	0.6087803444373394	0.8788758735596519	0.6002426796540765
C	0.6316771370762639	0.6765346489625147	0.6002662238735723
C	0.6729262078723147	0.6339504265374437	0.6003182940369763
C	0.5990035449061653	0.8018667162830196	0.6002502938781902
C	0.7961711907265513	0.5983214655003907	0.6002032766795949
C	0.3014201673457450	0.3809106074874212	0.5002178654953982
C	0.3872627091075050	0.3000076930407610	0.5002259528989756
C	0.2385919385710698	0.3977616003379835	0.5002118285878449
C	0.4052855553006426	0.2381105573512843	0.5002357065127465
C	0.8388978255444021	0.2385306409046211	0.5002308262995407
C	0.0025531344492711	0.3474923672356189	0.5002322854441146
C	0.7660967589011526	0.1660478495734452	0.5002533176565821
C	0.0860410805834594	0.3799980193684632	0.5002071516352975
C	0.6005310953975596	0.7663237145000333	0.5002606684128642
C	0.6199020860153049	0.9194977321747650	0.5002568429436449
C	0.6170103758167076	0.7033376623352681	0.5002838671898567
C	0.6543819633663434	0.0028925276804080	0.5002587079098180
C	0.3477249312484859	0.0009111589734946	0.5002602815397945
C	0.2329236610418161	0.8388858761481164	0.5003244695898630
C	0.3846480243666717	0.0845911081326220	0.5002482872608798
C	0.1600706882757597	0.7665020955143028	0.5004173839070369
C	0.9136988727359138	0.6192310135630151	0.5003076802254046
C	0.7609227803965879	0.6005974233290521	0.5002727069183815
C	0.9971671909860779	0.6540086444427565	0.5003403732857443
C	0.6991431314970663	0.6187406170672609	0.5002732799806975
C	0.1396977198572769	0.2722466333351455	0.0001121511951568
H	0.1024746956480158	0.2505103129671278	0.0726688800856378

H 0.1025628285644545 0.2506361046057928 0.9274632694369956
H 0.1816277991359559 0.2507602607351542 0.0000979648354848

[C] Optimized geometry for methyl radical bound to graphene.

(a) Total energy

-481.783504 eV

(b-1) Direct lattice vectors

a= (10.6595837724395750, 6.1554451173861313, 0.0000000000000000)
b= (-10.6595789398152352, 6.1554581291218966, 0.0000000000000000)
c= (0.0000000000000000, 0.0000000000000000, 12.0000000000000000)

(b-2) position of ions in fractional coordinates (direct lattice)

C 0.4335110250832557 0.5664889922224603 0.0022843199478118
C 0.3667447036337990 0.6332555517804508 0.0001740283938574
C 0.2335937905269816 0.5666692527437149 0.9997742591120442
C 0.0335508255312789 0.5662995453157436 0.9996548593862329
C 0.1669861637806065 0.6332048117202476 0.9986815102718367
C 0.8338957989689035 0.5664668705986458 0.0039851141153093
C 0.9670634938688920 0.6330526507581808 0.0014237157628543
C 0.2337105349075941 0.7662891804429677 0.9984058193321133
C 0.1670136326641298 0.8329867430255362 0.0007928440525049
C 0.0340130762080122 0.7663672712563923 0.0030542874147912
C 0.9679501041656877 0.8334645456919390 0.0112211023317883
C 0.8335657037691035 0.7661557158199486 0.0125932167671436
C 0.7674018135174663 0.6338173401053595 0.0073928066870437
C 0.6334866428179566 0.5664959160092380 0.0055923289327069
C 0.2336325512872790 0.9659867545480552 0.0030548855991981
C 0.1665357198754478 0.0320501420952795 0.0112214781324411
C 0.0351020383538767 0.9648978311914647 0.0192103807434520
C 0.9672488762765141 0.0327512307451983 0.0536467934085110
C 0.8310788322671883 0.9651279740109828 0.0207645865809312
C 0.7665888846085096 0.8335669105315304 0.0129703555083225
C 0.6332760916688258 0.7664769243425695 0.0053831466549283
C 0.5668058208595781 0.6330521691232818 0.0040492301358555

C	0.5667637768361971	0.8330456802567099	0.0027678980878036
C	0.6333778047930991	0.9660942422487437	0.0039150399947587
C	0.7666607981241071	0.0321578976479628	0.0120447877144088
C	0.0348719938883164	0.1689210408904600	0.0207644381813594
C	0.9678422404793281	0.2333391855449705	0.0120444511767559
C	0.8335127859987495	0.1664871741996024	0.0115100820029852
C	0.7673622856393720	0.2326377737830256	0.0055456142268753
C	0.6335575276169649	0.1661567958190986	0.0030537130542925
C	0.5668767226834674	0.0330068492242219	0.0015068484440448
C	0.0339057055531313	0.3666219794470180	0.0039149957829352
C	0.9669932858779191	0.4331232503781806	0.0015076549206583
C	0.8338431781003024	0.3664424110673750	0.0030541793520911
C	0.7671502872761238	0.4331268922149363	0.0033750740501830
C	0.6336477972045813	0.3663522465001492	0.0043364893731450
C	0.5668732587887035	0.2328498508845840	0.0033746772067147
C	0.5668807957056927	0.4331193550729182	0.0049394495190711
C	0.1669545687128746	0.4332363304533828	0.0027678155636224
C	0.1664333573642409	0.2334112500092402	0.0129703032325210
C	0.2335230253760727	0.3667238296411881	0.0053830590560082
C	0.3669481037738862	0.4331944614373242	0.0040493289770822
C	0.2338442435186252	0.1664342958026239	0.0125934451450647
C	0.3661827893115230	0.2325982451868143	0.0073929087465032
C	0.4335039472401618	0.3665132953703889	0.0055925062102702
C	0.3669475473652568	0.0329368023621228	0.0014233134789308
C	0.4335331686610076	0.1661042800105719	0.0039846784011459
C	0.3667953122857099	0.8330140291555566	0.9986809893788688
C	0.4337001745037199	0.9664489652867445	0.9996538177517564
C	0.4333305616374830	0.7664060745020151	0.9997741044214621
C	0.9681957351727135	0.0318036329373825	0.1861148386091855
H	0.9199710842219275	0.0800259334515232	0.2178177089269440
H	0.9199543361776108	0.9347385917003663	0.2161875168691125
H	0.0652604656447053	0.0800464163247625	0.2161883695386067

7. Full authors list in Ref. 33

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