Table IV. Spectroscopic Properties of *p*-Cresol and Tyrosine

p-Cresol: Ground state,[a,b] cm^{-1}	*p*-Cresol: Excited state,[a] cm^{-1}	Point group C_{2v} symmetry species[b]	Vibrational mode no.[c]	Tyrosine[d] excited state, cm^{-1}
468	422	A_1	6A	420
642	585	B_2	6B	Not detected
738	694	A_1	12	Not detected[e]
841	808	A_1	1	800
1251[f]	1272	A_1	7A	1250[g]

[a] Reference 30. [b] Reference 27. [c] Notation described in K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, **65**, 803 (1943). [d] Taken from Figure 2. [e] The 0 + 694 cm^{-1} transition is weak in *p*-cresol vapor; for *p*-cresol and tyrosine solutions, this band is completely masked by the 0 + 800 cm^{-1} band. [f] In contrast to the rest of the vibrations where the vibrational frequency of the excited state is lower than that of the ground state, vibration 7A has a slightly higher frequency in the excited state (ref 29). [g] In the vapor spectrum of *p*-cresol five bands are closely spaced around 0 + 1250 cm^{-1} (ref 30). These bands cannot be resolved in solution. The 0 + 1272 cm^{-1} transition appears to be the single strongest contributor to the intensity of the 0 + 1250 cm^{-1} band of tyrosine. In addition, the 0 + 420 + 800 cm^{-1} transition also may contribute in this region.

since tyrosine is a derivative of *p*-cresol[26] and has the same near-ultraviolet absorption spectrum as does *p*-cresol. Unfortunately the ultraviolet spectrum of *p*-cresol has not been analyzed completely. Supplementary information, however, is available from studies on phenol and other substituted benzenes.

The effective local symmetry of the phenolic ring in tyrosine appears to be C_{2v}. First an analysis of the infrared and Raman spectra of *p*-cresol indicates an effective symmetry of C_{2v}.[27] Secondly, the near-ultraviolet transitions of phenol have been described in terms of C_{2v} symmetry.[28,29] In view of the effective local symmetry being C_{2v}, the near-ultraviolet band of tyrosine can be identified as an $A_1 \rightarrow B_2$ electronic transition, as is also the case for phenylalanine.[4]

The symmetry species of the excited state vibrational modes were identified from the corresponding ground-state vibrations of *p*-cresol[27,30] (Table IV). The mode numbers for the vibrations were obtained by starting with the assignments for phenol.[28,29] The vibrational frequency of each mode, however, may be somewhat changed in disubstituted benzenes such as *p*-cresol and tyrosine. The magnitude of this change was estimated by calculating the frequency shift for each mode in going from toluene to *p*-xylene (see Tables XIX and XXII in ref 31). When this value was added to the fundamental frequency observed in the excited state of phenol,[28,29] the resulting frequency matches only one of the excited-state vibrational frequencies observed in *p*-cresol (Table III). Thus the identification of the vibrations of *p*-cresol and tyrosine seems reliable.

Consideration must also be given to the absorption intensity of the transitions involving the nontotally symmetrical vibration 6B. In both phenol[28,29] and *p*-cresol (ref 30 and Table III), these transitions are very weak. In the *p*-cresol vapor spectrum, vibration 6B apparently occurs in the 0 + 585 cm^{-1} transition. As would be expected from the weakness of this transition in *p*-cresol vapor,[30] the 0 + 585 cm^{-1} band is too weak to be detected in the tyrosine spectrum even at 77°K. Therefore, the near-ultraviolet absorption spectrum of tyrosine arises almost entirely from the 0–0 band and combinations involving only totally symmetrical vibrations.

Acknowledgments. We wish to thank Professor Albert Moscowitz and Professor Oscar Weigang for helpful discussions concerning the effects of solvation and vibronic coupling.

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(27) R. J. Jakobsen, *Spectrochim. Acta*, **21**, 433 (1965).

(28) W. W. Robertson, A. J. Seriff, and F. A. Matsen, *J. Amer. Chem. Soc.*, **72**, 1539 (1950).

(29) H. D. Bist, J. C. D. Brand, and D. R. Williams, *J. Mol. Spectrosc.*, **21**, 76 (1966).

(30) S. Imanishi, M. Ito, K. Semba, and T. Anno, *J. Chem. Phys.*, **20**, 532 (1952).

(31) See Table III, footnote *c*.

Communications to the Editor

Carbon Scrambling upon Electron Impact

Sir:

The occurrence of hydrogen scrambling accompanying fragmentation in the mass spectrometer has been demonstrated in many classes of compounds.[1] In toluene and related compounds scrambling involves ring expansion, some aspects of which have been probed by ^{13}C labeling.[2] For compounds where ring expansion is not possible it has been suggested,[3] by analogy with known photochemical processes, that scrambling might involve valence tautomerism. Some support for this hypothesis has been found[4] in the propensity for H/D scrambling in deuterated thiophenes and the absence of such scrambling in furans, a result which is paralleled by the photoisomerization of arylthiophenes[5] and the absence of such isomerization in arylfurans.[6] Further support for the ring atom scrambling mechanism in thiophenes comes from an electron impact study[7] of

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(1) References appear in R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 137 (1969).

(2) K. L. Rinehardt, *J. Amer. Chem. Soc.*, **90**, 2983 (1968). Compare also K. L. Rinehardt, A. C. Bucholtz, and G. E. Van Lear, *ibid.*, **90**, 1073 (1968); M. Marx and C. Djerassi, *ibid.*, **90**, 678 (1968); A. V. Robertson and C. Djerassi, *ibid.*, **90**, 6992 (1968).

(3) K. R. Jennings, *Z. Naturforsch.*, **22a**, 454 (1967). Compare K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 1116 (1968).

(4) D. H. Williams, R. G. Cooks, J. Ronayne, and S. W. Tam, *Tetrahedron Lett.*, 1777 (1968).

(5) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Berkhius, *J. Amer. Chem. Soc.*, **89**, 3501 (1967).

(6) A. Padwa and R. Hartman, *ibid.*, **88**, 3759 (1966).

(7) T. A. Elwood, P. F. Rogerson, and M. M. Bursey, *J. Org. Chem.*, **34**, 1138 (1969).

Table I. Ion Abundance Ratios in Selected Regions of the Mass Spectra (70 eV) of I-IV[a]

Compd[b]	Process	Ionic masses and abundances
I	$M\cdot^{+}$ [c]	133 (0.15) 134 (100) 135 (10.0) 136 (4.6) 137 (0.4)
II	$M\cdot^{+}$ [c]	134 (84.0) 135 (100) 136 (11.6) 137 (4.4) 138 (0.3)
I	$M\cdot^{+} - C_2H_2$	107 (7.4) 108 (100) 109 (7.7) 110 (4.4) 111 (0.8)
II	$M\cdot^{+} - C_2H_2$	107 (11.9) 108 (100) 109 (57.9) 110 (7.6) 111 (2.1)
II	$M^{2+} - C_2H_2$	107 (14) 108 (100) 109 (56)
I	$M\cdot^{+}$ − CS/CHS	88 (3.6) 89 (100) 90 (85) 91 (8.8) 92 (1.2)
II	$M\cdot^{+}$ − CS/CHS	88 (4.3) 89 (68.8) 90 (100) 91 (44.8) 92 (2.9)
III	$(M\cdot^{+} - CO_2)$ − CS/CHS	88 (3.1) 89 (100) 90 (20.5) 91 (5.4)
IV	$(M\cdot^{+} - CO_2)$ − CS/CHS	88 (4.2) 89 (100) 90 (40.5) 91 (10.0)
I	$CHS\cdot^{+}$	45 (100) 46 (2.8) 47 (4.5)
II	$CHS\cdot^{+}$	45 (100) 46 (37.1) 47 (5.0)

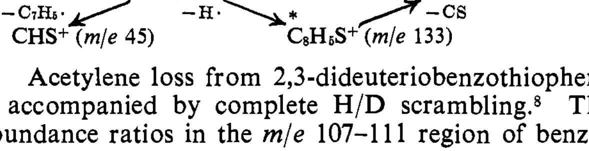
[a] Spectra were measured on an AEI MS 9 mass spectrometer. Each region is normalized for ease of comparison. Abundances appear in parentheses after the mass number. Each value represents an average taken from at least ten replicate scans made on two separate days. [b] I, benzothiophene; II, benzothiophene-2-^{13}C (52.2% enriched); III, benzothiophene-2-carboxylic acid; IV, benzothiophene-2-carboxylic acid-2-^{13}C (52.2% enriched). [c] Run at 17 eV.

arylthiophenes and arylfurans in which the *p*-fluorophenyl label gave results which matched those of deuterium labeling.[4]

In spite of the evidence for carbon scrambling in thiophenes no direct demonstration of this type of process has yet been presented. We judged benzothiophene a suitable compound for such a study since deuterium labeling[8] indicated a behavior similar to thiophene,[4] several processes being accompanied by complete and one by partial H/D scrambling. Furthermore, a heteroaromatic compound was preferred since the heteroatom acts as a label and only one ^{13}C atom need be introduced. Reaction of rhodanine-5-^{13}C (prepared from acetic acid-2-^{13}C with benzaldehyde followed by basic hydrolysis of the benzylidene adduct) yielded α-mercaptocinnamic acid-α-^{13}C which was oxidatively cyclized to benzo[*b*]thiophene-2-carboxylic acid-2-^{13}C.[9] Decarboxylation with copper in quinoline yielded benzo[*b*]thiophene-2-[^{13}C].[10]

Incorporation of ^{13}C into the benzothiophene, as determined from the molecular ion at low electron energy (Table I), was 52.2%. Determination on the molecular ion and the $M\cdot^{+} - OH\cdot$ ion of benzothiophene-2-carboxylic acid gave values of 52.2 and 52.3%, respectively. The fragmentations of benzothiophene of interest in this study appear in Scheme I. Observed ion abundances for the labeled and unlabeled benzothiophenes, normalized in each region of interest, are given in Table I.

Scheme I



Acetylene loss from 2,3-dideuteriobenzothiophene is accompanied by complete H/D scrambling.[8] The abundance ratios in the *m/e* 107–111 region of benzothiophene-2-^{13}C and of benzothiophene yield a C_6H_4S:$^{13}CC_5H_4S$ ratio of 100:52.2 for the 52.2% labeled compound.[11] Complete scrambling of the six carbon atoms bearing hydrogen atoms requires 100:53.4, complete scrambling of all eight carbon atoms requires 100:64.4, and in the absence of carbon scrambling a ratio of 100:0 could have been expected.[12] At low electron energy the $M\cdot^{+}$ − acetylene region is simplified by the absence of $M\cdot^{+} - C_2H_3\cdot$ and the C_6H_4S:$^{13}CC_5H_4S$ ratio (100:55) agreed within experimental error with that required for complete scrambling of the hydrogen-bearing carbon atoms.

$CHS\cdot$ loss from the benzothiophene molecular ion occurs with complete hydrogen scrambling.[8] This process, as well as CS loss, actually involves carbon scrambling as is evident from a comparison of the observed and calculated C_7H_5:C_7H_6 + $^{13}CC_6H_5$:$^{13}CC_6H_6$ abundance ratios. Our results (Table I), corrected for natural ^{13}C, yield the ratio 72.6:100:40.6 while complete scrambling of the six hydrogen-bearing carbon atoms requires 63.6:100:39.2 and an eight carbon scrambling mechanism requires 60.9:100:41.0. In the absence of carbon scrambling no $^{13}CC_6H_6$ ion would be expected. Scrambling is also evident in the metastable ions due to CS elimination from the molecular ion and the $M\cdot^{+}$ − H· ion.[13] It is interesting to contrast the carbon scrambling accompanying $C_7H_6S\cdot^{+}$ and $C_7H_5S^{+}$ formation in benzothiophene with formation of the same ions in benzothiophene-2-carboxylic acid where only about 15% carbon scrambling occurs, and even this could be due to benzothiophene generated thermally in the mass spectrometer source.

The explanation of the apparent hydrogen scrambling in benzothiophene in terms of carbon scrambling also encompasses CHS^{+} formation, which is accompanied by *partial* H/D scrambling in deuterated benzothiophene and thiophene.[8] The 52.2% ^{13}C-enriched benzothiophene yielded CHS^{+}:$^{13}CHS^{+}$ in the ratio 100:34.3,

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[8] R. G. Cooks, I. Howe, S. W. Tam, and D. H. Williams, *J. Amer. Chem. Soc.*, 90, 4064 (1968).

[9] This series of reactions has been used to prepare the unlabeled acid: E. Campaigne and R. E. Cline, *J. Org. Chem.*, 21, 39 (1956).

[10] From 1 g of labeled acetic acid (50–60 atom %) the carboxylic acid was obtained in 5% overall yield and was characterized by its mp, 137–139° (the unlabeled compound melts at 140–141° [9]), its uv, and its mass spectrum. The labeled benzothiophene (*ca.* 20 mg) was characterized by its uv and mass spectra.

[11] This calculation (and that for CHS^{+}:$^{13}CHS^{+}$) was made by subtraction of the unlabeled from the labeled spectrum. A small error is introduced by ignoring the contribution of the $M\cdot^{+} - C_2H_3\cdot$ process to *m/e* 108 in the labeled compound. If this process involves CH moiety scrambling the C_6H_4S:$^{13}CC_5H_4S$ ratio becomes 100:53. The compositions of the ions of interest in benzothiophene were confirmed by exact mass measurements and, although the $^{13}C/^{12}CH$ doublet could not be resolved, the absence of extraneous ions in the labeled compound was demonstrated at 12,000 resolution.

[12] This assumes exclusive acetylene loss from the five-membered ring. Loss from both rings, without scrambling, *could* give a 100:52.2 (or any other) ratio.

[13] Five metastables are expected in the partly labeled compound (two are coincident) and all were observed in approximately their expected abundance ratios except that due to ^{13}CS loss which was obscured by the normal ion at *m/e* 60.

while complete scrambling of all eight carbon atoms requires 100:7.0, scrambling of the six carbons bearing hydrogens requires 100:9.5, and no scrambling requires 100:108.2.

Our results clearly establish that carbon scrambling occurs in benzothiophene prior to formation of many mass spectral decomposition products and while scrambling processes involving C–H bond cleavage cannot be excluded, they are not necessary to explain the present results. The extent to which H/D scrambling in other systems is founded on ring atom scrambling is being investigated. It was of much interest to note that carbon scrambling also accompanies fragmentation of the *doubly charged* benzothiophene molecular ion, the $M^{2+} - C_2H_2$ daughter ions being formed in abundance ratios (Table I) very similar to those of the corresponding singly charged ions.

(14) National Science Foundation undergraduate summer research participant, 1969.

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Carbon Scrambling in Benzene upon Electron Impact

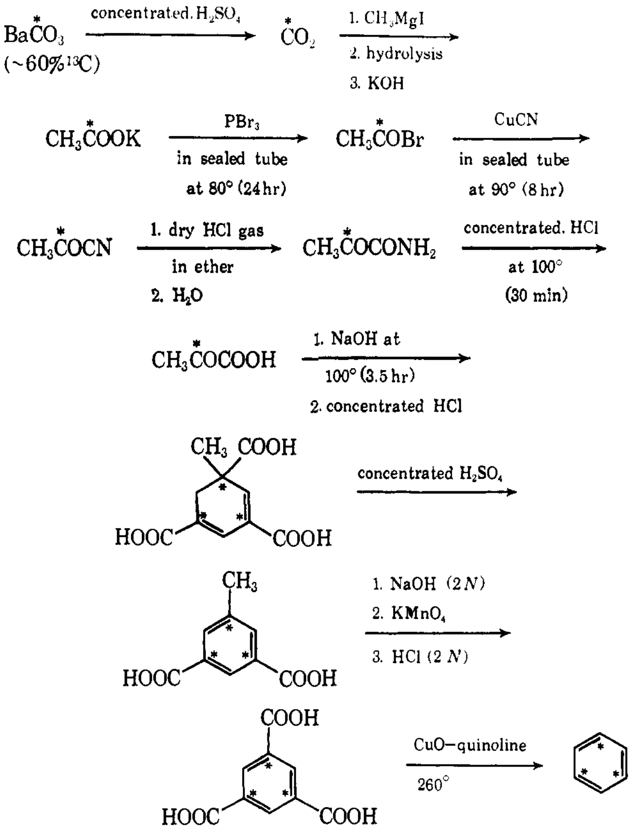
Sir:

The scrambling of aromatic hydrogens upon electron impact has been shown to occur in benzene,[1] pyridine,[2] and thiophene.[3] Similar scrambling in bicyclo aromatics and heterocycles has also been observed.[4] In benzene, the observed scrambling has been rationalized[1] by postulating carbon randomization, proceeding *via* valence isomerization involving structures such as benzvalene, prismane, and "dewar" benzene, in analogy to known photochemical transformations.[5] We now present evidence for carbon scrambling in benzene in the mass spectrometer.

1,3,5-$^{13}C_3$-Benzene required for mass spectral analysis was prepared by the sequence of reactions outlined in Scheme I. Experimental details have been described by Anker[6] and Hughes and Reid.[7,8]

The mass spectrum of unlabeled benzene shows peaks at *m/e* 52, 51, and 50, arising from the loss of C_2H_2 from the M^+, $M^+ - 1$, and $M^+ - 2$ ions, with corresponding "metastable peaks" at *m/e* 34.7, 33.8, and 32.9, respectively. Other than the metastable transition for loss of acetylene from the molecular ion, there are no metastable transitions from the molecular ion to daughter ions in the *m/e* 50–54 region. 1,3,5-$^{13}C_3$-Benzene prepared by the above sequence of reactions is not isotopically pure but is contaminated by $^{13}C_0$-, $^{13}C_1$-, and $^{13}C_2$-benzenes.[9] The loss of acetylene and ^{13}C-containing acetylenes from the M^+, $M^+ - 1$, and $M^+ - 2$ ions of $^{13}C_0$-, $^{13}C_1$-, $^{13}C_2$-, and $^{13}C_3$-benzenes gives rise to overlapping peaks in the *m/e* 50–55 region. Similar overlapping is encountered when "metastable peaks" arising from decomposition in the second field-free region are considered. This complication does not arise if "metastable peaks" arising from the loss of acetylene and ^{13}C-containing acetylenes from the molecular ion of 1,3,5-$^{13}C_3$-benzene in the first field-free region of a double focusing AEI MS9 mass spectrometer are considered.[10] These "metastable peaks" for the processes 81 → 55, 81 → 54, and 81 → 53 were examined. The ion with *m/e* 81 could only be 1,3,5-$^{13}C_3$-benzene[12] and the loss of 26, 27, and 28 mass units corresponds to the loss of C_2H_2, $^{13}CCH_2$, and $^{13}C_2H_2$, respectively.

Scheme I



If carbon atoms in benzene do not scramble prior to loss of acetylene, then 1,3,5-$^{13}C_3$-benzene can only lose $^{13}CCH_2$. However if the carbon atoms scramble prior to loss of acetylene, and if the scrambling is complete, C_2H_2, $^{13}CCH_2$, and $^{13}C_2H_2$ would be lost in the ratio of 20:60:20, respectively.[13] The experimental results[14] (the average of three sets of readings) show the loss of $21.4 \pm 3.8\%$ C_2H_2, $60.8 \pm 3.8\%$ $^{13}CCH_2$, and $17.8 \pm 1.8\%$ $^{13}C_2H_2$. This agrees closely with calculated val-

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(1) K. R. Jennings, *Z. Naturforsch.*, **22a**, 454 (1967).

(2) D. H. Williams and J. Ronayne, *Chem. Commun.*, 1129 (1967).

(3) D. H. Williams, R. G. Cooks, J. Ronayne, and S. W. Tam, *Tetrahedron Lett.*, 1777 (1968).

(4) R. G. Cooks, I. Howe, S. W. Tam, and D. H. Williams, *J. Amer. Chem. Soc.*, **90**, 4065 (1968); W. G. Cole, D. H. Williams, and A. N. H. Yeo, *J. Chem. Soc.*, *B*, 1284 (1968).

(5) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966), and references therein.

(6) H. S. Anker, *J. Biol. Chem.*, **176**, 1333 (1949).

(7) D. M. Hughes and J. C. Reid, *J. Org. Chem.*, **14**, 516 (1949).

(8) Modifications have been made in some of the experimental procedures in order to render them more suitable to the smaller quantity of materials involved.

(9) The mass spectral analysis of trimesic acid (1) shows an isotopic purity of 7.8% $^{13}C_0$, 27.0% $^{13}C_1$, 45.3% $^{13}C_2$, and 19.9% $^{13}C_3$. It is expected that the isotopic purity of the benzene derived from this acid should be the same.

(10) The intensities of these metastables can be determined with the aid of a "metastable defocuser."[11] The electrostatic analyzer was set initially at 4 kV.

(11) M. Barber and R. M. Elliot, paper presented at the 12th ASTM E-14 Meeting on Mass Spectrometry, Montreal, 1964; K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnet and J. G. Davis, Ed., United Trade Press, London, 1967, pp 105–109.

(12) No correction has been made for the natural ^{13}C isotope of 1,3-$^{13}C_2$-benzene.

(13) The derivation of these ratios is from $(3!/2!1!):(3 \times 3):(3!/2!1!)$.

(14) Partial overlap of the 80 → 54 and 80 → 53 "metastable peaks" with the 81 → 54 and 81 → 53 peaks, respectively, has been corrected for by assuming that the individual "metastable peaks" are gaussian.