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Determination of the Heats of Formation of the Isomeric Xylylenes by Ion Cyclotron Double-Resonance Spectroscopy

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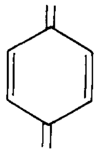
Abstract: Heats of formation of 50 and 53 kcal mol^{-1} have been measured for *p*- and *o*-xylylene by using pulsed-ion cyclotron double-resonance spectroscopy. In addition a lower bound of 76 kcal mol^{-1} has been obtained for the heat of formation of gaseous *m*-xylylene.

The family of C_8H_8 hydrocarbons comprises a variety of interesting and much studied compounds, ranging in stability from styrene to the highly strained cubane. One series of C_8H_8 isomers which have yet to be isolated are the xylylenes (1-3).



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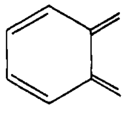

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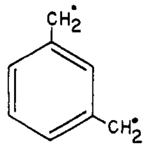

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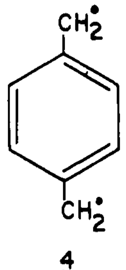
p-Xylylene (**1**) or *p*-quinodimethane[2] (3,6-bis(methylene)-1,4-cyclohexadiene) was originally detected as the reactive intermediate in the polymerization of the pyrolysis products both of *p*-xylene[2b] and of [2.2]paracyclophane.[2c] While unstable at room temperature in the condensed phase, electron diffraction[3] and photoelectron spectra[4] have been observed for the gaseous pyrolysate of [2.2]paracyclophane. By trapping the pyrolysate at liquid-nitrogen temperatures and dissolution of **1** in THF-d_8 at -80 °C, Pearson and co-workers were able to obtain an ^{1}H NMR spectra.[4a] This same group later succeeded in obtaining the UV and IR spectra of **1** trapped on a window at 77 K. Recently, it was reported[5] that **1** could also be obtained by the base-catalyzed elimination of methanol from 4-(methoxymethyl)toluene, this yielding the characteristic poly-*p*-xylylene product. Both these experimental studies as well as previous theoretical work[6] support a structure for *p*-xylene such as **1** as opposed to the alternative biradical form **4**. Structure **1** also appears to provide the best fit to the electron diffraction data.[3]



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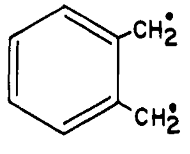

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o-Xylylene (**2**) or *o*-quinodimethane (5,6-bis(methylene)-1,3-cyclohexadiene) has been extensively studied by Michl and others.[7] While no condensed phase spectra have been observed, matrix UV, IR, and Raman spectra have been obtained on pyrolysis products from several precursors. All spectroscopic data are consistent with the *o*-quinoid structure **2** and not with the alternative biradical form **5**.[8] Such an assignment is also supported by theoretical work[6] and by the observation that *o*-xylylene, generated in solution by base-catalyzed elimination of methanol from 2-(methoxymethyl)toluene, forms an isolable Diels-Alder adduct with cyclopentene.[5]

The available literature on *m*-xylylene (**3**) or *m*-quinodimethane is much more sparse. The UV spectrum of the species, obtained as a product of the photolysis of either m-xylene or mesitylene in a glassy hydrocarbon matrix at 77 K, has been interpreted in terms of a biradical structure.[9] This is supported by theoretical work[6,8] which further suggested a triplet electronic ground state. Michl and co-workers[7a] have failed to uncover evidence for **3** by using methodology similar to that successfully employed by them for *o*- and *p*-xylylenes.

All three xylylenes undergo polymerization above -80 °C. The high reactivity of these molecules, more so than their low thermal stability, appears to be the major factor which has made their characterization difficult. It has, thus far, also precluded measurement of their relative thermochemical stabilities by conventional means. In such cases as these ion cyclotron resonance (ICR) spectroscopy offers a viable alternative means of obtaining thermochemical data. The basis of the experimental technique, which has now been successfully applied to the determination of the thermochemical stabilities of a variety of labile neutral molecules,[10] is the measurement of the proton affinity of the species in question by using the double-resonance bracketing technique.[10a,11] In this work we utilize this technique to determine the proton affinities of the three isomeric xylylenes. These values,

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(1) Regents Dissertation Fellow, 1979-1980.

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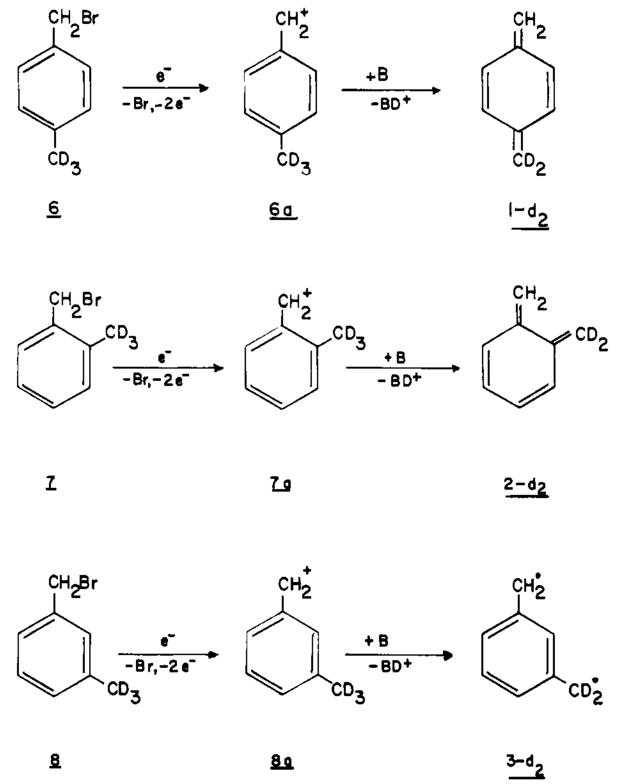
Scheme I



in conjunction with other thermochemical data, allow us to determine the heats of formation of these interesting and highly reactive molecules.

Results and Discussion

We have measured the proton affinities of the three xylylenes via Scheme I.

Each of the labeled methylbenzyl cations is formed from the corresponding α-bromoxylene precursor via electron impact and in the presence of some base B of known proton affinity. Under these conditions and with the assumption that neither label scrambling nor positional isomerization has occurred, formation of the appropriate xylylene may be inferred by detection of an ion of mass corresponding to BD^+. This will occur only if deuteron transfer (from methyl-d_3-benzyl cation to B) is exothermic, thermoneutral, or only slightly endothermic. The proton affinity of the neutral xylylene is taken to lie midway between the proton affinity of the weakest base capable of effecting deuteron abstraction (as confirmed by double resonance[10a,11]) and that of the strongest base incapable of reaction. Our experimental results are presented in Table I.

Due to the finite resolution of the gas-phase basicity scale, the difficulty in assessing how endothermic a deuteron transfer might be and still be observed, and the uncertainty in the absolute value for the enthalpy of protonation of our standard base, ammmonia,[12] we expect an error of no greater than 4 kcal mol^{-1} in the measured proton affinities. Given this degree of uncertainty, the proton affinities of *p*- and *o*-xylylene determined in this work, −11.6 ± 4 and −10.8 ± 4 kcal mol^{-1} relative to ammonia, respectively, are the same within experimental error. On the other hand, the proton affinity of **3** is markedly different. In fact, none of the bases available to us proved capable of abstracting deuterium from **8a**. This places a lower bound of −32.5 kcal mol^{-1} (relative to NH_3) on the proton affinity of *m*-xylylene.

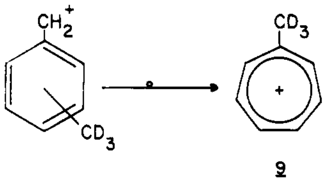
Table I. Observation by ICR Spectroscopy of Deuteron Abstraction from Methyl-d_3-benzyl Cations

abstracting base B	enthalpy of protonation of B (relative to NH_3),[a] kcal mol^{-1}	Is BD^+ observed?[b] 6a	7a	8a
2-F-pyridine	−6.6[c]	no		no
3-CF_3-pyridine	−8.3[c]	no	no	
$[(CH_3)_3C]_2S$	−8.7[c]	no		
2-Cl-pyridine	−10.2[c]	no		
3-Cl-pyridine	−10.7[c]		no	
$CF_3CH_2N(CH_3)_2$	−10.9[c]		yes	
$CH_3CH_2NH_2$	−12.5	yes		
$CH_3(CH_2)_2NH_2$	−14.2	yes	yes	no
$(CH_3)_2CHNH_2$	−15.2	yes	yes	
$CH_3NHCH_2CH_3$	−19.4			no
$[(CH_3)_2CH]_2NH$	−26.0[c]			no
$(CH_3CH_2)_3N$	−28.5			no
4-$(CH_3)_2$N-pyridine	−32.5[c]			no

[a] Unless otherwise noted, from: R. W. Taft In "Proton Transfer Equilibria", E. F. Caldin and V. Gold, Eds., Wiley-Halstead: New York, 1975, p 31. The published gas phase basicities have been slightly modified in view of higher ambient temperatures in the ICR spectrometer than previously believed. [b] Observation of BD^+ derived from benzyl cation confirmed by both fixed H_1-swept ω_2 scan and fixed ω_2-swept H_1 scan (see ref 10a). [c] Unpublished data of R. W. Taft.

It is possible that the inability to observe deuteron abstraction in the meta compound may be due to a kinetic effect; e.g., the rate of deuteron transfer might be slower than is capable of being observed in the time frame of the ICR experiment. However, these authors see no inherent reason for such a difference in deuteron transfer rate in the ortho or para isomers and in the meta isomer, other than the basic thermochemical stability differences.

Before preceeding, we should comment on the structural integrity of the benzyl cations. Rearrangement of this system to methyltropylium **9** seems to be ruled out given that different



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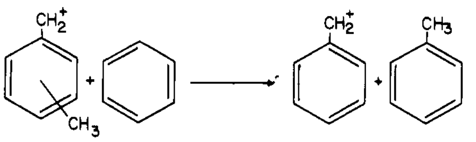
deprotonation thresholds have been obtained for each of the isomeric methylbenzyl cations or, more precisely, for the meta isomer relative to the ortho and para forms. This same observation also appears to preclude the possibility of interconversion of the precursor cation to a common form. Work of McLafferty on the $C_8H_9^+$ manifold should also be noted.[13] Using collisional activation mass spectroscopy, he has found that the isomeric methylbenzyl cations retain unique structures with regard to both types of rearrangements. Such a result is also in accord with MINDO/3 calculations performed by Dewar[14] on the $C_7H_7^+$ system.

To be able to ascribe relative stabilities and absolute heats of formation to the xylylenes, we also require heats of formation for the precursor benzyl cations. Unfortunately, there exist no reliable experimental thermochemical data on these ions. We have, therefore, obtained heats of formation for the methylbenzyl cations by combining calculated energies of isodesmic reactions[15] (eq 1)



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(12) The original value of 202.3 kcal mol^{-1} for the absolute proton affinity of ammonia derived from ICR spectroscopy[2] has been revised upward by more recent work: 203.6 kcal mol^{-1} (S. T. Ceyer, P. W. Tiedmann, B. H. Mahon, and Y. T. Lee, *J. Chem. Phys.*, **70**, 14 (1979)); 207 kcal mol^{-1} (F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4067 (1974)); 209.2 kcal mol^{-1} (R. G. McLoughlin and J. C. Traeger, *ibid.*, **101**, 5791 (1979)).

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Table II. 3-21G Geometry of Benzyl Cation[a,b]

bond lengths, Å		bond angles, deg	
C_1C_2	1.356	$C_3C_2C_3'$	118.9
C_2C_3	1.434	$C_2C_3C_4$	120.2
C_3C_4	1.362	$C_3C_4C_5$	119.3
C_4C_5	1.400	$C_4C_5C_4'$	122.3
H_1C_1	1.074	$H_1C_1H_1'$	116.7
H_2C_3	1.072	$H_2C_3C_2$	119.1
H_3C_4	1.069	$H_3C_4C_3$	120.9
H_4C_5	1.072		
$E = -267.38046$ au			

[a] Held to C_{2v} symmetry. [b] Numbering as per structure

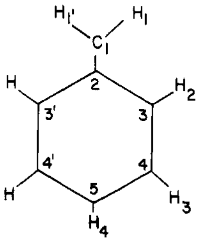

Table III. 3-21G Geometry of Toluene[a,b]

bond length, Å		bond angles, deg	
C_1C_2	1.518	$C_3C_2C_3'$	118.6
C_2C_3	1.388	$C_2C_3C_4$	120.8
C_3C_4	1.384	$C_3C_4C_5$	120.2
C_4C_5	1.384	$C_4C_5C_4'$	119.5
H_1C_1	1.086	$H_1C_1H_2$	108.0
H_2C_1	1.083	$H_2C_1H_2'$	108.2
H_3C_3	1.073	$H_1C_1C_2$	110.5
H_4C_4	1.072	$H_2C_1C_2$	111.0
H_5C_5	1.072	$H_3C_3C_2$	119.5
		$H_4C_4C_3$	119.8
$E = -286.40186$ au			

[a] Held to C_s symmetry. [b] Numbering scheme as per structure

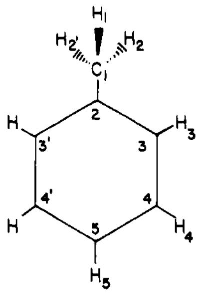

Table IV. 3-21G Energies of Isomeric Methylbenzyl Cations[a]

isomer	energy, hartrees	isomer	energy, hartrees
ortho	−306.20506	para	−306.21112
meta	−306.20395		

[a] Geometries as per text.

Table V. Experimental and Calculated Heats of Formation of Some C_8H_8 Hydrocarbons

compd	$\Delta H_f°$(exptl), kcal mol^{-1}	$\Delta H_f°$(calcd),[a] kcal mol^{-1}
styrene	35.3[b]	35.2
benzocyclobutene	47.7[c]	49.2
p-xylylene	50[d]	49.3
o-xylylene	53[d]	54.2
cyclooctatetraene	71.1[b]	71.3

[a] Calculated as per ref 28. [b] Reference 18. [c] Reference 27. [d] This work.

with experimental heats of formation for benzene, toluene, and benzyl cation. The structure and energy for benzyl cation and toluene have been calculated by using nonempirical molecular orbital theory and the recently introduced 3-21G split-valence basis set.[16] They are presented in Tables II and III. The 3-21G level energy for benzene has previously been reported.[17] The energies for the isomeric methylbenzyl cations, obtained by using the optimized 3-21G benzyl cation structure and substitution of a methyl group (optimized structure based on propane[17b]), appear in Table IV. With use of these data, ΔE values of 2.4, 1.7, and 6.2 kcal mol^{-1} for reaction 1 starting from *o*-, *m*-, and *p*-methylbenzyl cations, respectively, have been obtained. Given the experimental heat of formation for benzene (19.8 kcal mol^{-1})[18] and toluene (12.0 kcal mol^{-1}),[18] we only require the experimental heat of formation of benzyl cation, along with the above determined ΔE of reaction, to determine the heats of the methylbenzyl cations.

The heat of formation of benzyl cation has been the subject of much controversy. Published values range from 213 to 220 kcal mol^{-1} with theory favoring the upper end of the range.[14,19] The most recent data is based on the ionization potential of benzyl radical, as measured by photoelectron spectroscopy, combined with the heat of formation of benzyl radical.[20] While the former quantity (the IP of benzyl radical) seems to be relatively well established, recent work in this laboratory and in others finds the accepted published value for the heats of formation of the corresponding radical to be too low.[21,22] Our own value for $\Delta H_f°$ for benzyl free radical (48.0 kcal mol^{-1})[21] used in conjunction with the ionization potential from photoelectron spectroscopy (7.2 eV)[20] yields a heat of formation for benzyl cation of 214 kcal mol^{-1}.

Such a value is consistent with a heat of formation of 213 kcal mol^{-1} for benzyl cation arrived at in an independent fashion, from the equilibrium constant for chloride exchange between the benzyl and *tert*-butyl cations,[19b] together with the heats of formation of the neutral reactants as well as that for *tert*-butyl cation. The heat of formation for the *tert*-butyl cation of 165 kcal mol^{-1}, itself still subject to some controversy,[23] has been arrived at by combining Pacansky's value of 10.5 kcal mol^{-1} for the heat of formation of the corresponding free radical[24] together with the adiabatic ionization potential of the radical as determined by Beauchamp and Houle.[25]

Using a value of 214 kcal mol^{-1} for $\Delta H_f°$ for benzyl cation, we arrive at heats of formation of 206, 204, and 205 kcal mol^{-1} for *p*-, *o*- and *m*-methylbenzyl cations, respectively. These data,

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(15) For discussion see: W. J. Hehre, *Acc. Chem. Res.*, **9**, 399 (1976).

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(17) (a) $E_{3\text{-}21G}$(benzene) = −229.41945 au. (b) R. A. Whiteside, J. S. Binkley, R. Krishman, D. J. DeFrees, M. B. Schlegel, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Archive.

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(23) (a) 8.4 kcal mol^{-1}: M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, **11**, 969 (1979). (b) 8.4 kcal mol^{-1}: K. Y. Choo, P. C. Beadle, L. W. Piszkieicz, and D. M. Golden, *ibid.*, **8**, 45 (1976). (c) 9.92–12.6 kcal mol^{-1}: R. M. Marshall, J. M. Purnell, and P. D. Storey, *J. Chem. Soc., Faraday Trans. 1*, **72**, 85 (1976). (d) 11.0–12.9 kcal mol^{-1}: J. A. Walker and W. Tsang, *Int. J. Chem. Kinet.*, **11**, 867 (1979). (e) 10.3 kcal mol^{-1}: D. A. Parkes and C. P. Quinn, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1952 (1976). (f) 10.5 kcal mol^{-1}: G. M. Atri, R. R. Baldwin, G. A. Evans, and R. R. Walker, *ibid.*, **74**, 366 (1978).

(24) J. Pacansky and J. S. Chang, submitted for publication. We thank Dr. Pacansky for a copy of his manuscript in advance of publication.

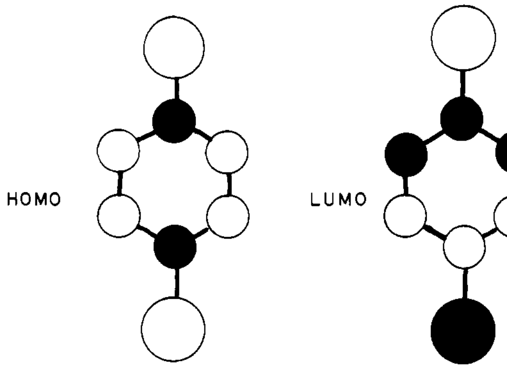
(25) F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4067 (1979).

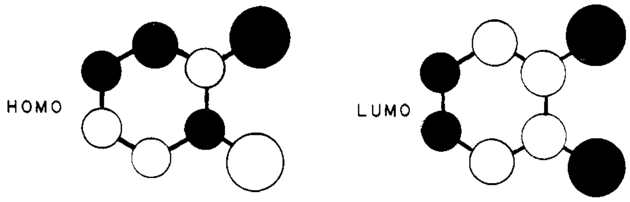
together with the heat of formation of the proton (367 kcal mol^{-1})[26] and the absolute proton affinity of ammonia (−205 ± 2 kcal mol^{-1}),[12] may in turn be used to obtain heats of formation of 50 ± 4 kcal mol^{-1} for *p*-xylylene, 53 ± 4 kcal mol^{-1} for *o*-xylylene, and greater than 76 ± 4 kcal mol^{-1} for *m*-xylylene. The significant difference in thermochemical stabilities between the ortho or para compounds and the meta isomer is consistent with the lack of success of Michl and co-workers[7a] in forming the latter under conditions appropriate for generation of *o*- and *p*-xylylene.

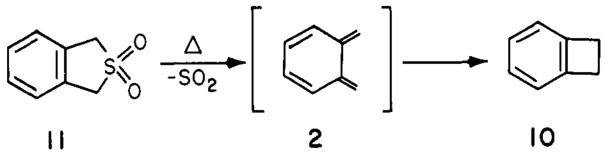
The only other experimental data for the heats of formation of the isomeric xylylenes is for the ortho isomer. Roth and co-workers[27] have estimated its value to be 58 kcal mol^{-1}, on the basis of the heat of formation of benzocyclobutene, and activation barriers measured for reactions of the transient neutral.

Further confirmation of our experimental heats of formation may be obtained from Benson's group additivity rules.[28] Heats of formation of the xylylenes as well as several other C_8H_8 hydrocarbons predicted in this manner are compared to their respective experimental quantities in Table V. Overall, the level of agreement is excellent.

The data in Table V suggest that it is the kinetic instability of *o*- and *p*-xylylene (rather than thermodynamic in stability) which has precluded their isolation. Examination of the frontier molecular orbitals of *p*-xylylene suggests that the terminal methylene groups may act either to donate or to accept electron density. The high propensity of these species for self-polymerization is, therefore, not unexpected. Similar conclusions follow from examination of the valence molecular orbital of *o*-xylylene. Here there also exists the possibility of electrocyclic ring closure (i.e., to form **10**). Such a process, involving the intermediacy of *o*-xylylene, has been suggested as the probable pathway to formation of benzocyclobutene (**10**) from 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide[29] (**11**). *o*-Xylylene should, of course, also be highly reactive under Diels–Alder conditions. This is evidenced by the fact that Diels–Alder addition has been used as a chemical trap for the species.[5,30]

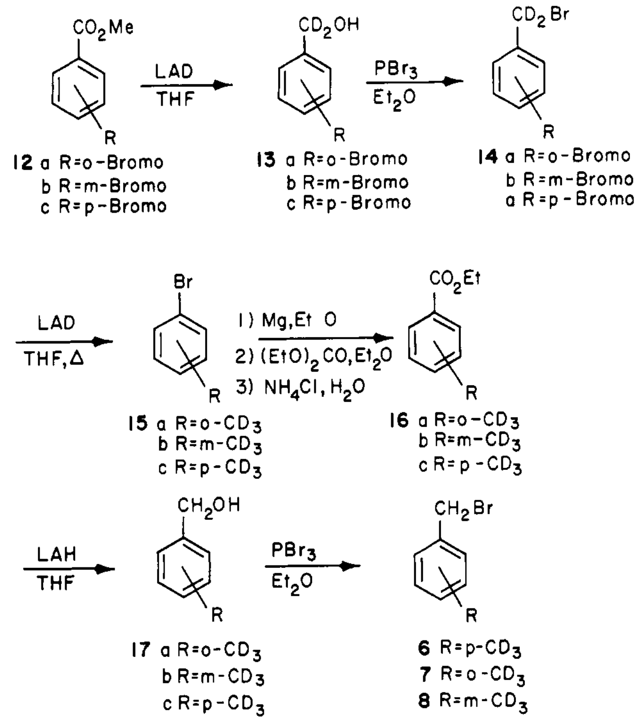






11 **2** **10**

Scheme II



Experimental Section

All ICR measurements were performed on a spectrometer described previously.[11] Ionization energies were typically 17–18 eV. Argon buffer gas was utilized to eliminate excited ionic species. Typical sample mixtures were in the ratio of partial pressures 4:1:100, α-bromoxylene:reagent base:argon buffer, with a total pressure of 1 × 10^{-5} torr. Reactions were observed from 75 to 100 ms after the grid pulse to ensure sufficient time for the ions to come to thermal equilibrium. Double-resonance experiments were performed first in the conventional fixed H_1–swept ω_2 mode and then confirmed by using a fixed ω_2–swept H_1 method.[10a] Unless otherwise noted, all organic materials were purified by preparative VPC. Argon (Linde 99.9995%) was used as supplied.

General Synthetic Procedures. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Literature physical properties are for the undeuterated analogues. Infrared spectra (IR) were recorded on a Perkin-Elmer IR 283 infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A56/60 or EM-360 spectrometer. Chemical shifts are given in part per million (ppm) downfield from tetramethyl silane in δ units.

For preparative VPC, a Varian aerograph, Model 920, equipped with thermal conductivity detector and helium carrier gas was used. The packed column used was 6 ft × $^{1}/_{4}$ in., 10% SE-30 on 60/80 Chrom W (copper). The bromide precursors were synthesized via Scheme II.

Most reagent grade chemicals were dried prior to their use by standard methods. Unless otherwise indicated, organic compounds were obtained from Aldrich Chemical Co. and inorganic compounds were obtained from Ventron Corp.

2-Bromobenzyl-α,α-d_2 Alcohol (13a).[31] Into a 2-L three-necked round-bottom flask fitted with pressure-equalizing addition funnel, reflux condenser, and magnetic stir bar and maintained under static nitrogen atmosphere was placed lithium tetradeuterioaluminate (LAD) (2.92 g, 70 mmol; Merck) and 250 mL of anhydrous THF. The addition funnel was charged with a solution of methyl 2-bromobenzoate (24.8 g, 115 mmol) in 250 mL of anhydrous THF. The ester was added over 1 h with stirring. The reaction was allowed to stir for 0.5 h more and then carefully quenched by the slow addition of solid sodium sulfate decahydrate (Glauber's salt), followed by stirring for 1 h. The clear organic layer was decanted, and the salts were extracted in a Soxhlet apparatus with THF. The organic layers were combined and dried over solid

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anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was recrystallized from ligroin to yield **13a** as white needles (15 g, 69%): mp 78.5–80.5 °C (lit. 79–82 °C); NMR ($CDCl_3$) δ 2.5 (s, 1 H), 7.0–7.7 (m, 4 H); IR (Nujol) 3400 (m), 3300 (m), 2200 (w), 2080 (m), 1565 (m), 1230 (m), 1210 (m), 1132 (m), 1095 (m), 1082 (s), 1065 (m), 1032 (m), 1020 (s), 975 (s), 945 (m), 740 (vs) cm^{-1}.

3-Bromobenzyl-α,α-d_2 Alcohol (13b). Following the same procedure as for **13a**, using methyl 3-bromobenzoate (20 g, 93 mmol) and LAD (2.14 g, 51 mmol), one obtains a yellow oil. Distillation (140–144 °C (17 mm)) yields 16.6 g of **13b** as a water white liquid (92%): NMR ($CDCl_3$) δ 3.7 (s, 1 H), 7.1–7.5 (m, 4 H); IR (neat) 3320 (vs, br), 3060 (w), 2195 (m), 2120 (w), 2080 (m), 1660 (m), 1568 (s), 1475 (s), 1420 (s), 1225 (s), 1095 (s), 1085 (s), 1070 (s), 1055 (s), 995 (m), 920 (m), 960 (s), 887 (m), 820 (m), 795 (m), 755 (s), 690 (m), 660 (s) cm^{-1}.

4-Bromobenzyl-α,α-d_2 Alcohol (13c). Following the same procedure as for **13a**, using methyl 4-bromobenzoate (20 g, 93 mmol) and LAD (2.14 g, 51 mmol), one obtains a yellow solid. Recrystallization from ligroin afford 16.7 g of **13c** as white needles (94%): mp 76–78 °C (lit. 76 °C); NMR ($CDCl_3$) δ 2.4 (s, 1 H), 7.25 (A_2B_2, J_{AB} = 18 Hz, $\delta(H_A)$ 7.10, $\delta(H_B)$ 7.40, 4 H); IR (KBr pellet) 3310 (vs, br), 2200 (w), 2130 (w), 2080 (w), 1910 (w), 1970 (w), 1595 (m), 1485 (vs), 1400 (s), 1225 (s), 1092 (s), 1070 (vs), 1010 (vs), 970 (vs), 912 (w), 860 (m), 798 (s), 772 (vs) cm^{-1}.

2-(Bromomethyl-d_2)bromobenzene (14a).[32] Phosphorus tribromide (12.18 g, 4.3 mL, 45 mmol) was added to a stirred solution of **13a** (12.2 g, 65 mmol) in anhydrous ethyl ether over a period of 2 h. The mixture was then refluxed for 2 h and then quenched by pouring onto 300 g of ice. The organic layer was separated and the aqueous phase extracted with two portions of ether. The combined organic layers were then washed with saturated aqueous sodium bicarbonate and water. The solvent was removed via distillation. Distillation of the remaining yellow oil (115–117 °C (10 mm)) afforded **14a** as a water white liquid (16.3 g, 67%): NMR ($CDCl_3$) δ 6.9–7.6 (m, 4 H); IR (neat) 3050 (w), 2180 (w), 1565 (m), 1560 (m), 1470 (s), 1458 (m), 1438 (s), 1275 (m), 1220 (m), 1160 (w), 1121 (w), 1065 (m), 1025 (s), 942 (m), 928 (s), 850 (w), 822 (w), 789 (w), 748 (vs), 710 (m), 650 (m), 585 (w) cm^{-1}.

3-(Bromoethyl-d_2)bromobenzene (14b). Following the same procedure as for **14a**, using phosphorus tribromide (24.12 g, 8.4 mL, 89 mmol) and **13b** (24.3 g, 128 mmol) afforded **14b** as white needles (29.3 g, 91% yield). No further purification was undertaken: mp 40–41 °C (lit. 41 °C); NMR ($CDCl_3$) δ 7.0–7.5 (m, 4 H); IR (neat) 3040 (w), 2180 (w), 1960 (w), 1815 (w), 1762 (w), 1590 (m), 1560 (s), 1470 (m), 1420 (s), 1222 (m), 1160 (w), 1090 (w), 1065 (m), 1055 (m), 992 (w), 935 (s), 905 (w), 882 (s), 825 (w), 808 (m), 780 (vs), 685 (vs), 655 (w) cm^{-1}.

4-(Bromoethyl-d_2)bromobenzene (14c). Following the same procedure as for **14a**, using phosphorus tribromide (15.0 g, 5.19 mL, 55 mmol) and **13c** (15 g, 79 mmol) afforded white needles from ethanol (19.9 g, 96%): mp 62.3–63 °C (lit. 61 °C); NMR ($CDCl_3$) δ 7.2–7.5 (A_2B_2, $\delta(H_A)$ 7.38, $\delta(H_B)$ 7.58, J_{AB} = 8.25 Hz, 4 H); IR (melt) 2270 (w), 2180 (w), 1910 (w), 1582 (m), 1480 (m), 1395 (m), 1270 (m), 1095 (s), 1065 (s), 1050 (m), 1005 (s), 948 (m), 922 (m), 820 (vs), 800 (m), 772 (m), 702 (m) cm^{-1}.

2-Bromotoluene-α,α,α-d_3 (15a).[32] To a three-necked round-bottom flask, fitted with pressure equalizing addition funnel and magnetic stir bar (all under static nitrogen atmosphere), were added lithium tetradeuterioaluminate (1.35 g, 32 mmol) and 100 mL of anhydrous THF. The addition funnel was charged with a solution of **14a** (9.74 g, 39 mmol) in 100 mL of anhydrous THF, and the solution was added with stirring over 45 min. The reaction mixture was then refluxed for 3 h. upon being cooled, the reaction was quenched by the slow addition of solid sodium sulfate decahydrate (Glauber's salt) and the mixture stirred for 3 h. The organic layer was decanted, and the salts were extracted in a Soxhlet apparatus for 1 h. The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed via distillation to afford a yellow oil. Distillation (100 °C (35 mm)) yielded **15a** as a water white liquid (3.87 g, 60%): NMR ($CDCl_3$) δ 6.8–7.6 (m, 4 H); IR (neat) 3060 (m), 3015 (w), 2230 (w), 2210 (w), 2145 (w), 2115 (w), 1598 (w), 1568 (m), 1475 (s), 1460 (m), 1435 (s), 1270 (m), 1125 (w), 1068 (s), 1037 (s), 1019 (vs), 942 (m), 740 (vs), 670 (m), 650 (s) cm^{-1}.

3-Bromotoluene-α,α,α-d_3 (15b). Following the same procedure as for **15a**, using LAD (3.4 g, 81 mmol) and **14b** (24.6 g, 98 mmol) afforded via distillation (110 °C (83 mm)) 10.85 g of **15b** as a water white liquid (64%): NMR ($CDCl_3$) δ 6.9–7.4 (m, 4 H); IR (neat) 3060 (m), 2230 (m), 2210 (m), 2130 (m), 2060 (m), 1600 (s), 1565 (s), 1478 (s), 1422 (s), 1390 (m), 1295 (m), 1228 (s), 1170 (m), 1085 (s), 1070 (vs), 1050 (vs), 1002 (s), 918 (s), 890 (s), 818 (vs), 787 (s), 750 (vs), 760 (s), 661 (s) cm^{-1}.

4-Bromotoluene-α,α,α-d_3 (15c). Following the same procedure as for **15a**, using LAD (2.5 g, 57 mmol) and **14c** (17.6 g, 70 mmol) afforded a low melting yellow solid. Distillation (110 °C (83 mm)) afforded a water white liquid which solidified upon standing (6.46 g, 53%): NMR ($CDCl_3$) δ 6.95–7.45 (A_2B_2, $\delta(H_A)$ 6.91, $\delta(H_B)$ 7.52, J_{AB} = 8.5 Hz, 4 H); IR (neat) 3020 (w), 2220 (w), 2200 (w), 2125 (m), 2055 (w), 2045 (w), 1485 (s), 1400 (m), 1388 (w), 1235 (m), 1178 (w), 1105 (m), 1070 (s), 1042 (m), 1010 (s), 878 (s), 765 (vs), 665 (w) cm^{-1}.

Ethyl 2-Methyl-d_3-benzoate (16a).[33] Into a three-necked round-bottom flask fitted with pressure equalizing addition funnel and a magnetic stir bar (all under static nitrogen atmosphere) were placed magnesium turnings (0.56 g, 23 mmol) and 20 mL of anhydrous ethyl ether. The addition funnel was charged with **15a** (3.89 g, 23 mmol) in 50 mL of anhydrous ethyl ether. The magnesium turnings were stirred and 5 mL of the bromide was added to initiate Grignard formation (some slight warming was necessary). The remainder of the bromide was added at such a rate to maintain gentle reflux and at the completion of addition, stirred for 0.5 h longer.

Into a second three-necked round-bottom flask fitted as above was placed freshly distilled diethyl carbonate (4.13 g, 36 mmol) in 5 mL of anhydrous ethyl ether. The Grignard reagent formed above was transferred to the addition funnel under anhydrous conditions. Stirring was initiated and the Grignard was added as fast as reflux would permit. Stirring was then continued for 0.5 h. The reaction mixture was allowed to stand overnight and then quenched by pouring onto 120 g of ice. The reaction mixture was then hydrolyzed with 15 mL of 30% aqueous sulfuric acid. The organic layer was separated and the aqueous layer extracted with one portion of ether. The combined organic phases were washed with 5% aqueous sodium bicarbonate, water, 5% aqueous sodium thiosulfate, and water and then dried over anhydrous sodium sulfate. The solvent was then removed via distillation and the crude product distilled (85 °C (3.5 mm)) to yield 1.59 g of **16a** as a water white liquid (36%): NMR ($CDCl_3$) δ 1.4 (t, J = 7.5 Hz, 3 H), 4.35 (q, J = 7.5 Hz, 2 H), 7.0–7.6 (m, 3 H), 7.8–8.05 (m, 1 H); IR (neat) 3070 (m), 3030 (m), 2980 (s), 2940 (m), 2900 (m), 2230 (m), 2130 (w), 2050 (w), 1720 (vs), 1602 (m), 1575 (m), 1490 (s), 1478 (m), 1465 (m), 1450 (s), 1390 (m), 1368 (s), 1290 (vs), 1255 (vs), 1175 (m), 1140 (s), 1125 (s), 1085 (vs), 1052 (s), 1020 (m), 955 (w), 905 (w), 852 (w), 795 (w), 750 (w), 722 (vs), 685 (w), 659 (m) cm^{-1}.

Ethyl 3-Methyl-d_3-benzoate (16b). Following the same procedure as for **16a**, using magnesium turnings (0.5 g, 21 mmol), **15b** (3.6 g, 21 mmol), and diethyl carbonate (3.64 g, 31 mmol), we obtained via distillation (68 °C (0.75 mm)) 1.1 g of **16b** as a water white liquid (33%): NMR ($CDCl_3$) 1.35 (t, J = 7 Hz, 3 H), 4.35 (q, J = 7 Hz, 2 H), 7.15–7.55 (m, 2 H), 7.65–8.5 (m, 2 H); IR (neat) 3060 (w), 3015 (w), 2980 (m), 2935 (w), 2900 (w), 2229 (w), 2208 (w), 2133 (w), 2062 (w), 1722 (vs), 1610 (m), 1585 (m), 1480 (w), 1465 (w), 1435 (m), 1390 (w), 1365 (m), 1285 (vs), 1212 (vs), 1170 (w), 1105 (s), 1078 (m), 1052 (w), 1020 (w), 925 (w), 730 (s), 662 (w) cm^{-1}.

Ethyl 4-Methyl-d_3-benzoate (16c). Following the same procedure as for **16a**, using magnesium turnings (0.8 g, 32 mmol), **15c** (5.5 g, 32 mmol), and diethyl carbonate (5.6 g, 47 mmol), we obtained via distillation (50 °C (0.5 mm)) 1.96 g of **16c** as a water white liquid (37%): NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 3 H), 4.29 (q, J = 7 Hz, 2 H), 7.18–8.01 (A_2B_2, $\delta(H_A)$ 8.3, $\delta(H_B)$ 6.9, J_{AB} = 9 Hz, 4 H); IR (neat) 3040 (w), 2980 (m), 2835 (w), 2805 (w), 2230 (w), 2210 (w), 2130 (w), 2050 (w), 1725 (s), 1615 (m), 1575 (w), 1511 (w), 1470 (w), 1465 (w), 1445 (w), 1410 (m), 1392 (w), 1370 (m), 1315 (m), 1275 (vs), 1232 (m), 1178 (s), 1105 (s), 1048 (w), 1020 (m), 900 (m), 872 (w), 850 (w), 732 (s) cm^{-1}.

2-Methyl-d_3-benzyl Alcohol (17a). Following a procedure similar to that for the reduction of methyl 4-bromobenzoate to **13a**, using lithium tetrahydroaluminate (LAH) (0.24 g, 63 mmol) and **16a** (1.59 g, 100 mmol) yielded via distillation (72 °C (2 mm)) 1.10 g of a water white liquid which solidified on cooling (87%): NMR ($CDCl_3$) δ 2.0 (s, 1 H), 4.7 (s, 2 H), 7.25 (s, 4 H); IR (neat) 3340 (vs, br), 3070 (s), 3020 (s), 2890 (s), 2225 (m), 2205 (m), 2120 (m), 2050 (w), 1760 (m), 1605 (m), 1570 (w), 1490 (s), 1450 (vs), 1415 (m), 1375 (m), 1285 (m), 1255 (m), 1220 (m), 1190 (s), 1045 (vs), 1005 (vs), 945 (m), 895 (w), 840 (m), 755 (vs), 735 (vs), 715 (s), 688 (m), 605 (w), cm^{-1}.

3-Methyl-d_3-benzyl Alcohol (17b). Following the same procedure as for **17a**, using LAH (0.14 g, 3.62 mmol) and **16b** (1.1 g, 6.58 mmol), we obtained via Kugelrohr distillation (75 °C (2 mm)) 610 mg of **17b** as a water white liquid (75%): NMR ($CDCl_3$) δ 2.7 (s, 1 H), 4.6 (s, 2 H), 7.2 (s, 4 H); IR (neat) 3340 (vs, br), 3050 (m), 3020 (m), 2870 (m),

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2220 (w), 2200 (w), 2120 (w), 1435 (m), 1360 (w), 1255 (w), 1215 (w), 1160 (m), 1085 (w), 1020 (vs, br), 918 (m), 882 (m), 835 (w), 750 (s), 720 (s), 680 (m) cm^{-1}.

4-Methyl-*d*$_3$-benzyl Alcohol (17c). Following the same procedure as for **17a**, using LAH (244 mg, 5.89 mmol) and **16c** (1.95 g, 11.7 mmol), we obtain via recrystallation from heptane **17c** as white needles (872 mg, 61.9%): mp 56 °C (lit. 59–60 °C); NMR ($CDCl_3$) δ 1.6 (s, 1 H), 4.6 (s, 2 H), 7.3 (s, 4 H); IR (neat) 3360 (s, br), 3090 (w), 3050 (m), 3010 (m), 2930 (m), 2870 (m), 2230 (w), 2205 (w), 2170 (w), 2050 (w), 1617 (w), 1518 (s), 1460 (m), 1418 (s), 1370 (w), 1205 (m), 1180 (w), 1025 (vs), 1015 (vs), 885 (s), 775 (s), 718 (s), 675 (w) cm^{-1}.

2-Methyl-*d*$_3$-Benzyl Bromide (7). Following a procedure similar to the one used in the conversion of **13a** to **14a**, using phosphorus tribromide (960 mg, 3.54 mmol) and **17a** (640 mg, 5.11 mmol), we obtained via Kugelrohr distillation (80 °C (3 mm)) **7** as water white liquid which solidified on standing (512 mg, 77%): NMR ($CDCl_3$) 4.5 (s, 2 H), 7.2 (s, 4 H); IR (neat) 3060 (m), 3020 (s), 2975 (m), 2925 (m), 2865 (m), 2225 (m), 2205 (m), 2120 (w), 2070 (w), 2050 (w), 1605 (m), 1578 (m), 1490 (s), 1452 (s), 1442 (s), 1375 (w), 1299 (w), 1282 (m), 1235 (m), 1215 (vs), 1193 (s), 1160 (w), 1135 (w), 1085 (m), 1045 (m), 945 (m), 892 (w), 875 (w), 837 (m), 755 (vs), 715 (m), 685 (s), 600 (s), 582 (m) cm^{-1}.

3-Methyl-*d*$_3$-benzyl Bromide (8). Following the same procedure as for **7**, using phosphorus tribromide (913 mg, 3.37 mmol) and **17b** (616 mg, 4.87 mmol), we obtained via Kugelrohr distillation (80 °C (2.5 mm)) **8** as a water white liquid: NMR ($CDCl_3$) δ 4.4 (s, 2 H), 7.2 (s, 4 H); IR (neat) 3100 (w), 3035 (w), 3020 (m), 2875 (w), 2230 (w), 2210 (w), 2130 (w), 2060 (w), 1608 (m), 1588 (w), 1485 (m), 1440 (m), 1265 (m), 1212 (s), 1165 (w), 1082 (m), 1050 (w), 922 (m), 905 (w), 835 (w), 760 (s), 715 (m), 690 (s), 605 (s), 558 (w) cm^{-1}.

4-Methyl-*d*$_3$-benzyl Bromide (6). Following the same procedure as for **7**, using phosphorus tribromide (474 mg, 1.74 mmol) and **17c** (431 mg, 3.45 mmol), we obtained via Kugelrohr distillation (80 °C (3.5 mm)) **6** as a water white liquid which solidified on standing (436 mg, 68%): NMR ($CDCl_3$) δ 4.2 (s, 2 H), 7.05–7.4 (A_2B_2, $\delta(H_A)$ 7.34, $\delta(H_B)$ 7.13, J_{AB} = 9 Hz, 4 H); IR (neat) 3130 (w), 3090 (w), 3050 (m), 3030 (m), 3005 (m), 2870 (w), 2230 (q), 2210 (w), 2130 (m), 2050 (m), 1915 (w), 1615 (m), 1515 (s), 1439 (m), 1415 (s), 1225 (vs), 1205 (s), 1185 (w), 1105 (w), 1045 (w), 1018 (w), 950 (w), 890 (s), 828 (m), 785 (s), 708 (s), 682 (s), 595 (m) cm^{-1}.

Silabutadienes and Their Silylene Isomers. An ab Initio Study

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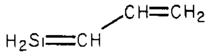
Abstract: 1-Silabutadiene (**1**), 2-silabutadiene (**2**), and their respective singlet silylene isomers allylsilylene (**3**) and methylvinylsilylene (**4**) are investigated through ab initio double ζ + d(Si) SCF calculations. The calculated SCF relative stabilities (**4** < **2** < **1** < **3**) should be modified by correlation effects to the **2** < **4** < **1** < **3** ordering. π-Conjugation in silabutadienes is put in evidence through an analysis of energy shifts and π charge transfers which are predominantly $Si{=}C{\to}C{=}C$ in **1** while $C{=}Si{\leftarrow}C{=}C$ in **2**. This conjugation strongly stabilizes 1-silabutadiene (**1**) with respect to its silylene isomer **3**, while the conjugation in **2** is balanced by the $\pi_{C=C} \to 3p_{zSi}$ delocalization occurring in **4**.

I. Introduction

The field of theoretical stability of π-bonded silicon compounds has been substantially explored. Since the previous works of Gordon[1] and Strausz et al.,[2] many ab initio calculations using extended basis sets and including CI have appeared (for reviews, see ref 3 and4). A general feature in organosilicon unsaturated compounds is that the preferred forms are cycles (when possible) or silylenes rather than silico olefin forms. The simplest case, silaethylene, which bears one unsaturation on two centers, has been studied extensively.[5-7] Goddard's most reliable results concerning the (lower) singlet states predict silaethylene to lie only 0.4 kcal/mol above methylsilylene.[7] The next series concerns three centers and one unsaturation, namely, C_2SiH_6; Gordon's SCF calculations[6] predict the preferred forms to be dimethylsilylene and silacyclopropane (apart from the stable vinylsilane in which the silicon atom is not involved in the unsaturation). Barthelat et al.[8] have explored the case of two unsaturations on three centers (C_2SiH_4) showing the most stable isomers were silacyclopropylidene and silacyclopropene. The C_3SiH_4 isomers correspond to three unsaturations on four centers; Gordon[9] has calculated silacyclobutadiene to be more stable than silatetrahedrane, as for carbon analogues. An interesting series deals with two unsaturations on four centers, allowing conjugation of a Si=C bond with a C=C bond. One may wonder whether the conjugation in silabutadienes could stabilize the Si=C bonds with respect to the silylene forms. In the literature is actual mention of the occurrence of transient 1-silabutadienes[4] and 2-silabutadienes.[4,10,11]

This work is an ab initio study, mainly at the SCF level, of the stability and electronic structure of some C_3SiH_6 isomers limited to the 1- and 2-silabutadienes (**1** and **2**) and to their corresponding



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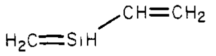

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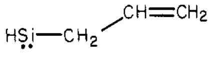

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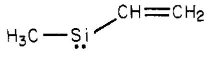

4

linear silylene isomers, namely, allylsilylene (**3**) and methylvinylsilylene (**4**).

Calculations on silaethylene, methylsilylene, and vinylsilylene are also reported which allow (i) comparisons with other all electron calculations, (ii) geometrical assumptions, and (iii) an estimate of possible correlation effects in **1** to **4**.

II. Computational Details

All the SCF results reported here are obtained from the PSHONDO algorithm[12] which introduces the pseudo-potentials of Durand and Barthelat[13] into the HONDO program.[14] For carbon

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